UNIVERSITAT ROVIRA I VIRGILI

ORGANIC MICROPOLLUTANTS IN REVERSE OSMOSIS WATER TREATMENTS, PRESENCE AND REJECTION

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ORGANIC MICROPOLLUTANTS IN REVERSE OSMOSIS WATER TREATMENTS, PRESENCE AND REJECTION.

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DOCTORAL THESIS

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Departament de Química Analítica i Química Orgànica

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FAIG CONSTAR que aquest treball, titulat "ORGANIC MICROPOLLUTANTS IN REVERSE OSMOSIS WATER TREATMENTS, PRESENCE AND REJECTION", que presenta CAROLINA MARTÍNEZ DE PEÓN per a l'obtenció del títol de Doctora, ha estat realitzat sota la meva direcció al Departament de Química Analítica i Química Orgànica d'aquesta universitat.

HAGO CONSTAR que el presente trabajo, titulado "ORGANIC MICROPOLLUTANTS IN REVERSE OSMOSIS WATER TREATMENTS, PRESENCE AND REJECTION", que presenta CAROLINA MARTÍNEZ DE PEÓN para la obtención del título de Doctora, ha sido realizado bajo mi dirección en el Departamento de Química Analítica i Química Orgànica de esta universidad.

Tarragona, 14 de novembre de 2014.

El/La/Els director/a/s de la tesi doctoral
El/La/Los director/a/es de la tesis doctoral

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INDEX

CHAPTER 1

INTRODUCTION

The current Doctoral Thesis presented here is a part of the collaboration between the CTQ (Chemistry Technology Centre), the Chromatography and Environmental Applications Group of the Analytical and Organic Chemistry Department at the Universitat Rovira i Virgili, and the Dow Water and Process Solutions department of the Dow Chemical Company.

The work has been done through the ITACA-INPRONTA project (Technology research for treatment, reuse and control for future sustainability in water treatment) and it is included in the squad ITACA-INNPRONTA 2011. The aim of the project is the research on new concepts of advanced purification of industrial and urban waste water, minimizing impacts on the environment. This Thesis has contributed to the elaboration of some activities evaluating integrated membrane systems.

Different sections are included in the introduction chapter of this Thesis. The first section, some water problems are described, as well as the different water treatments, quality parameters and regulations. The second section, a description of advance membrane treatments is included and reverse osmosis is studied to eliminate micropollutants from the water. The third section, the most common families of organic micropollutants studied in environmental waters are described. Some of these families are currently regulated. In addition, the analytical methodologies for these compounds determination are also described. Finally, the characterization of the organic fouling in reverse osmosis membranes and how it could interfere in the water treatment process by the advance treatments is described.

1.1. Water

Water is not only a resource, it is a life source and one of our most precious natural sources. Water is a vital for human, animal and plant health. Therefore, the responsibility to ensure a secure, sustainable and healthy water supply for the environment and communities should be shared for everyone in the world. Our quality of life depends on it. Water is essential for human survival and welfare. In addition, water is a key component to many sectors of the economy. Moreover, as the human population continues growing, water resources are becoming limited. Definitely, it will intensify the pressure on water resources [1].

There are more than 326 million trillion gallons of water on Earth. Over the 97 % of the water in the earth is found in the oceans as salt water. Less than 3 % of water on Earth is fresh water and of that amount, more than two-thirds is locked up in ice caps, glaciers and snowy mountain ranges. That leaves only 1 % of the available water on earth to us for our daily water supply needs. It is still thousands of trillions of gallons, but it is a very small amount compared to all the water available. The fresh water supplies are stored either in the soil, as aquifers, or in the ground, lakes, rivers, and streams on the surface. Only this amount is regularly renewed by rain and snowfall, and could be available on a sustainable basis [1].

1.1.1 Water sources and supplies

Water has sources and supplies which are applied in different ways including direct consumption, irrigation, agricultural, industrial production, industrial effluents, the treatment of sewage, fisheries, hydropower, navigation and environmental protection [2]. As a general term, water resources refer to the supply of groundwater and surface water in a given area. In addition, the value of water to people differs across cultures and further complicates the characteristics of the resource depending on the availability.

A lot of efforts have to be taken into account to balance supply and demand in order to plan for sustainability in the near future. Studies of water resources have to be realistic and proper accounting of seasonal and annual variability of water flow as well as the interactions between surface water and ground water. Moreover, the most important fact is the realistic evaluation of social, political and economical factors which help to determine the water availability.

Figure 1 shows the different consumers of water in the world as percentages. Depending on natural precipitation, the degree of development and human population, the percentages could vary from different regions. It is observed that agricultural usages represent the largest consumer of water, approximately 69 %. About 18 % is used in urban and rural homes, hotels and offices. The remaining 13 % is used in manufacturing and mining activities [1].

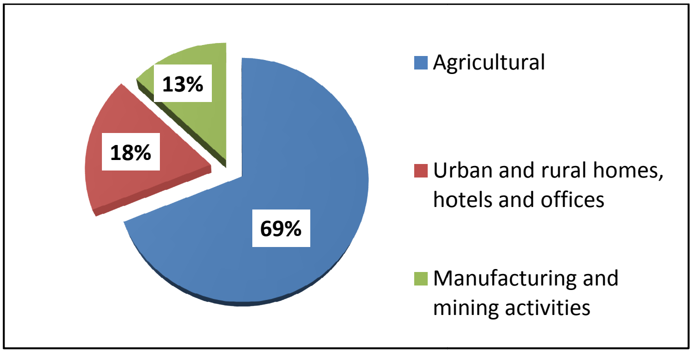

Figure 1. Different water consumers.

Social and physical characteristics

Access to water is a basic human right. Clean water reduces the frequency of diseases, being considered a social benefit shared by all users of the same water source. The public health impacts of inadequate water supply and sanitation has serious social and economic consequences for all. Classifying water as a basic human right introduces further social logistic in terms of equally distribution. In fact, only a fraction of water consumption is actually used for life preserving. A large portion of urban water is used for convenience and comfort. Equitable distribution of the safe drinking water is difficult due to clearly 1.1 billion people still lacking access to it [2]. Moreover, the moral dimensions of water management are a problem because of the property rights issues, underlying the economic water allocation.

Water is a renewable resource available by the natural hydraulic cycle. Furthermore, water provides habitats for aquatic life and river systems provide humidity for vegetation and terrestrial biota, transporting nutrients between one ecosystem and another. However, some natural water sources can become polluted due to the contamination by human actions.

The use of water has increased faster in the modern times. During the first years of the last century, about 200 % of the world per capita water use has increased. However, due to industrial and agriculture pollution, significant part of water resources has become unusable and has led to ecological and human health disasters. It is recognized worldwide that more than 20 % of all freshwater fish species are now threatened or endangered because of reservoirs, saltwater intrusions, ground water aquifers threatened by exhaustion and water withdrawals. These inefficient and harmful uses of water have led to concerns that water physical value is not reflected in its cost, becoming an economic question [2].

1.1.2 Water problems, diseases and pollution

More than 3.4 million people die each year from water, sanitization, and hygiene-related causes. Approximately, one of nine people lack access to an improved water source. Providing potable water to communities, especially among developing nations is a major problem. Provision of drinking water is expensive and difficult.

In general terms, water pollution is any chemical, physical or biological change in the quality of water that has a harmful effect on any living organism that drinks or uses or lives in it [3]. There are several types of water pollutants which will be cover in the next sections. One of the classes is those agents causing diseases, including bacteria, viruses, protozoa and parasitic worms that enter sewage systems and untreated waste.

The oxygen demand wastes are a second type of water pollutants, which might be decomposed by aerobic bacteria, requiring oxygen for growing. With the presence of these populations of aerobic bacteria, they can deplete oxygen levels in the water and consequently, causing the death of other organisms in the water such as fish.

Other class of water pollutants is the soluble inorganic pollutants, including acids, salts and toxic metals. High concentrations of these compounds in water could result unsuitable to drink and will cause the death of aquatic life.

Eutrophication is an important type of water contamination, natural nutrient enrichment of streams and lakes. Eutrophication is commonly increased by human activities, for instance agriculture. The enrichment is mainly caused by an increase in nitrate and phosphate concentrations and it has a negative influence on water life due to the extensively growth of water plants such as algae. As a consequence, the water absorb less light and certain aerobic bacteria will become more active depleting oxygen levels, making water life impossible for fish and other organisms.

Water could also be polluted by organic compounds such as oil, plastics and pesticides, which are harmful to humans and all plants and animals in the water. Agriculture has also been affected due to groundwater is contaminated by chemicals such as fertilizers and pesticides. The routine application of fertilizers and pesticides are being recognized as water pollution. Waste water from manufacturing as well as chemical processes in industries has also contributed to water pollution. Industries have to be assured of having adequate water supply as well as to ensure that the water use in industrial processes is managed efficiently.

In most manufacturing processes, heat is produced and released into the environment considered as a waste. The way to discard the heat is to release it into the surface water. The heat released in the water has negative effects on the life water organisms. This pollution is commonly known as thermal pollution or heat pollution. The heat water will decrease the solubility of oxygen in the water and it will cause water organisms to breath faster. Many water organisms will then die from oxygen shortages becoming also more susceptible to diseases.

Suspended sediment is also dangerous water pollution because it causes reduction of light absorption in the water and the particles spread dangerous compounds such as pesticides through the water. Additionally, other minor constituents can be macro-solids such as sanitary napkins, nappies/diapers, children's toys, dead animals/plants, and gases such as hydrogen sulphide, carbon dioxide, methane, and emulsions such as paints, adhesives, and emulsified oils.

The last group but not the less important is the soluble radioactive compounds, which can cause cancer, birth defects and genetic damage being dangerous water pollutants. Summarizing, pollutants can be classified as follows in the Table 1.

Table 1. Classification of the majority water pollutants [4].

Dissolved Substances	Organic Materials (biodegradable and non-biodegradable substances)	Urea, fruit sugars, soluble proteins, drugs, pharmaceuticals, soaps and detergents. Toxins such as pesticides, poisons, herbicides.
	Inorganic Materials	Nutrients, used in part or totally by microorganisms. Ions including metal and heavy metal ions.
Colloids	Non-settleable small drops of oils and greases Organic and inorganic small solid particles	
Suspended Solids	Organic particles	Microorganisms (bacteria, viruses, worm eggs, protozoa), including pathogens. Other organic materials (faces, hair, residual particles from food, plant material, humus, paper fibres). Macro solids.
	Inorganic Particles	Sand, grit, clay, minerals. Partly organic and partly inorganic particles.

1.1.3 Water treatment

The treatment of the water is a suitable process for returning to its natural state. This process involves science and engineering and the treatment includes physical, mechanical, chemical and biological methodologies. The conversion of used water into acceptable water for the environment is called waste water treatment. Municipal and domestic waste water treatments convert used water, treated as a waste, into environmentally acceptable water. Every urban centre requires such a facility.

The conventional treatment consists of different processes including coagulation, flocculation, clarification and filtration. Moreover, disinfection at full scale is followed at the end of the process [5]. Generally, all water treatments include the removal of solids, algae, bacteria, plants, organic and inorganic compounds. The removal of solids is usually performed by filtration and sedimentation. In addition, bacteria digestion is also an important process to remove harmful pollutants.

A typical overview of a waste water treatment process is presented in Figure 2.

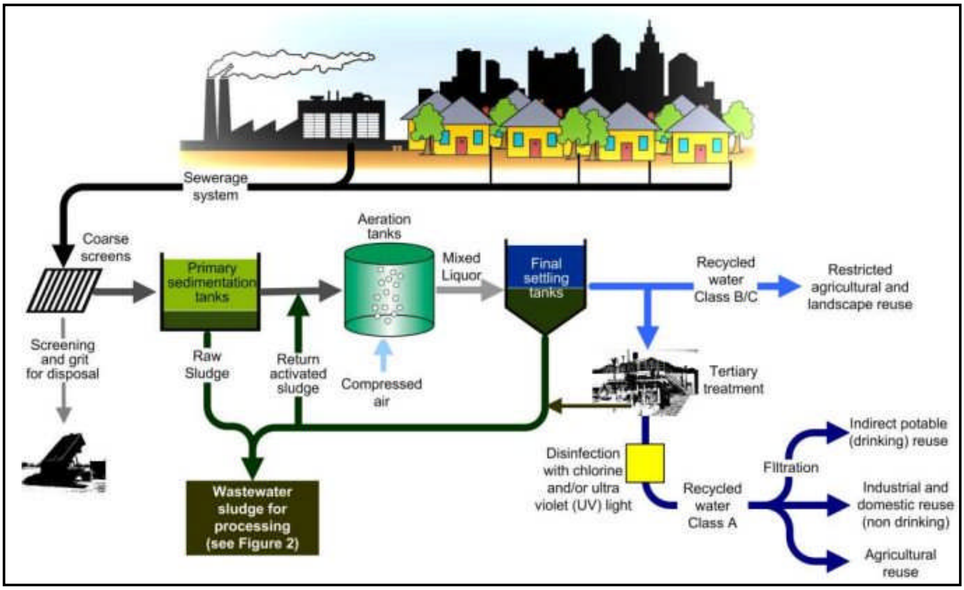

Figure 2. Conventional waste water treatment [5].

In this overview, mixed influent is used coming from industrial and municipal waste water sources. The first unit operation is a coarse screen that removes large solids parts like leaves, sticks and plastic residue. The liquid stream runs by gravity into a primary sedimentation tank where sand and silt are removed by sedimentation. After this step, the waste water enters the aeration tank where oxygen (and optionally nutrients) is fed to enable biological degradation of the organic components. The mixed liquor flows then into a final settling tank where water and the mixed liquor suspended solids are separated by gravity settling. The water flows out of the system to be discharged or reused while the mixed liquor suspended solids (waste water sludge) are partly returned to the aeration tanks and mostly collected for processing.

The conventional treatment is often preceded by pre-sedimentation, then followed by powdered activated carbon (PAC) addition, also granular activated carbon (GAC) used as a filter media, and in some cases be followed by GAC adsorption. Conventional treatment could be also preceded by pre-oxidation. Common oxidants for the disinfection process in the conventional treatment are chlorine, chloramines, chlorine dioxide or permanganate [5].

The coagulant alters and destabilizes negatively charged particulate, dissolved, and colloidal contaminants. The commonly used metal coagulants fall into two general categories: those based on aluminium and those based on iron. The aluminium coagulants include aluminium sulphate, aluminium chloride and sodium aluminate. The iron coagulants include ferric sulphate, ferrous sulphate, ferric chloride and ferric chloride sulphate. Other chemicals used as coagulants include hydrated lime and magnesium carbonate. Turbidity and total organic carbon (TOC) are measures of particulates and dissolved organics impacting coagulation [6]. During coagulation, liquid aluminum sulfate or polymer are added to untreated raw water. Enhanced coagulation is now widely practiced for removing disinfection by-product (DBP) precursors, and it also removes inorganic, particulates, and color causing compounds. Removing these contaminants using coagulation depends on the amount of coagulant added. It is important to determine the optimal dose for coagulation. In addition, the temperature also impacts the coagulation process because it affects the viscosity of the water. Therefore, lower temperature waters can decrease the hydrolysis and precipitation kinetics. For some treatment objectives, other parameters like iron, manganese or sulfate impact coagulation.

During flocculation, there are two primary destabilization mechanisms in water treatment: charge neutralization and sweep flocculation. Adding excess coagulant beyond charge neutralization results in the formation of metal coagulant precipitates. The metal hydroxide compounds, such as aluminum hydroxide and iron hydroxide, are heavy, sticky and larger in particle size. Sweep flocculation occurs when colloidal contaminants are entrained or swept down by the precipitates as they become in suspension.

Following flocculation, agglomerated particles enter into the clarification unit where they are removed by sedimentation, by gravity or they are floated from the surface of the clarification unit. Then, in the sedimentation processes, the majority of the solids are removed by gravitational sedimentation. The particles that did not settle, and remained suspended, are removed during the filtration process.

Dual-media filter comprised of anthracite and sand is the most commonly used filter type in the conventional treatment process. Moreover, sand mono-media and multi-media filters, as well as the granular activated carbon filter, are also used in water treatment. The majority of suspended particles are removed in the top portion of the media filter during filtration process.

Water is disinfected before it enters the distribution system to ensure that any disease-causing bacteria, viruses, and parasites are destroyed. As mentioned before, chlorine is used because it is a very effective disinfectant, and residual concentrations can be maintained to protect against possible biological contamination in the water distribution system.

As mentioned before, throughout the world, water scarcity is being recognized as a present or future threat to human activity. Therefore, it is required to find alternative water resources such as desalination. Desalination refers to any process that removes salts and minerals from saline water. Salty water is desalinated to produce drinking water for human consumption as well as for irrigation [7]. Reverse osmosis is currently the most commonly method for desalination. Although some substances dissolved in water, such as calcium carbonate, can be removed by chemical treatment, other common constituents, like sodium chloride, require more technically sophisticated methods, collectively known as desalination. In the past, the difficulty and expense of removing various dissolved salts from water made saline waters an impractical source of potable water. Desalination technology has been around for the better part of the last century. Many countries, municipalities, oil and gas, mining, resorts, with services and ships have the need to produce fresh water by desalination because of their lack of natural sources of potable water. Therefore, desalination technology has brought clean water and hence commercial and industrial development to different parts of the world that otherwise may have remained unproductive. Not only has development been enhanced by this technology but, more importantly, the health of many people has been improved by the supply of sanitary fresh water supplies [7].

1.1.4 Water analysis

The purpose of the waste water treatment plant (WWTP) and desalination plants is to ensure that treated water can be either returned to the natural water cycle without harming the environment (discharge) or treated up to a quality that meets the needs of end use application of the reused water. The treatment plants are always obliged to comply with certain minimum requirements, which depend on local legislation. These threshold values can only be monitored correctly and treatment processes can only be controlled economically with the help of accurate and reliable analysis. To be able to comply with the legal requirements on treated water, plant operators must control the treatment process carefully, so that they can intervene promptly to prevent limit values from being exceeded. Besides chemical and physical methods, depending on the type of water to be treated, different essential parameters should be analyzed. For instance, waste water treatment is essentially based on biological treatment by microorganisms in activated sludge. Knowledge of the nutrient requirements and the composition of the activated sludge are therefore needed if the plant is to operate at maximum efficiency. On the other hand, desalination systems are more focused on determining complete ions analysis [7].

Our research will be more focused on waste water treatment plant. Therefore, in this section it is more detailed the general quality parameters regarding waste water.

The general waste water quality parameters always include basic parameters such as particle and solids analysis, including total suspended solids (TSS) and turbidity, nutrient analysis (C:N:P), salinity, conductivity, pH, chemical oxygen demand (COD), biological oxygen demand (BOD), total organic carbon (TOC) and temperature. These parameters provide rough idea on the efficiency of the waste water treatment process, level of treatment steps needed to reach final effluent quality.

Taking into account all mentioned before, the main water analysis and basic parameters to be considered for analyzing are described below, including nutrients, carbon, nitrogen, phosphorous, microbiological quality and chemical quality.

Nutrients

A balanced nutrient ratio is essential if the microorganisms are to function efficiently. The most important of these nutrients are carbon, nitrogen and phosphorus. Other trace elements needed to build cells, such as potassium, magnesium, manganese, iron, copper, zinc and nickel, vitamins and growth factors are usually present in municipal waste water, or they provide by the microorganisms in the activated sludge.

Nitrogen and phosphorus compounds are not toxic, but encourage the growth of algae in surface waters, which results in oxygen depletion of the surface water through eutrophication, a problem mentioned before. The elimination of ammonium, nitrite, nitrate, total nitrogen, orthophosphate and total phosphate plays a key role in waste water treatment processes.

The content of the individual nutrients in waste water should correspond to the needs of the bacteria in the activated sludge, and there should be a balanced relationship between C, N and P. This is crucial to the effectiveness of the biodegradation processes. During aerobic waste water treatment, the C:N:P ratio should be in the range between 100:10:1 and 100:5:1. However, all sorts of industrial plants, regional differences in eating habits (disposal of different kitchen wastes through the drains), and the nature of the soil and drinking water cause waste water to vary widely in its composition. The composition of the individual nutrients is measured individually and described below.

Carbon

Carbon is the principal component of the organic substances found in waste water. It is biodegraded by the microorganisms in activated sludge mostly in the aerobic zone of the process although it participates in other zones of more advanced treatment processes. The microorganisms use carbon compounds to build their cell structures and to generate energy. Common compound parameters to be determined are COD, BOD and TOC, all measurements can be conducted according to Standard Methods 5220B [5].

COD gives a value of the amount of the oxygen necessary to chemically oxidize the substances present in waste water. BOD is an expression for the quantity of oxygen required for biological degradation of organic matter in a waste water sample, expressed as BOD5 for 5 days of incubation, the most common incubation period. BOD measurement is therefore used as a basis for the detection of biologically degradable organic matter in water. BOD measurement is therefore an important measurement of the effects of domestic and industrial waste water on sewage plants and outflow points. The ratio of COD and BOD5 parameters is a measure of the biodegradability of the waste water pollution load. If the COD:BOD_5 ratio does not exceed 2:1, the biodegradability is said to be good. Higher values indicate the presence of poorly biodegradable substances.

During the last years, TOC has gained importance in waste water analysis. In particular, in relation with COD, TOC offers specific information regarding the source and type of the organic load in waste water. TOC is also much faster analysis than BOD and may be used for active process monitoring and control. TOC in waste water streams is required in an increasing number of territories, enforced by environmental ruling or compliance.

As all organic carbon compounds are determined and specified in terms of carbon mass, TOC is an exactly definable absolute quantity and is directly measurable (mg $C\cdot L^{-1}$). TOC on its own sheds no light on the oxidisability of the measured carbon or the amount of oxygen needed for its biodegradation. However, the ratio COD:TOC can provide important information about the presence of certain organic compounds, such as alcohols and proteins.

In addition, waste water researchers frequently use dissolved organic carbon (DOC), UV254, and specific ultraviolet absorption (SUVA254) to obtain information about the organic carbon in natural waters. These parameters are not specific but they give a general idea of organic content and are very easy to obtain. The principle behind this method is that UV-absorbing constituents will absorb UV light in proportion to their concentration. UV254 is an indicator of organic constituents and SUVA is an indicator of the humic content of water. These parameters are also included in the USEPA's Disinfectants/Disinfection By-Products (D/DBP) Rule [8]. Measurement methods and protocols for these parameters are described in Standard Methods for the Examination of Water and Waste water (published by the American Public Health Association, Water Environment Federation, and the American Water Works Association) [5, 9-10], USEPA's Enhanced Coagulation and Enhanced Precipitative Softening Guidance Manual [11], and the recently published USEPA Method 415.3 [12].

Nitrogen

In the influent of waste water treatment plants, nitrogen is present in organically bonded form (organic N) and as ammonium nitrogen (NH_4-N). During biological waste water treatment, organic N is converted to NH_4-N by the bacteria in the activated sludge. This NH_4-N and the NH_4-N from the influent are converted to nitrite, which in turn is converted to nitrate (nitrification). The nitrogen compounds that are not biodegraded in the activated sludge are converted under anoxic conditions (absence of dissolved O_2) to elementary nitrogen (denitrification). This escapes into the atmosphere as N_2.

Nitrogen compounds are determined as organic N, inorganic N (NH_4-N, NO_2-N, NO_3-N) and TN (total nitrogen). This parameter is determined frequently in the waste water sector, to obtain information about the level of degradation in waste water treatment plants. Nitrogen is one of the five major elements found in organic materials such as protein. This fact was recognized by Johan Kjeldahl, who used it as a method of determining the amount of protein in samples taken from a wide variety of organisms [13]. The Kjeldahl nitrogen in the sample is first converted to ammonia by metal-catalyzed acid digestion. The resulting ammonia is then separated from the sample by distillation. The ammonia released is captured in a dilute sulfuric acid solution. For inorganic nitrogen, Standard Methods 4500 [14] can be used to measure ammonium (NH_4^+) and nitrogen oxide compounds (NO_x) based on spectrophotometry.

Phosphorous

In the environment, phosphorus switches between organic and inorganic forms due to the action of bacteria. Inorganic phosphate (often used as a synonym for orthophosphate) is an essential plant nutrient, and promotes the growth of algae and other aquatic plants in surface waters. Then, orthophosphate species are the only form of phosphorus that can be use by micro-organisms and plants and converted to organic phosphorus. That is why WWTP should be prepared to eliminate phosphates, for example biologically, with nitrification and denitrification or chemically, with adequate chemicals.

The phosphorous load in the influent of a waste water treatment plant is made up of orthophosphate-phosphorus, polyphosphates and organic phosphorus compounds. Together, they give the sum parameter ‘total phosphorus’. During biological waste water treatment, polyphosphates and organically bonded phosphorus are converted to orthophosphate. The P demand of the organisms is due to the special role of phosphorus in their energy metabolism. P is needed to form the cell membrane and DNA. Some of the excess phosphorus in waste water is eliminated biologically (bio-P) by fixing within the solids in an anaerobic treatment zone. The rest can be removed by chemical-physical phosphate precipitation. In the absence of phosphorus in the incoming waste water, WWTPs can add phosphorus as nutrient to aid treatment efficiency. There are several methods available following the Standard Methods for the Examination of Water and Wastewater [15].

Microbiological quality

Water is the most important potential common source of infectious diseases, caused by a variety of bacteria, viruses and protozoa. Generally, the largest microbiological risk with water is associated with ingestion of water that is contaminated with human or animal faeces, since they can be a source of pathogenic bacteria, viruses, protozoa and helminthes. Therefore, the used water quality indicators are usually associated with the intestinal tract; their presence indicates the fecal contamination of the water source [16-17].

Elimination of the faecal microbial contamination is especially important in point of source, municipal waste water treatment plants. When waste water is reused, a certain set of microbiological quality limits are always required. Depending on the end use of the water, the limits vary. The most stringent effluent quality limits is for water reuse applications where treated waste water can be consumed by humans (indirect and direct potable reuse, irrigation). The water regulations will be covered later on this Tesis.

Chemical quality

Water is contaminated through its use by broad range of chemical components. These components find its origin in human uses (anthropogenic source), domestic, industrial or agricultural use of the original water source. Not all of the components discharged in the water make their way to the waste water treatment system due to adsorption in clay or other sediment, especially for components from agricultural source. For example, the presence of a wide variety of pharmaceutical and personal care products (PPCP) in water and waste water has been frequently reported. These compounds are a source of concern because they are used and released in large quantities and their physical and chemical properties contribute to their widespread distribution into the environment. The presence of small concentration of PPCP has been associated to chronic toxicity, endocrine disruption and the development of pathogen resistance. The consequences can be long-lasting in aquatic organisms as they are subjected to multigenerational exposure [18]. The presence of micropollutants also endangers the reuse of treated waste water, a generally proposed solution to achieve a sustainable water cycle management. Furthermore, many of the components are difficult to biodegrade but can be removed to certain extend through biosorption [18] on the biomass which is removed from the WWTP or through more advanced processes (e.g. enzymatic, catalytic, ozone). The different organic compounds that are found can be classified as follows based on its origin, including agricultural water use (such as pesticides, herbicides), industrial and domestic water use PPPCPs, endocrine disrupting components (EDCs), disinfection by-products (DBPs), fats, oils and greases (FOG), fragrance allergens, odours and volatile organic compounds (VOCs).

During the last decade, the use of many chemical substances without any control and studies about their behavior in the environment has become a focus of interest for the European Union (EU). Face to their capacity to be persistent and to have a potential estrogenic activity, the aim of the registration evaluation and authorization of chemicals (REACH) system which came into force in June 2007 is to protect human health and the environment from the impact of more than 32 millions of chemical substances registered to the Chemical Abstract Service [19-21].

1.1.5 Quality parameters of importance in different end user applications

Human activities commonly affect the distribution, quantity, and chemical quality of water resources. The range in human activities that affect the interaction of ground water and surface water is broad. In the present section the most important applications are described, which are drinking water, industrial and agricultural applications.

Drinking water

The majority of surface water on the planet is neither potable nor toxic. This remains true when seawater in the oceans (which is too salty to drink) is not counted. Another general perception of water quality is the property that tells whether water is polluted or not. In fact, water quality is a complex subject, in part because water is a complex medium intrinsically tied to the ecology of the Earth.

Contaminants that may be in untreated water include microorganisms such as viruses, protozoa and bacteria, inorganic contaminants such as salts and metals, organic chemical contaminants from industrial processes, pesticides and herbicides, and radioactive contaminants. Water quality depends on the local geology and ecosystem, as well as human uses such as sewage dispersion and industrial pollution.

Water quality regulated by the International Organization for Standardization (ISO) is covered in the next section 1.1.6, including the water regulations.

Industrial

The quality parameters for industrial quality water from municipal waste water effluent do not differ drastically from standards used for industrial water treatment using conventional water sources such as surface or well waters. The key requirements and treatment targets are written around total dissolved solids (TDS)/conductivity, turbidity, individual inorganic species (Cl^-, Na^+, Mg^{2+}, Ca^{2+}, NH_4^+, NO_3^-, SO_4^{2-}, SiO_2, HCO_3^-, P), trace elements and heavy metals, TOC and pH. The differentiator to conventional water sources is that concentrations of certain parameters, like NH_4^+, NO_3^-, TOC, can be much higher in municipal waste water effluent than in conventional brackish waters and thus they can become the most stringent quality limit. Therefore, industrial water end use application requires treatment with advance tertiary membrane treatments, such as RO membranes.

Agricultural

In agricultural end user applications the main quality parameters have health or agricultural significance. The health significance is related to the pathogenic organisms present in the waste water and the treated water quality is controlled by specific indicator organisms.

The physical and mechanical properties of the soil, such as dispersion of particles, stability of aggregates, soil structure and permeability, are very sensitive to the type of exchangeable ions present in irrigation water [22].

Important agricultural water quality parameters include a number of specific properties of water that are relevant in relation to the yield and quality crops, maintenance of soil productivity and protection of the environment [23]. These parameters mainly consist of certain physical and chemical characteristics of the water. The primary waste water quality parameters of importance from an agricultural viewpoint are: Total Dissolved Solids/Conductivity, temperature, color, hardness, anions and cations (Ca^{2+}, Mg^{2+}, Na^+, K^+, CO_3^{2-}, HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-, PO_4^{3-}), especially phytoxic species (B, Cl^-, Na^+, HCO_3^-), trace elements: Al, Be, Co, F, Fe, Li, Mn, Mo, Se, Sn, Ti, W,V, heavy metals: As, Cd, Cr, Cu, Pb, Hg, Zn, and pH.

1.1.6 Water regulations

Many countries have a national environmental protection agency (EPA). These agencies and departments are responsible for all aspects of the environment; regulation of sanitation and waste water management activities is just one of their duties. National environmental protection bodies often set national environmental quality standards, which in turn are the responsibility of state or provincial environmental agencies to enforce. In some cases, the detailed definition and implementation of standards is delegated to state EPAs, or to river basin or watershed management boards, which are responsible for water quality within a defined watershed.

Many developed countries specify standards to be applied in their own country. In Europe, this includes the European Drinking Water Directive [24] and in the USA the United States EPA establishes standards as required by the Safe Drinking Water Act [25]. For countries without a legislative or administrative framework for such standards, the World Health Organization (WHO) publishes guidelines on the standards that should be achieved [26]. In addition, the WHO set up some guidelines for drinking-water quality which are the international reference point for standards setting and drinking-water safety. The latest guidelines drew up by the WHO are those agreed in Geneva, 1993.

Where drinking water quality standards do exist, most are expressed as guidelines or targets rather than requirements, and very few water standards have any legal basis or, are subject to enforcement. Two exceptions are the European Drinking Water Directive and the Safe Drinking Water Act in the USA, which require legal compliance with specific standards. These directives have been introduced before. Furthermore, in Europe, this includes a requirement for member states to enact appropriate local legislation to mandate the directive in each country. Routine inspection and, where required, enforcement is enacted by means of penalties imposed by the European Commission on non-compliant nations. Therefore, on the 23th of October of 2000, the Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for the Community action in the field of water policy or, in other words, the EU Water Framework Directive [27].

Regarding the Spanish legislation in terms of water quality, there are two standards to follow: the EU Water Framework Directive, mentioned before, and the Spanish Directive, within the *Real Decreto* 2090/2008 [28].

There is no guideline for some of the elements and substances which are taken into account in the present Thesis. This is because there are not sufficient studies about the effects of the substance on the organism, and therefore it is not possible to define a guideline limit. In other cases, the reason for a non-existing guideline is the impossibility of that substance to reach a dangerous concentration in water, due to its insolubility or its scarcity.

Summarizing this water section, increasing demand for water and development of water scarce areas are driving the needs for additional water resources. The two foreseeable non-conventional water sources which could answer this global challenge are desalinated sea water and treated wastewater. Therefore, membrane filtration is an advanced water treatment technology which can treat municipal and industrial water to almost any purified state. Membranes have very well defined physical properties which guarantee rejection of various contaminants including pathogens, enabling re-use of treated waste water in about any application including high quality industrial process water and drinking water.

In the following section, these advanced membrane water treatments are being described.

1.2. Reverse osmosis membrane treatments

Membrane technology has become a widely accepted separation technology over the past decennia for water treatments. Membranes can work with lower energy consumption than traditional thermal and distillation processes. Membranes are used for play a key role in water process from groundwater, surface water or waste water [29].

Membrane filtration has become the technology of choice for industries seeking to reuse their waste water and minimize water discharges, due to the growing global demand for clean water and the increasing environmental concern. In the present Doctoral Thesis, several analytical methodologies have been applied in order to study the water treated by reverse osmosis membranes and the obtained water.

1.2.1 Separation technologies

The various filtration technologies which currently exist can be categorized on the basis of the size of the particles that they can remove from a feed stream. Therefore, membranes are classified according to the pore diameter: as wide pore (pore diameter between 10 nm and 50 microns) and fine pore (diameter between 1 and 10 nm) [30].

Some of these membranes have almost perfect and parallel cylindrical pores, and they are being obtained from a polymer layer with a thickness between 10 and 20 microns. In dense membranes, the influent stream must pass through the material which constitutes the membrane. Then, it is produced a separation between the molecular level of the soluble species and solvent particle species. These are also called semi-permeable or perm-selective membranes, and they are used to separate mixtures of gases or liquids, as well as in the desalination processes of reverse osmosis. In other words, the solution diffusion model, which is not covered in this thesis, makes two assumptions. The first is that the solvents dissolve inside the membrane, and thereafter they diffuse through the dense film according to the present concentration gradient. In the reverse osmosis, separation occurs because of the different solubility and mobility of each specie throughout the membrane.

To resolve the issue of insufficient water for sustainable development, countries recognize that membrane processes will play an increasingly significant role as the dominant technology in water purification.

The filtration processes commonly used for desalination and water reclamation include macrofiltration, microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO) and ion exchange resins. Water reclamation typically employs microfiltration/ultrafiltration to pretreat biologically treated waste water before the RO process. As a general scheme, in Figure 3 the main filtration technologies are shown.

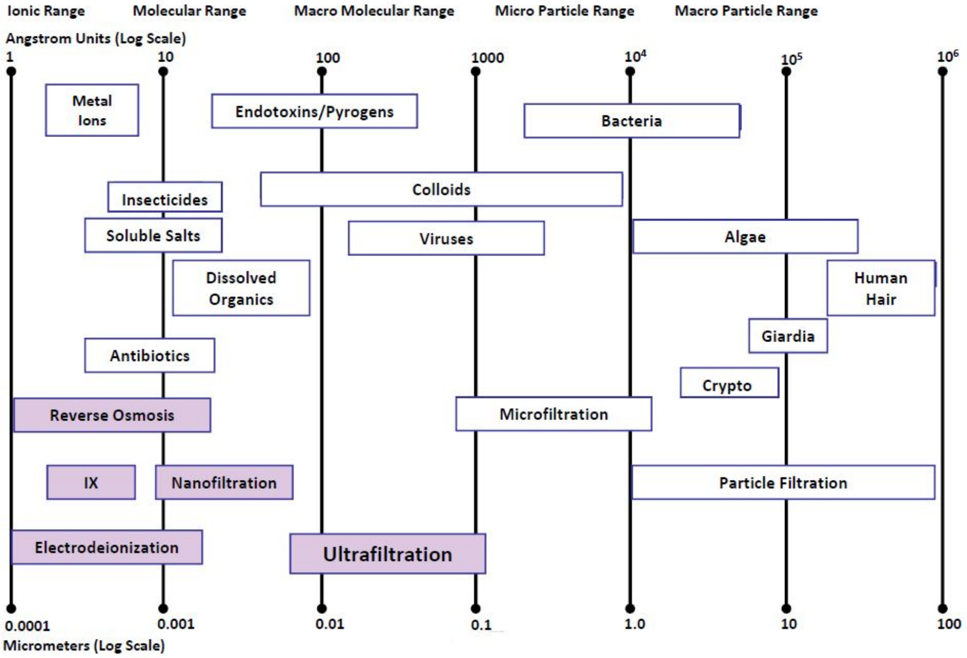

Figure 3. Membrane filtration spectrum.

Microfiltration

Microfiltration removes particles in the range of approximately 0.1 µm to 1 µm. In general, suspended particles and large colloids are rejected while macromolecules and dissolved solids pass through the MF membrane. Applications include removal of bacteria, flocculated materials, or TSS (total suspended solids). Membrane pressures are typically 0.7-1 bar [30].

Microfiltration membranes have pore diameters that range typically from 0.1 µm to 1 µm [31]. These pores are basically similar to the pores used by the ultrafiltration membranes but bigger. Its filtration mechanism is also described by the pore flow model as it achieves separation using the same sieving mechanism.

Ultrafiltration

Ultrafiltration membranes have pore diameters that range typically from 1 nm to 0.1 µm [32], and are designed to remove contaminants such as particles, microorganisms (including viruses), suspended solids, precipitated metals (such as Fe or Mn), colloids, and macromolecules. The driving force is typically a pressure gradient between the filtrate and the feed membrane side, with a membrane pressure typically between 1 bar to 7 bar [30] depending on the pore size. The separation principle is the sieving mechanism (size exclusion) and it is described by the pore flow filtration model. The filtration principle results into a convective flux across the membrane. All dissolved salts and smaller molecules pass through the membrane. Substances rejected by the membrane include colloids, proteins, microbiological contaminants, and large organic molecules. Most UF membranes have molecular weight cut-off values between 1,000 and 150,000 Da.

The ultrafiltration membranes technology most widely used is the pressurized technology. It uses a pressure vessel to accommodate bundles of hollow fibers. UF membrane filtration also offers solutions for large-scale municipal applications which produce potable water from a variety of source waters. UF filtration can be used as an alternative for media filtration, flocculation, sediment purification techniques or adsorption (e.g. active carbon filters, ion exchangers) [33-34].

Nanofiltration

Nanofiltration refers to a membrane process which rejects particles in the approximate size range of 1 nm, hence the term nanofiltration. NF membranes have pore diameters that range from 0.5 nm to 1.5 nm. These pores have the particularity of being between truly microporus membranes and clearly dense films. Therefore, mass transfer through nanofiltration membranes is described using both pore flow and solution diffusion models. This happens because if membrane polymer chains are very stiff, the molecular motion of the polymer is restricted, and semi-permanent microcavities are formed which are interconnected.

NF operates in the realm between UF and reverse osmosis. Organic molecules with molecular weights greater than 200-400 g·mol^{-1} are rejected. Also, dissolved salts are rejected in the range of 20-98%. Salts which have monovalent anions (e.g. sodium chloride or calcium chloride) have rejections of 20-80%, whereas salts with divalent anions (e.g. magnesium sulfate) have higher rejections of 90-98%. Typical applications include removal of color and total organic carbon (TOC) from surface water, removal of hardness or radium from well water, overall reduction of total dissolved solids (TDS), and the separation of organic from inorganic matter in food and waste water applications. Transmembrane pressures are typically 3.5 to 16 bar [30].

Reverse Osmosis

Reverse osmosis is a process which decreases the particles down to the molecular level in order to create clean pure water. RO is the finest level of filtration available. The RO membrane acts as a barrier to all dissolved salts and inorganic molecules, as well as organic molecules with a molecular weight greater than approximately 100 $g \cdot mol^{-1}$. Water molecules, on the other hand, pass freely through the membrane creating a purified product stream. RO rejects by particle size as well as by charge exclusion. Rejection of dissolved salts is typically 95% to 99%.

RO is often used in the production of ultrapure water for use in the semiconductor industry, power industry (boiler feed water), and medical/laboratory applications. Utilizing RO prior to ion exchange dramatically reduces operating costs and regeneration frequency of the ion exchange resin system. Operational pressures for RO typically range from 5 bar for brackish water to greater than 84 bar for seawater [30].

In the present Doctoral Thesis, the main focus is reverse osmosis membrane processes. Therefore, more detailed information about this membrane technology is described.

1.2.2 Reverse osmosis membranes

Since the development of RO, NF and UF as practical unit operations in the late 1950's and early 1960's, the scope for their application has been continually expanding. Initially, reverse osmosis was applied to the desalination of seawater and brackish water. Increased demands on the industry to conserve water, reduce energy consumption, control pollution and reclaim useful materials from waste streams have made new applications economically attractive. In addition, advances in the fields of biotechnology and pharmaceuticals, coupled with advances in membrane development, are making membranes an important separation step, which, compared to distillation, offers energy savings and does not lead to thermal degradation of the products.

New products have been developed and existing products have undergone improvements in their ability to improve permeate quality and lower the total cost of water. In general, RO membranes now offer the possibility of higher rejection of salts at significantly reduce operating pressures, and therefore, reduce costs. NF membrane technology provides the capability of some selectivity in the rejection of certain salts and compounds at relatively low operating pressures [29].

In the present Doctoral Thesis, the main focus is reverse osmosis membrane processes. Therefore, more detailed information about this membrane technology is described.

RO systems are used to produce high quality water at a certain flow rate from low quality influent water at a certain feed pressure and with a minimum of maintenance. The main performance criteria of an RO system is the effluent flow rate at a given pressure (or the pressure at a given flow rate) and the salt rejection. The corresponding criteria for the membrane performance are the water permeability and the salt permeability. A third important performance criterion is the pressure drop from the feed side to the concentrate side. Trouble arises if one or more of these three performance criteria do not meet the design values.

Membrane characteristics

The composite polyamide flat sheet product of several manufacturers dominates modern RO membrane technology. New chemical formulas are constantly being developed. The construction and configuration of the membrane element is schematically shown in the Figure 4. Three different parts are differentiated, including the feed spacer, the membrane leaf and the permeate spacer.

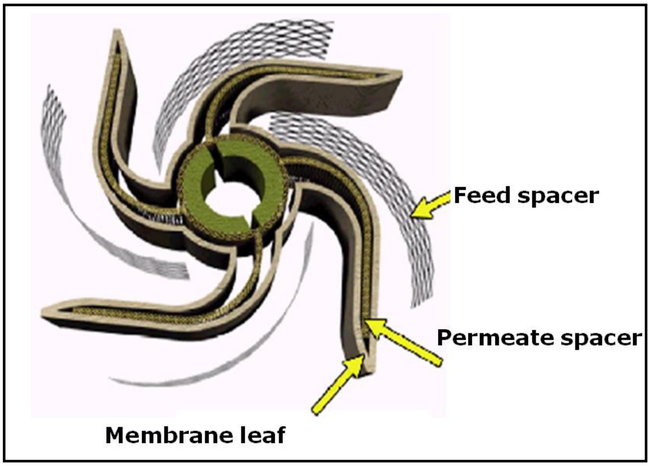

Figure 4. Spiral wound RO membrane.

The membranes used in the RO process are usually either made from polyamides or from cellulose sources. Cellulose acetate membranes in both flat sheet and hollow fine-fiber configuration are still manufactured [35].

The membrane properties which influence this process of transport or permeation are the thickness, the physic-chemical interactions between analyte, water and membrane, such as solubility of the permeate species in the membrane, the electric charge and the density, the width and the tortuosity of the pores and the charge mobility of ions transported. The mass transport across the membrane may be due to the diffusion of molecules from the external phase, or a convective flow, caused by an electric field or by a gradient of concentration, temperature or pressure acting separately or simultaneously.

1.2.3 Dow Water and Process Solutions (DW&PS)

For over 50 years, Dow Water & Process Solutions, a business unit of The Dow Chemical Company has been a leading supplier of advanced water purification and separation technologies worldwide [29]. Their membrane technologies are used throughout the world to improve the quality of drinking water and the water that is critical to essential industrial process like chemical processing, power generation and the manufacturing of food and pharmaceuticals.

The Dow FILMTEC™ membrane is a thin film composite membrane consisting of three layers: a polyester support web, a microporous polysulfone interlayer, and an ultra thin polyamide barrier layer on the top surface. Each layer is tailored to specific requirements. A schematic diagram of the membrane is shown in Figure 5.

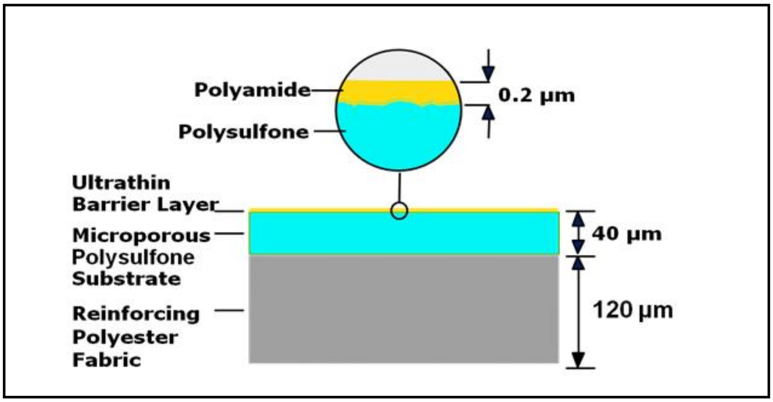

Figure 5. Schematic cross-section of a Dow FILMTEC™ thin film composite membrane.

FILMTEC™ produces different types of polyamide and piperazine membranes for use in water purification. The first is the FT30 chemistry, which is an aromatic polyamide and is used in all FILMTEC™ reverse osmosis membranes patented by John Caddotte at

FILMTEC™ in 1969 and NF90 nanofiltration membrane, which is a mixed aromatic and aliphatic polyamide used in all nanofiltration membranes and was also initially developed by John Caddotte at FILMTEC™. The membranes cover a flux performance range from 1 to 14 l/m^{2}h bar [30].

Figure 6 represents the approximate structure of the FT-30 aromatic polyamide membrane. The presence of both amine and carboxylate end groups are shown.

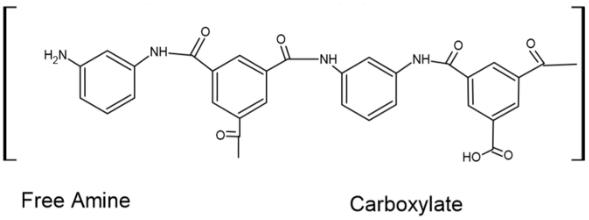

Figure 6. Barrier layer of the FT30 aromatic polyamide membrane [30].

As mentioned before, the parameters which characterize the performance of a membrane are the water permeability and the solute permeability. The ideal reverse osmosis membrane has very high water permeability and a zero salt permeability.

1.2.4 Reverse osmosis operation parameters

In practice, RO and NF membranes are applied as a cross-flow filtration process, as it is represented in the Figure 7.

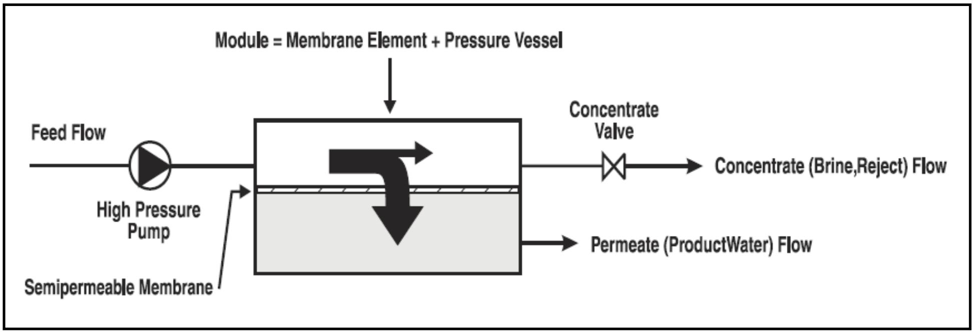

Figure 7. Cross-flow membrane filtration [30].

Cross-flow membrane filtration is used for the removal of small particles and dissolved salts. Cross-flow membrane filtration uses a pressurized feed stream which flows parallel to the membrane surface. It is represented in the Figure 7. A portion of this stream passes through the membrane, leaving behind the rejected particles in the concentrated remainder of the stream. Thus, one feed stream is separated into two exit streams: the solution passing through the membrane surface (permeate or effluent) and the remaining concentrate stream.

The main operational parameters in RO influencing water and salt transport across the membrane are recovery, rejection, salt passage, flow and flux.

Recovery is the ration between influent water that emerges from the membrane system as product water effluent or permeate. Rejection is the percentage of solute concentration removed from system by the membrane. Salt passage is the opposite of "rejection", it is the percentage of dissolved constituents (contaminants) in the influent water allowed to pass through the membrane. Flow is the rate of influent/effluent water introduced to the membrane element or membrane system, usually measured in gallons per minute (gpm) or cubic meters per hour (m^3/h). Flux is the rate of permeate flow per unit of membrane area, usually measured in gallons per square foot per day (gfd) or liters per square meter and hour (l/m^2h).

Permeate flux and salt rejection are the key performance parameters of a reverse osmosis or a nanofiltration process. Under specific reference conditions, flux and rejection are intrinsic properties of membrane performance. Flux and rejection of a membrane system are mainly influenced by variable parameters including: pressure, temperature, recovery, feed water and salt concentration. In practice, there is normally an overlap of two or more effects. Table 2 summarizes these factors.

All these factors can be understood with the solution diffusion model [30]. The performance of a specified RO system is defined by its feed pressure (or permeate flow, if the pressure is specified) and its salt passage.

The following equation describes that the permeate flow F_w through an RO membrane is directly proportional to the wetted surface area S multiplied by the net driving pressure $(\Delta P - \Delta \pi)$. The proportionally constant is the membrane permeability coefficient or A-value. Water flux equation has the form:

$$F_w = (A)\ (S)\ (\Delta P - \Delta \pi) \qquad \text{[Equation 1]}$$

The salt passage is by diffusion; hence the salt flux F_s is proportional to the salt concentration difference between both sides of membrane.

The proportionally constant is the salt diffusion coefficient or B-value.

$$F_s = B\,(C_{fc} - C_p) \qquad \text{[Equation 2]}$$

Where: C_{fc} is the feed concentrate average concentration and C_p is the average permeate concentration.

Table 2. Factors influencing reverse osmosis performance [30].

Factors	**Permeate Flow**	**Salt Passage**
Pressure increase	Increase	Decrease
Temperature increase	Increase	Increase
Feed flow increase	Increase	Increase
Feed salt concentration increase	Decrease	Increase

Performances issues are typically experienced as a reduced normalized permeate flow rate and an increased normalized salt passage (changes are only perceived as a problem if these are significant).

The permeability of solutes decreases (the rejection increases) with an increase in the:

- Degree of dissociation: weak acids, for example lactic acid, are rejected much better at higher pH when the dissociation is high.
- Ionic charge: e.g. divalent ions are better rejected than monovalent ions.
- Molecular weight: higher molecular weight species are better rejected.
- Non-polarity: less polar substances are rejected better.
- Degree of hydration: highly hydrated species, e.g. chloride, are better rejected than less hydrated ones, such as nitrate.
- Degree of molecular branching: such as isopropanol is better rejected than n-propanol.

Membrane systems are typically designed and operated at constant water productivity. Membranes with high water permeability require a low feed pressure and thus a low energy to operate at a given flux.

Table 3 shows a comparison of the performance of different membranes based on a given flux as typically encountered in membrane systems.

Table 3. Performance of some commercial FILMTEC™ membranes [30].

	SW30HR-380	**BW30-4040**	**XLE-440**
Feed pressure (psi)	800	225	125
Feed pressure (bar)	55	15.5	8.6
Sodium chloride NaCl (Rejection %)	99.60	99.50	99.00

Standard test conditions at 18 GFC (gallon/(ft^2·day) (30 l/m^{2}h), (32000 mg/L NaCl concentration, 25ºC, pH 8, 8% recovery per SW30HR-380 element; 2000 mg/L NaCl concentration, 25ºC, pH 7-8, 15% recovery per BW30-4040 and XLE-440 elements.

As a general rule, membranes with high water permeability (low feed pressure) also have a higher salt permeability compared to membranes with lower water permeability.

1.2.5 Membrane fouling

The primary objective of RO influent water pretreatment is to ensure that the RO membrane is not adversely affected by fouling, scaling or chemically and physically degraded due to they are the main limitation of RO processes. Fouling refers to particulate matter such as silt, clay, suspended solids, biological slime, algae, silica, iron flocks and other suspended matter that adheres to and accumulates on the membrane surface. Scaling is referred to as the buildup of a mineral salt layer on the membrane surface due to both direct surface crystallization and deposition of precipitated salt crystals onto the membrane surface. More specifically, colloidal fouling refers to the entrapment of particulate or colloidal matter such as iron flocks or silt, biological fouling (biofouling) is the growth of a biofilm, and organic fouling is the adsorption of specific organic compounds such as humic substances and oil on to the membrane surface.

The evaluation of the performance symptoms helps to identify the causes. Certain combinations of symptoms may indicate the direct cause, which are summarised in Table 4.

Table 4. Symptoms indicating the direct cause [30].

DIRECT CAUSE	SYMPTOMS OBSERVED		
	Permeate Flow	**Salt Passage**	**Pressure Drop**
Scaling fouling	Decrease	Increase	Increase
Biofouling	Decrease	Normal	Increase
Organic fouling	Decrease	Decrease	Normal
Chemical and mechanical damage	Increase	Increase	Normal
Leaks, mechanical damage	Normal	Increase	Normal

Fouling typically occurs in the lead membrane elements, such as initial stages, and progresses gradually toward the tail elements. Typically, scaling occurs in the last elements, where the salt concentration in the feed is high. The type of pretreatment system depends on a large extent on feed water source, such as well water, surface water, industrial and municipal waste water. The visual inspection of the element may already reveal the cause of the problem. Figure 8 shows an example of sand from a media filter deposited onto the face of the lead element.

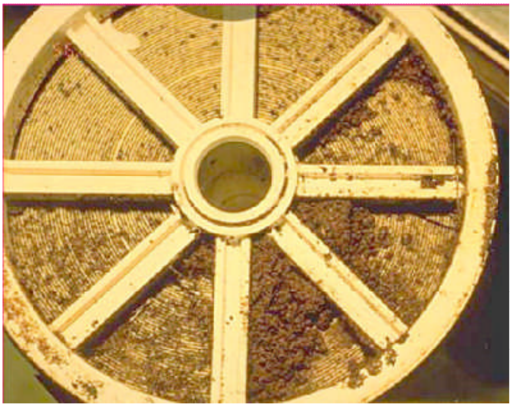

Figure 8. Particulate fouling [30].

Particle fouling can be prevented by using appropriate pre-treatment methods. These include sand and multimedia filters and cartridge filters; the finest pre-filtration method is UF.

Metal fouling is very common. As an example, iron fouling can be recognized just by its typical red/brown color. Humid metal hydroxide fouling feels soft to the touch and can be wiped off easily, as it is shown in Figure 9.

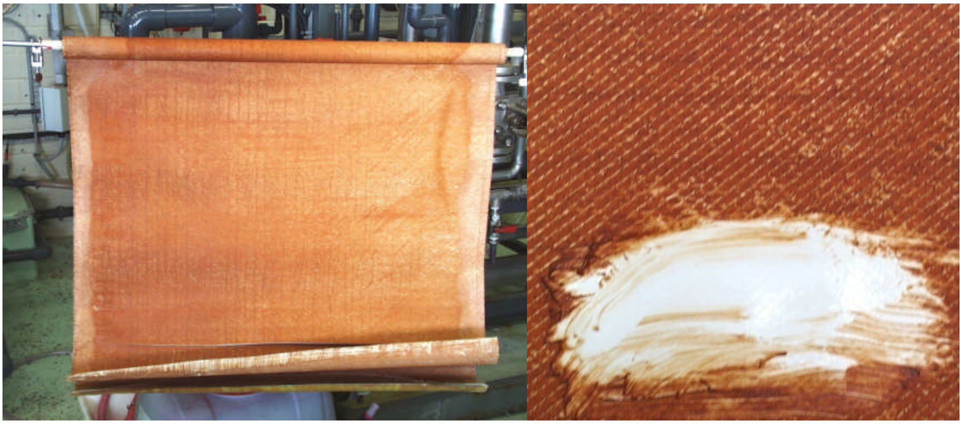

Figure 9. Iron fouling [30].

Biofouling is the development of a layer of bacteria and other microorganisms, embedded in their products, such as extracellular polymers (EPS), on the surface of the membrane and feed spacer. It occurs due to the feed water has a high biogrowth potential and the operation procedures are not adequate. Biofouling may lead to feed spacer being pushed out from the scroll as seen in Figure 10.

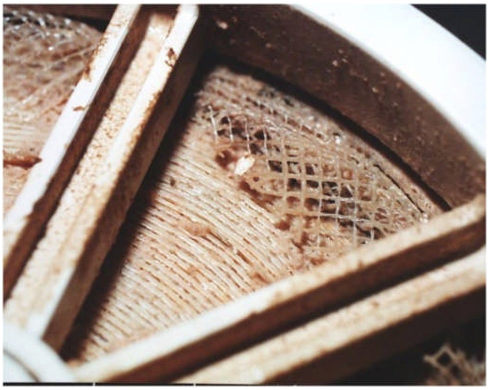

Figure 10. Biofouling causing displacement of feed spacer because of the fouling layer [30].

Organic fouling means the coating of the membranes with organic substances from the raw water, such as natural organic matter (NOM), including humic substances, or anthropogenic pollutants, oil and grease, or polymers from the pretreatment section, such as coagulants and scaling inhibitors.

Finally, the chemical damage is caused by chemicals in the influent water, in a cleaning, sanitizing or preservation solution. The most common problem is oxidation of the barrier layer of the membrane by chlorine or other oxidizing agents. The damaged membranes need to be replaced.

Once the direct cause(s) of performance problems have been identified, the root cause can be found, and corrective and preventive measures can be addressed. This will be discussed in the following for fouling, scaling, mechanical damage and chemical damage.

1.2.6 Membrane cleaning

Membranes may be cleaned regularly during its operational life. The frequency and type of cleaning depends on the quality of the feed water and degree of fouling. Pre-treatment of the influent water prior to the RO process is basically designed to reduce contamination of the membrane surfaces as much as possible.

Typically, fouling of the membrane surfaces is caused by different factors, including inadequate pretreatment system, pretreatment upset conditions, improper materials selection (pumps, piping), failure of chemical dosing systems, inadequate flushing following shutdown, improper operational control, slow build-up of precipitates over extended periods (barium, silica), changes in feed water composition and biological contamination of feed water.

Cleaning can be accomplished very effectively because of the combination of pH stability and temperature resistance of the membrane and the element components. However, if cleaning is delayed too long, it could be difficult to remove the fouling completely from the membrane surface. Cleaning will be more effective the better it is tailored to the specific fouling problem. Therefore, the type of foulants on the membrane surface should be determined prior to cleaning. There are different ways to accomplish this, such as analyze plant performance data, analyze influent water (a potential fouling problem may already be visible there), check results of previous cleanings, analyze foulants collected with a membrane filter pad used for the silt density index (SDI) value determination, analyze the deposits on the cartridge filter, inspect the inner surface of the feed line pipe and the feed end scroll of the FILMTEC™ element. Specifically, the characterization of the organic fouling will be covered in the section 1.4 of the introduction.

Elements should be cleaned when one or more of the below mentioned parameters are applicable [15]:

- The normalized permeate flow drops 10%
- The normalized salt passage increases 5 - 10%
- The normalized pressure drop increases 10 - 15%

If you wait too long, cleaning may not restore the membrane element performance successfully. In addition, the time between cleanings becomes shorter as the membrane elements will foul or scale more rapidly.

Differential Pressure (dP) should be measured and recorded across each stage of the array of pressure vessels. If the feed channels within the element become plugged, the dP will increase.

1.3. Organic micropollutants in aquatic environments

As mentioned earlier, different families of micropollutants are studied in this Thesis, which have different physic-chemical properties. In the following sections, the compounds included in each group are described in more detail, as well as their chemical properties and their ecotoxicological risk.

The term micropollutants refer to organic or mineral compounds with toxic, persistent and bioaccumulative properties that could have a negative effect on the environment and organisms. The presence of all of these micropollutants, including pharmaceuticals, disinfection by-products, personal care products and industrial additives in aquatic systems has been the focus of much public concern and also scientific consideration during the last decades [36]. Therefore, the continuously increasing contamination of surface and ground-waters with these pollutants is one of the key environmental problems.

Currently, recent improvements in analytical techniques allowing the detection of trace levels (typically parts per trillion) of organic micropollutants in the water environment have led to concern about potential negative impacts on ecological and human health. These organic micropollutants have been detected in waste water effluents, receiving waters, drinking water sources, and even some treated drinking waters [37]. Although, most of these compounds are not currently regulated, the public has expressed interest and concern about the potential presence of these contaminants in water.

1.3.1 Micropollutants studied

Several studies have investigated the exposure of wildlife to organic micropollutants and observed detrimental effects, such as feminization, and reproductive and developmental problems [38]. In fact, more research is needed by toxicologists since the risks associated with exposure to trace levels of many different types of organic micropollutants that could potentially interact are difficult to evaluate.

The micropollutants families studied in this Thesis are volatile organic compounds, endocrine disrupting compounds, pesticides, fragrance allergens, odours and disinfection by-products. All of them are described below and they have been studied due to their presence in the different waters studied.

Volatile organic compounds

Volatile organic compounds (VOCs) are carbon-containing compounds that evaporate easily from water into air at normal air temperatures. They are the gases released when organic matter evaporates and those gases are present in our atmosphere at all times.

Concentrations of many VOCs are consistently higher in indoors (up to ten times higher) than in outdoors. Most VOCs found in the environment result from human activity. When VOCs are spilled or improperly disposed of, a portion will evaporate, but some will soak into the ground. In soil, VOCs may be carried deeper by rain, water or snow melt and eventually reach groundwater. When VOCs migrate underground to nearby wells, they can eventually end up in drinking water supplies.

VOCs include a variety of chemicals, some of which may have short- and long-term adverse health effects. VOCs are emitted by a wide array of products, including paints and lacquers, paint strippers, cleaning supplies, pesticides, building materials and furnishings, office equipment such as copiers and printers, correction fluids and carbonless copy paper, graphics and craft materials including glues and adhesives, permanent markers, and photographic solutions. Organic chemicals are widely used as ingredients in household products. Paints, varnishes, and wax all contain organic solvents, as do many cleaning, disinfecting, cosmetic, degreasing and hobby products. Fuels are made up of organic chemicals. Figure 11 shows the sources of volatile organic compounds according to EPA government in 2013 [5].

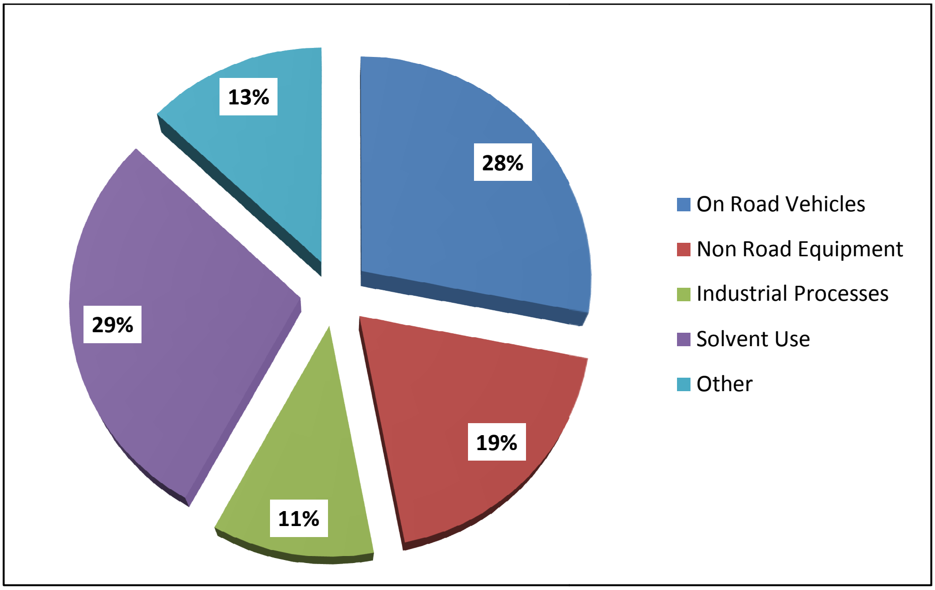

Figure 11. Sources of VOCs.

The ability of organic chemicals to cause health effects varies greatly from those that are highly toxic, to those with no known health effect. The extent and nature of the health effect will depend on many factors including level of exposure and length of time exposed. Many organic compounds are known to cause cancer in animals; some are suspected of causing, or are known to cause, cancer in humans, as mentioned before in previous studies [32]. In this Thesis, 54 VOCs have been studied which are showed in Appendix section. The VOCs regulated by the Directive 2008/105/CE [39] are marked in bold.

Endocrine disrupting compounds

Endocrine disrupting compounds (EDCs) are chemicals which have the potential to disturb hormonal equilibrium in living organisms [40]. These compounds, mistakenly recognized by estrogenic receptors, are treated the same as those naturally present in the organisms. The compounds cannot, however, perform the functions of those naturally present and, therefore, disturb regulatory mechanisms throughout the organism.

EDCs penetrate the natural environment and can be assimilated by living organisms during production processes and use. Synthetic compounds with estrogenic properties, which can be found in the natural environment and in food, include several pesticides and herbicides, organochlorine compounds, polycyclic aromatic hydrocarbons, alkylphenols, phthalates, polychlorinated biphenyls and dioxins, flame retardants and bisphenol A and its derivatives [41]. Most compounds are not regulated yet. However, they may be probable compounds for EDCs regulation with the collection of sufficient data to prove their toxic effects on human health [42]. The U.S. EPA tried to establish the Endocrine Disruptor Screening Program (EDSP) to develop official screening methods and toxicity testing strategies for approximately 87.000 compounds [43].

Reclaiming waste water will help to supplement the existing drinking water supplies but has a range of potentially adverse health outcomes, including hormonal effects. In considering wastewater reuse, emphasis will need to be placed on EDCs because of the current public concern coupled with the lack of scientific knowledge. Improved understanding of the action of EDCs is required to assess and minimize the risks associated with human exposure to harmful substances in reclaimed water. In this Doctoral Thesis some EDCs have been selected, which the most are found in the waters studied. The EDCs studied are showed in the Appendix section.

Pesticides

The term "pesticide" includes all chemicals that are used to kill or control pests [44]. Pesticides are, however, generally toxic for living organisms and are difficult to degrade, being toxic agents with persistent bioaccumulative effects [45]. The use of pesticides also constitutes a risk for water quality in agricultural areas due to the fact that these components may pass through the soil and subsoil and pollute surface waters and groundwater.

A fundamental contributor to the Green Revolution has been the development and application of pesticides for the control of a wide variety of insectivorous and herbaceous pests that would otherwise diminish the quantity and quality of food produce. The use of pesticides coincides with the "chemical age" which has transformed society since the 1950s. In areas where intensive monoculture is practised, pesticides were used as a standard method for pest control.

While agricultural use of chemicals is restricted to a limited number of compounds, agriculture is one of the few activities where chemicals are intentionally released into the environment because their capacity to kill. Agricultural use of pesticides is a subset of the larger spectrum of industrial chemicals used in modern society. Because the environmental burden of toxic chemicals includes both agriculture and non-agricultural compounds, it is difficult to separate the ecological and human health effects of pesticides from those of industrial compounds that are intentionally or accidentally released into the environment. However, there is overwhelming evidence that agricultural use of pesticides has a major impact on water quality and leads to serious environmental consequences.

The impact on water quality by pesticides is associated with some factors, including active ingredient in the pesticide formulation, contaminants that exist as impurities in the active ingredient, additives which are mixed with the active ingredient (wetting agents, diluents or solvents, extenders, adhesives, buffers, preservatives and emulsifiers) and degradation products that are formed during chemical, microbial or photochemical degradation of the active ingredient.

In this Doctoral Thesis, some pesticides have been selected. They are showed in Appendix section, and they have been proposed for regulation by the European Commission, on the 31th of June of 2012 [46].

Fragrance allergens

Most personal care products (PCPs) as well as many household products contain fragrances among their ingredients. The International Fragrance Association (IFRA) defines fragrances as any basic substance used in the manufacture of fragrance materials for its odorous, odour enhancing or blending properties [47]. Fragrance ingredients may be obtained by chemical synthesis from synthetic, fossil or natural raw materials or by physical operations from natural sources.

Fragrance allergens are a group of chemicals incorporated in most cosmetic and other personal care products including baby care ones. Some of the suspected allergens not only pose the risk of causing contact allergies, but also can cause systemic effects [48]. Although the main route of exposition to these cosmetic ingredients is, in general, the direct application of cosmetics on the skin, the contact with water containing these fragrances should be also considered. As they are important components of daily use products, allergen fragrances are continuously introduced into the environment at high quantities, mainly via urban wastewater effluents. Bath waters as well as the residual waters from many residential communities enter the environment via direct spill into superficial waters or through disposal into the sewage treatment system, contributing to water pollution and causing environmental concern.

Currently there is not any European legislation that control fragrance allergens in waters. Legal restrictions only limit the use of 26 fragrance ingredients suspected of causing skin reactions. These regulations restrict the presence of potential fragrance allergens in cosmetic products of 0.01% (100 $mg \cdot kg^{-1}$) for rinse off and 0.001% (10 $mg \cdot kg^{-1}$) for leave-on products [49-51]. In this Thesis 10 fragrance allergens have been selected, which are listed in Appendix section.

Odour compounds

Odour emissions affect quality of life, leading to psychological stress and symptoms such as insomnia, loss of appetite and irrational behaviour [52-53]. Therefore, waste water professionals have found the need to address odours as a primary concern in the design and operation of collection and treatment facilities in order to control odour emissions. However, there is not any European legislation that control odour compounds in waters.

Taste and odour problems are common in water utilities. They continue to be one of the most difficult issues faced by the water treatment industry due to they are major factors influencing the perception of the consumers of drinking water quality. Consumers generally think that if their drinking water smells badly, then it is probably not safe to drink.

Most of the odours are organic compounds present in the water which react with disinfectants or oxidation processes. Moreover, the causes of the odour problems have been attributed to microbial byproducts, disinfectants and disinfection by products, and distribution system materials. A part from the water source, odours may also form during treatment and distribution. Therefore, it is important for water utilities to detect their source and to determine the identity and origin of these compounds. In this Thesis, 8 odour compounds have been studied and they are presented in the Appendix section.

Disinfection by-products

Disinfection by-products (DBPs) are formed when a disinfectant, such as chlorine, ozone, chloramines or chlorine dioxide, reacts with natural organic matter (NOM) and/or bromide/iodide in source waters. Chlorination is the most commonly employed chemical disinfectant in drinking water treatment nowadays. Concerns regarding the potential health effects of DBP prompted several industrialized countries to develop a number of regulations. Of more than known 600 DBPs, only 11 are currently regulated in the United States and in other countries [54-57]. However, more DBPs (>500) were identified in drinking waters [58-62] for which little or no toxicological information is known.

Recent research has identified new emerging unregulated DBPs, which are more genotoxic than those that are currently regulated, and the use of new alternative disinfectants (chloramines, ozone and chlorine dioxide) could increase their formation [63]. Emerging DBPs include iodinated-acids, iodinated-trihalomethanes (I-THMs), bromonitromethanes, haloamides, and nitrosamines (including nitrosodimethylamine, NDMA). New research on emerging DBPs should be performed. Therefore, some of these emerging DBPs have been considered to study in this Doctoral Thesis.

NOM is of concern because it serves as precursor to the formation of DBPs. It has been extensively studied, but still remains a complex and heterogeneous mixture of specific but mostly difficult to identify compounds and varies significantly from one source to another [64]. NOM could also be defined as a mixture of two separate fractions: the hydrophobic (non-polar or hydrophobic) substances, generally of terrestrial origin and the hydrophilic (polar or hydrophilic) substances, typically of biological origin. To better understand the reactivity of NOM towards the formation of DBPs, NOM is generally characterized by measuring its total organic carbon (TOC) or dissolved organic carbon (DOC) concentration, its ultraviolet (UV) absorbance, generally at 254 nm to exhibit the amount of aromatic material, and its potential to form DBPs. NOM provides the precursor material from which DBPs are formed. Therefore, the amount (described as DOC or TOC) and the nature (described as UV_{254}) of NOM will give some insights into the DBPs formed.

These by-products may lead to increased health risks if present at $\mu g \cdot L^{-1}$ levels. A generation ago, when these contaminants were first discovered in drinking water [65-

66], concentrations of several hundred µg·L^{-1} were common. Nowadays, after many years of actively avoiding trihalomethanes (THM) production, most water-works supply tap water with less than 20 µg·L^{-1}. THMs have been considered probable human carcinogens (kidney, liver, bladder cancers) [67] and have been regulated in drinking water by The United States Environmental Protection Agency (EPA or sometimes USEPA) with a mandatory Maximum Contaminant Level (MCL) of 100 µg·L^{-1} of total THM [68]. However, recently a new level of 80 µg·L^{-1} has been proposed by the Europen government as a cause of miscarriages. However, in the actual European and therefore Spanish Legislation [69] the limit of the total THM concentration is 100 µg·L^{-1}.

Next in prominence after THMs are the halogenated acetonitriles (HANs) [70], the halogenated nitromethanes (HNMs) [71] and the halogenated ketones (HKs) [72]. Most of these compounds are made from two-carbon fragments. They are found in chlorinated waters at levels one-third to one-half of the THM level. When they are eventually regulated explicitly, it is expected that they will receive MCLs in the 30-80 µg·L^{-1} range. Epidemiological studies have suggested a link between consumption of drinking waters containing elevated levels of DBPs and adverse human health outcomes, particularly bladder cancer and reproductive effects [73-74]. In this Doctoral Thesis, 20 DBPs have been studied and they are presented in the Appendix section.

As mentioned before, the occurrence of micropollutants in the aquatic environment is of increasing interest. Therefore, modern sensitive techniques are employed worldwide for their determination [75], which are further described in the following section.

1.3.2 Determination of micropollutants in waters

In recent years, pollutants in the aquatic environment are a major concern because their potential adversely effects on human health or affect the safety of the ecosystem. Some of the micropollutants are regulated for water quality monitoring, according to US EPA standards and the World Health Organization (WHO) guidelines, as commented before in section 1.1.6. However, most of these micropollutants are not currently regulated [76]. Therefore, the micropollutants were originally called priority pollutants instead of toxic pollutants because few toxically data was available. For many years, the research priorities have been focused on priority pollutants and more recently, increasing use of novel analytical techniques that allow detection of structures of contaminants has been necessary used.

Although the presence of organic micropollutants in the environment has caused a lot of interest from the water industry, research community, media and public, there remain many unknowns. Improvements in establishing standard and reliable methods for organic micropollutants analysis are also needed if these compounds must be routinely monitored or regulated in our waters in the future.

Extraction techniques for water samples

Since water should be considered as the live-based solvent, most of these chemical compounds are easily water soluble. Therefore, aqueous environmental matrices are the main points at which these compounds are likely to be found. Moreover, domestic and industrial sewage systems are the sites at which higher concentrations have already been found. However, a level of parts per billion or trillion is the most likely range of concentrations expected for most emerging organic contaminants. Therefore, specific sample pretreatment techniques involving pre-concentration and clean-up processes are necessary, before selective and sensitive analysis techniques for their determination in environmental matrices. Therefore, several techniques have been applied for sample preparation [77], such as liquid-liquid extraction (LLE) [78], solid phase extraction (SPE) [78-84], solid phase microextraction (SPME) [85], stir-bar sorptive extraction (SBSE) [86] and liquid-phase microextraction (LPME) [87-88]. The environmental application is a main cause due to the increased public awareness that environmental contaminants are a health risk.

In this Doctoral Thesis, headspace (HS)-SPME has been selected as the sample preparation technique because it allows complete elimination of organic solvents in the pretreatment step and decreases the number of steps needed for sample preparation becoming an accepted technique for the determination of volatile and semi-volatile substances, as well as it could be a totally automated technique when combined with GC.

The SPME device is constructed of a silica fibre coated with a thin layer (5-100 μm) of a suitable polymeric sorbent or immobilized liquid. The coated fibre is placed inside a needle, itself placed within a syringe-like arrangement. SPME can be used for the direct extraction of analytes from gaseous and liquid media by immersing the fibre expressed from the syringe in them. It can also be used for analysing the composition of liquid and solid samples by extracting the analytes from the headspace above them. After extraction, the fibre is placed within the feeder of the measuring monitoring instrument, where the analytes sorbed on the extraction fibre are desorbed. SPME is based on a partition mechanism and the establishment of equilibrium between the analyte and the sample matrix. In such cases, the final effect is ruled by the two parameters: partition coefficient of the analyte between the sample matrix and the retaining phase, and the ratio of volumes of this phase (the sorbent) and the sample. Taking into account limited opportunities of increasing the volume of the sorbent, the partition coefficient remains the decisive factor in the SPME technique.

The first development was the use of sol-gel technology for coating the silica fibres. The pioneering work was performed by Pawlizing [89]. Other authors, such as Chong et. al. [90], used this method to prepare sol-gel polydimethylsiloxane (PDMS) fibres. Unlike commercial PDMS fibres the sol-gel variety have the PDMS chemically bonded to the silica core, which increases their thermal stability and surface area by creation of a highly crosslinked network. Titanium and zirconium-based materials have also been prepared; these have increased the pH and mechanical stability of SPME fibres [89-91].

This sol-gel technology has been further used to prepare poly(ethylene glycol) (PEG) [92], polydimethylsiloxane/divinilbenzene (PDMS/DVB) and PDMS/DVB/carboxene (PDMS/DVB/CAR) [93], PDMS/poly(vinyl alcohol) (PDMS/PVA) [94], and polytetrahydrofuran (PTHF) [95] coated fibres. All of these, with the exception of PEG, are relatively apolar polymers.

SPME is widely applied in analytical practice because of its undoubted advantages simplicity of operation, short extraction time, solvent-free operation, possibility of automation, straightforward linkup with GC, and relatively good results of the isolation of trace amounts of analytes. On the other hand, some difficulties of this type of analysis are the need for derivatisation in some occasions before GC determination and problems associated. Basic principles of the technique, and general guidelines, have been discussed in detail in several books and reviews [96-98].

Although SPME, especially in combination with GC, is a well established sample-preparation technique, its application to the determination of polar analytes in water samples is still an emerging field. Only research groups are currently developing different sorbents for incorporation into microextraction fibres. Some of these are specifically intended for the determination of polar analytes in water samples. Polyacrilate (PA) and PEG coatings are commercially available, extraction efficiency for highly polar analytes is still limited and the development of more polar coatings is of interest.

SPME has been applied to the analysis of VOCs, widely monitored in water supplies. SPME has been widely used for the extraction of volatile and semi-volatile organic compounds from environmental, biological and food samples [99-102]. The type of polymer coating on the needle is chosen to match the characteristics of the VOCs of interest, for example in the studies performed by Nakamura et al. [103-105], three types of SPME fibers CAR/PDMS, DVB/PDMS and 100 μm PDMS were evaluated to achieve the method detection limits and linear range required in Japanese water regulation. The 100 μm PDMS fibre was found to be the best coating to obtain a wide range of linearity for the target compounds in multiple-component system.

Some fragrance allergens have also been included in this Thesis due to they have been previously reported in water samples. For example, the methodology used was based on SPME GC-MS by Becerril et al. [106], which allowed the reliable determination of 15 selected fragrance allergens frequently found in baby bath-waters using the intermediate polarity fibre of PDMS/DVB, described above. An experimental screening design was performed 3 x 2, which allowed studying temperature at three levels (50, 75 and 100 ºC) and the two extraction modes (HS and direct SPME), were selected. Finally, the best conditions selected were HS-SPME at 100 ºC. To overcome difficulties on obtaining good resolution between compounds and with other matrix components, especially in cosmetic samples, several methods based on multidimensional chromatography have also been proposed by other authors [107-108].

Odorous from waste water collection systems and treatment facilities affecting quality of life have given local populations reasons to complain for decades. In order to characterize the composition of the malodorous emissions, several methods could be applied. However, in many cases, these techniques are not sensitive enough and it is necessary to concentrate the sample. Since the introduction of the SPME as a sample preparation technique, it has become an accepted method for the determination of volatile and semi-volatile. As a result, most authors have chosen this technique for the analysis of odorous compounds in waste water and air samples. Kleeberg et al. [109] analysed waste gas from a fat refinery using SPME. The fibre was exposed to the sample, collected in a sampling bag at ambient temperature and a total of 56 substances including aldehydes, terpenes and esters were identified.

Moreover, Godayol et al. [110], determined odour-causing organic compounds in waste water treatment plants by HS-SPME. They evaluated the experimental conditions affecting the extraction process (temperature, time and salt content) by applying a factorial design at two levels. Using a DVB/CAR/PDMS fibre and the optimized HS-SPME conditions, calibration curves were constructed with detection limits between 0.003 to 0.6 $\mu g \cdot L^{-1}$.

Monitoring of pesticide residues has received much attention in the last few years. Before the chromatographic measurement, appropriate sample pretreatments are generally required to clean up or pre-concentrate the target species [111]. Li Hong-Ping et al. [111] examined six different types of SPME fibres and compared. The parameters affecting the efficiency in HS-SPME process, such as sampling time and temperature, desorption temperature and time were also studied to obtain the optimal conditions. The selected conditions were 12 minutes of samples extraction, in the headspace during the stirring solution (20 mL, 300 rpm) and the desorption was at 310ºC in the GC injector.

The characteristics of EDCs, such as their occurrence of EDCs at trace concentration levels and with extremely diverse groups, make the detection and analysis procedures quite challenging. To overcome difficulties in the analysis, various methods have been developed. Several extraction methods have been already developed and applied with respect to proper alterations to improve performance. Common extraction techniques that can be applied in practice are as follows: SPE, SPME and LPME.

As a general trend, several extraction techniques can be used for the extraction of disinfection by-products from water samples such as LLE, HS-SPME and HS-SDME [112-114]. In addition, SPE method was used to provide MS confirmation of semivolatile DBPs. SPME method was used in comparison with the LLE method in the last sampling quarter of the study [115]. Moreover, LLE method was used for quantifying bromochloromethyl acetate and the haloacetamides [116].

As mentioned before and due to all of these advantages, HS-SPME has been selected in the present Thesis as the sample preparation technique. Moreover, different determination techniques could be applied for the analysis of the different micropollutants studied.

Determination techniques for micropollutants

As mention earlier, analytical methods based on gas chromatography, liquid chromatography followed by mass spectrometry or tandem mass spectrometry are the most commonly used techniques for the quantification of organic micropollutants in water [117-127]. However, in spite of the recent technical progress, the instrumental quantification limits of the micropollutants are still high, around μg/L. Therefore micropollutants quantification in water requires a first step of extraction and preconcentration in order to evaluate them at very low concentrations (Directive 2000/60/EC) [128].

Generally, VOCs require a method with detection at the sub-$\mu g \cdot L^{-1}$ levels, headspace GC-MS, purge and trap GC-MS and SPME GC-MS have been applied to their analysis [103-

105]. For instance, Nakamura et al. achieved method detection limits of 0.001 - 0.05 $\mu g \cdot L^{-1}$ for 22 VOCs [105].

Gas chromatography flame ionization detection (GC-FID) and GC-MS are frequently used to identify and quantify some components of gas odour mixtures [129]. Additionally, in order to ascertain the contribution of the detected compounds in the odour perception, olfactometry analysis have been carried out [130-132]. In addition, chromatographic techniques have been considered as the best methods to determine pesticides in varied sample matrices. The need for higher selectivity and sensitivity, as well as the necessity for confirmation has been successfully achieved by coupling GC or liquid chromatography (LC) with MS and tandem mass spectrometry (MS/MS).

Currently, the most prevailing methodological approach designed to analyze EDCs incorporates a mass-based analysis process. Depending on the target compounds, various combinations of instruments and detectors can be applied to obtain improved analytical results, such as GC-MS, HPLC-MS, LC-UV, and GC-tandem mass spectrometer [133-135].

Most of the halogenated DBPs, including THMs, tribromochloromethane, haloacetonitriles, haloketones, haloacetaldehydes, halonitromethanes were analyzed and quantified using GC-electron capture detection (ECD) method [136]. A purge-and-trap-GC-MS method was used to analyze for VOCs and certain volatile chemicals that have been reported as possible DBPs (mono- and dihalogenated methanes, carbon tetrachloride, methylethyl ketone) and to provide MS confirmation of other volatile DBPs [116,136].

Non-halogenated carbonyl compounds and chloroacetaldehyde were derivatized with pentafluoro-benzylhydroxylamine (PFBHA), and the oxime products were extracted and analyzed by GC-ECD. The halogenated furanones were extracted from water, derivatized with boron trifluoride in methanol, back extracted, and analyzed by GC-ECD [137].The haloacetic acids were measured using acidic and salted LLE, derivatization with acidic methanol, and GC-ECD analysis [138]. Another haloacid, 3,3-dichloropropenoic acid, was analyzed by a similar method, substituting diazomethane for acidic methanol in the derivatization step [139].

Taking into account all of these methodologies studied, our final approach of this Doctoral Thesis was to apply the HS-SMPE and GC-MS methods to evaluate the RO membranes efficiency. Furthermore, determining different families of organic compounds in membrane surfaces will help us to obtain more information regarding organic compounds present in the membrane fouling.

1.4. Characterization of organic fouling

In spite of great advances in membrane technology, membrane fouling is still one of the major limitations for practical applications of membrane processes. Membrane fouling is caused by the adsorption, accumulation or precipitation of dissolved constituents on the membrane surfaces and it can reduce permeate flux and increase operating pressure which are related to the energy requirements and cost effectiveness.

Membrane fouling is inherent in the operation of membrane systems as no pretreatment method exists for perfect removal of foulants, including organic compounds resulting from undesirable bioactivity. Understanding the characteristics of fouling layers under various filtration conditions is an essential step toward overall improvement of membrane operations. Fouling can occur in two ways: fouling layer formation and adsorption of foulants. Cake fouling can be sensibly decreased after water backwashing or back-flushing. While, fouling due to the adsorption of foulants can only be counteracted to a certain extent by aggressive chemical cleaning. Furthermore, fouling can be affected by the interaction between foulants. When the influent contains a mixture of contaminants, the adsorption of a single foulant decreases by competitive sorption processes. Figure 12 shows a membrane with typical layer of organic and biofouling.

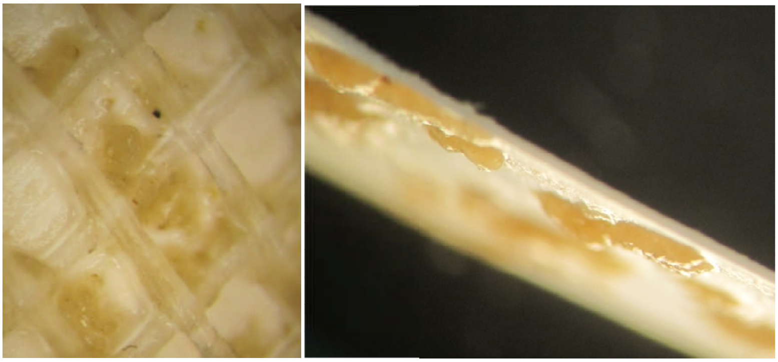

Figure 12. Organic and biologincal fouling on membrane surface.

One way to find strategies to minimize the fouling is to characterize the foulants found in the membranes, because as a result, it is possible to understand how the fouling could be reduced or avoided. The majority of studies have focused on the effects of single foulants or controlled synthetic samples. Therefore, an understanding of membrane fouling caused by influent water is necessary to optimize the membrane performance. This Thesis was conducted also to investigate possible organic foulants as well as their characterization in the membrane surface, classifying potential foulants present in the water by different families. Advanced characterization of organic foulants using various analytical methods, those based on gas chromatography and mass spectrometry tools, is believed to provide valuable insights into the fouling characteristics in a large scale application of RO membranes for municipal water reclamation.

The physical dissection of a RO membrane called autopsy and the resulting analysis of its foulants can be one of the most definitive methods of troubleshooting an RO system. The RO membrane elements should be packed in plastic bags and stored at 4°C until the autopsy to determine foulant accumulation onto the membrane surface, which have to be performed within 24h after their removal from the installation. RO autopsy involves opening lengthwise the membrane. Autopsy can also be the key to determining how to prevent fouling of new membranes and to maximize the efficiency of this key piece of water treatment equipment. This test is destructive, and the membrane element is not returned. The procedure begins with a physical examination of the intact element. Firstly, the process starts looking for physical damage to various parts of the element. Next, the process continues looking for evidence of gross fouling on the leading edges of the rolled membrane in the end cap. Fouling in this area can restrict water flow through the element. Therefore, the next step is to collect foulant of the membrane surface, and analyze it for chemical composition.

If foulant can be collected from the membrane surface, samples will be analyzed qualitatively and quantitatively. Sophisticated analytical tools are available to analyze the composition of the foulant and of chemical degradation of the membrane: ICP (Inductively Coupled Plasma Optical Emission Spectroscopy) is used to identify metals and their concentrations, ESCA (Electron Spectroscopy for Chemical Analysis) is primarily used to determine oxidation by halogens and element composite, and GC-MS can be used to identify low concentrations of organic foulants. Most of the major methods included also visual observation, loss on ignition (LOI), heterotrophic plate count [140], phospholipids, polysaccharides, total organic carbon (TOC), pyrolisis/GC-MS for some hydrophobic organics characterization [141-142], scanning electron microscopy (SEM), energy dispersive X-ray (EDX) and fourier transform infrared spectroscopy (FTIR) to investigate the complex fouling in RO membranes [143-145].

Those methodologies are focusing on characterise, as a general trend, the inorganic and organic fouling identifying specific functional groups in RO membrane fouling. In addition, few studies have focused on describing the classes of polymers and microorganisms that are associated with membrane biofouling, analyzing also organic and biological compounds [146-150]. However, there still remains a basic lack of understanding about which specific foulants, such as microorganism cells and their fragments, natural organic matter (NOM), extracellular polymeric substances (EPS), and byproducts of microbial metabolism, govern membrane organic fouling. Despite extensive studies on the relationship between membrane surface properties and membrane fouling, the roles of specific surface functional groups in RO membrane fouling under different solution conditions are still poorly understood [151-155].

Previous research reported that relatively hydrophilic and non-charged fractions, comprising of polysaccharides and protein-like substances, may be responsible for severe fouling formation in membrane systems which were tested with respect to water reclamation [156-157]. Another study demonstrated that decreasing pH, increasing ionic strength, and presence of calcium ions can increase the fouling formation with relatively hydrophilic organic matters in the RO membranes [158]. Some studies have also focused on relationship between physical and chemical properties of OM and membrane fouling formation [159-162]. Although many studies have been conducted to find out the important factors which can contribute to fouling formation, such as feed water characteristics, including relative hydrophobicity and hydrophilicity of the organic matter, levels of key constituents such as pH, ionic strength, presence of multivalent metal ions and colloids and membrane properties including molecular weight cut-off, surface charge, hydrophobicity and morphology and operating conditions such as temperature and permeate flux [163-166], understanding of membrane fouling by OM in a large scale municipal water reclamation plant is still lacking as most previous research has been performed under controlled laboratory conditions. The fouling phenomena of the practical membrane applications cannot be completely represented by laboratory-scale experiments [167].

In addition, other authors have been focused on OM characterization in the influent water by different analytical techniques which were focused in identifying major constituent of organic foulants and determining the NOM fraction and functional groups, as well as their molecular weight [168]. RO processes can either directly or indirectly remove NOM from water, depending on their operational conditions and the specific characteristics of the NOM such as its molecular weight, carboxylic acidity and humic substances content [169-170]. However, more recent studies done by Fabris et al. and Sharp et al. [171-172] have shown that low molecular weight NOM compounds, such as those found in the present study, are considered the most difficult to remove by conventional coagulation. Moreover, some investigations have found that hydrophilic NOM (non-humic acids, including fatty acids), might be a significant membrane fouling compounds. These analytical techniques included pyrolisis and mass spectroscopy [173], high performance size exclusion chromatography with ultraviolet and dissolved organic carbon detections, and FTIR [174-175]. Moreover, some studies have been applied advanced water characterization techniques, such as excitation emission matrix fluorescence spectroscopy (EEM) and liquid chromatography with organic carbon detection (LC-OCD) for the characterization of foulants [176], as well as high resolution mass spectrometry for molecular characterization of dissolved organic matter [177]. These studies have also determined two fouling indices: the total fouling index and the hydraulically irreversible fouling index, comparing them with the organic foulant results.

On the other hand, several sample preparation techniques mentioned before for micropollutants determination by GC-MS, could be applied for the extraction of organic compounds from RO influent water samples, such as LLE, single drop microextraction and SPE, whereas HS-SPME can selectively extract organic compounds and no solvents are required.

In the present Doctoral Thesis, some methodologies have been applied for organic fouling characterization as well as the implementation of new analytical techniques for organic foulants determination in water samples. Advanced characterization of organic foulants is believed to provide valuable insights into the fouling characteristics in a large scale application of the UF and RO membranes for municipal water reclamation.

1.6. References

[1] Gleick, P.H., Chalecki, E.L., and Wong, A. 2002. Measuring water well-being: Water indicators and indices. In: The World's Water 2002–2003. Gleick, P.H., editor.Washington, DC: Island Press, pp. 87–112.

[2] The Encyclopedia of the Earth, http://www.eoearth.org/view/article/157013/, (last accessed, July 2014).

[3] Water Treatment Solutions, http://www.lenntech.com/watercontamination.htm, (last accessed, July 2014).

[4] Wiesmann, Choi, Dombrowski, Fundamentals of Biological Wastewater Treatment, Wiley-VCH, 2007.

[5] USEPA, United States Environmental Protection Agency, http://iaspub.epa.gov, (last accessed, July 2014).

[6] Hach Lange Anwendungsbericht "Dr. Lange TOC Küvetten-Test entspricht der Europanorm", May 1998 (DOC042.00.00153).

[7] C. Fritzmann, J. Lowenberg, T. Wintgens, T. Melin, Desal. 216 (2007) 1.

[8] USEPA, United States Environmental Protection Agency, http://water.epa.gov/lawsregs/rulesregs/sdwa/stage2/regulations.cfm, (last accessed, July 2014).

[9] Standard Methods for the Examination of Water and Wastewater, Published by the American Public Health Association, Water Environment Federation, and the American Water Works Association 21st Edition 2005.

[10] Standard Methods, http://www.standardmethods.org/, (last accessed, July 2014).

[11] US EPA's Enhanced Coagulation and Enhanced Precipitative Softening Guidance Manual Unites States, May 1999.

[12] US EPA Method 415.3. Determination of total organic carbon and specific UV absorbance at 254 nm in source water and drinking water. Ohio (United States), 2003.

[13] Kjeldahl Method, http://www.brooklyn.cuny.edu/bc/ahp/SDKC/Chem/SD_KjeldahlMethod.html, (last accessed, July 2014).

[14] Hach Lange "Nitrogen parameters: Nitrification, Denitrification", December 2008 (DOC040[1].52.10015).

[15] Clesceri, L.S., Greenberg, A. E., Eaton A. D. 1998. Standard Methods for the Examination of water and waste water, 20th Edition, American Public Health Association, NW Washington, DC 20005-2605.

[16] Madigan M.T., Martinko J.M., Brock biology of micro-organisms, 10th Edition, 2003, Chapter 28, page 935-949.

[17] World Health Organization: Guidelines for drinking water quality, incorporating first addendum. Vol 1, recommendation -3rd Edition.

[18] Zümriye Aksu, Application of biosorption for the removal of organic pollutants: a review. Process Biochemistry, Volume 40, Issues 3-4, March 2005, Pages 997-1026.

[19] T. Petry, R. Knowles, R. Meads, Regul. Toxicol. Pharm. 44 (2006) 24.

[20] E.P. Council, Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC, Off. J. Eur. Union (2006) 850.

[21] American Chemical Society, http://www.acs.org, (last accessed, August 2014).

[22] Ayers and Westcot, FAO Irrigation and Drainage Paper No 29 Rev. 1 (FAO 1985).

[23] Pescod Wastewater treatment and use in agriculture FAO irrigation and drainage paper 47 (FAO 1992).

[24] European Commission, http://ec.europa.eu/environment/water/water-drink /index_en.html, (last accessed, July 2014).

[25] USEPA, United States Environmental Protection Agency, http://www.epa.gov, (last accessed, August 2014).

[26] WHO, World Health Organization guidelines, http://www.who.int/publications /en, (last accessed, September 2014).

[27] The EU Water Framework, http://ec.europa.eu/environment/water/water-framework/index_en.html, (last accessed, September 2014).

[28] Spanish Directive, http://www.magrama.gob.es/es/agua/legislacion/legislacion _nacional.aspx, (last accessed, September 2014).

[29] International Desalination Society, http://ida.water.usgs.gov/ida/, (last accessed, August 2014).

[30] Dow Water and Process Solutions, FilmTecTM Manual, http://www.dow-waterandprocess.com, (last accessed, August 2014).

[31] L.V. Saboyainsta, J.L. Maubois, Le Lait 80 (2000) 541.

[32] P. Burba, B. Aster, T. Nifant'eva, V. Shkinev, B.Y. Spivakov, Talanta 45 (1998) 977.

[33] Geankoplis, C. J. 1993. Transport Processes and Unit Operations, 3rd Edition, Prentice Hall, Englewood Cliffs, New Jersey.

[34] McCabe, W. L., Smith, J. C. 1993. Unit operations of Chemical Engineering, 5th Edition, McGraw-Hill, New York.

[35] Miguez, C., Urcela, R., Míguez, M. 1998. Tratamiento del agua por procesos de membrana. Principios, procesos y aplicaciones. McGraw-Hill, American Water Works Association Research Foundation, Lyonnaise des Eaux y Water Research Commission of South Africa.

[36] H.H. Dieter, Int. J. Hyg. Envir. Heal. 217 (2014) 117.

[37] A. A. Alturki, N. Tadkaew, J. A. McDonald, S. J. Khan, W. E. Price, L. D. Nghiem, J. Membr. Sci. 365 (2010) 206.

[38] H. Amjad, I. Hashmi, M.S.U. Rehman, M.A. Awan, S. Ghaffar, Z. Khan, Ecotox. Environ. Safe. 91 (2013) 25.

[39] Directive 2008/105/CE, http://ec.europa.eu/environment/water/water-dangersub/pri_substances.htm, (last accessed September 2014).

[40] Hyun-Shik C., Kwang-Ho C., Byungwhan L., Sang-June C., J. Hazard. Mater. 172 (2009) 1.

[41] S.D. Kim, J. Cho, I.S. Kim, B.J. Vanderford, S.A. Snyder, Water Res. 41 (2007) 1013.

[42] R.V. Kuiper, R.F. Canton, P.E.G. Leonards, B.M. Jenssen, M. Dubbeldam, P.W. Wester, M. van den Berg, J.G. Vos, A.D. Vethaak, Ecotoxicol. Environ. Saf. 67 (2007) 349.

[43] U.S. EPA, Special Report on Environmental Endocrine Disruption: An Effects Assessment and Analysis, Office of Research and Development, Washington, DC, EPA/630/R-36/012, (1997).

[44] K. Nishtha, R.S. Lokhande, J.K. Dhar, J. Environment Sci., 1 (2012) 1.

[45] F. Hernandez, J. Beltran, F. J. López, J.V. Gaspar, Anal. Chem. 72 (2000) 2313.

[46] European Commission-Environment. http://ec.europa.eu/environment /water /waterdangerousub/pri_substances.htm, (last accessed August 2014).

[47] International Fragrance Association, http://www.ifraorg.org/, (last accessed August 2014).

[48] E. Becerril, J.P. Lamas, L. Sanchez-Prado, M. Llompard, Talanta 83 (2010) 464.

[49] SCCNFP/0017/98 Final Fragrance Allergy in consumers (1999).

[50] REGULATION (EC) No 1223/2009 of The European Parliament and of the Council of 30 November 2009 on Cosmetic Products (recast), Official Journal of European Union L342 (2009) 59.

[51] C.P. Weisel, S.D. Richardson, B. Nemery, G. Aggazzotti, E. Baraldi, R.B. Ernest III, B.C. Blount, K.-H. Carlsen, P.A. Eggleston, F.H. Frimmel, M. Goodman, G. Gordon, S.A. Grinshpun, D. Heederik, M. Kogevinas, LaKind Judy S., M.J. Nieuwenhuijsen, F.C. Piper, S.A. Sattar, Environ. Health Persp. 117 (2009) 500.

[52] C. Hort, S. Gracy, V. Platel, L. Moynault, Chem. Eng. J. 152 (2009) 44.

[53] P. Gostelow, S.A. Parsons, R.M. Stuetz, Water Res. 35 (2001) 579.

[54] U.S. Environmental Protection Agency. 1996. National primary drinking water regulations: monitoring requirements for public drinking water supplies; Final rule. Fed. Reg. 61(94) 24354–24388.

[55] U.S. Environmental Protection Agency. 1998. National primary drinking water regulations: disinfectants and disinfection byproducts; final rule. Fed. Reg. 63 (241) 69389–69476.

[56] U.S. Environmental Protection Agency. 2000. Conducting a risk assessment of mixtures of disinfection by-products (DBPs) for drinking water treatment systems. NCEA-C-0791. Cincinnati, OH: U.S. Environmental Protection Agency.

[57] U.S. Environmental Protection Agency. 2006. National primary drinking water regulations: Stage 2 disinfectants and disinfection byproducts rule. Fed. Reg. 71 (2) 387–493.

[58] S.D Richardson, A.D.Jr. Thruston, C. Rav-Acha, L. Groisman, I. Popilevsky, O. Juraev, V. Glezer, A.B. McKague, M.J. Plewa, E.D. Wagner, Environ. Sci. Technol. 37 (2003) 3782.

[59] S.D. Richardson, A.D.Jr. Thruston, T.V. Caughran, P.H. Chen, T.W. Collette, T.L. Floyd, K.M. Schenck, B.W. Lykins, Environ. Sci. Technol. 33 (1999) 3368.

[60] S.D. Richardson, A.D.Jr. Thruston, T.V. Caughran, P.H. Chen, T.W. Collette, T.L. Floyd, K.M. Schenck, B.W. Lykins, Environ. Sci. Technol. 33 (1999) 3378.

[61] Richardson, S. D. 1998. Drinking water disinfection byproducts. In The encyclopedia of environmental analysis and remediation, Vol. 3, ed. R. A. Meyers, pp. 1398–1421. New York: John Wiley & Sons.

[62] S.D. Richardson, A.D.Jr. Thruston, T.W. Collette, K.S. Patterson, B.W. Lykins, Environ. Sci. Technol. 28 (1994) 592.

[63] W. Chu, N. Gao, D. Yin, S.W. Krasner, J. Hazard. Mater. 43 (2013) 4698.

[64] L. Jinfeng, T. Zhang, J. Ma, Z. Chen, J. Hazard. Mater. 162 (2009) 140.

[65] E. Gasia-Bruch, P. Sehn, V. García-Molina, M. Busch, O. Raize, M. Negrin, Desal. Water Treat. 31 (2011) 178.

[66] V. Uyak, I. Koyuncu, I. Oktem, I. Toroz, J. Hazard. Mater. 152 (2008) 789.

[67] M. Villanueva , K.P. Cantor, J.O. Grimalt, N. Malats, D. Silverman, A. Tardon, R. Garcia-Closas, C. Serra, A. Carrato, G. Castaño-Vinyals. R. Marcos, N. Rothman, X. Real, M. Dosemeci, M. Kogevinas, J. Epidemiol. 165 (2007) 148.

[68] U.S. Environmental Protection Agency. 2006. National primary drinking water regurations: Statge 2 disinfectants and disinfection byproducts rule. Fed. Reg. 71 (2): 387.

[69] Real Dectreto 1400/2003, Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008. http://eurlex.europa.eu/, (last accessed August 2014).

[70] I. Kristiana, C. Joll, A. Heitz, (2012) J. Chromatogr. A 1225 (2012) 45.

[71] I. Montesinos, M.J. Cardador, M. Gallego, J. Chromatogr. A 1218 (2011) 2497.

[72] M. Serrano, M. Silva, M. Gallego, J. Chromatogr. A 1218 (2011) 8295.

[73] K. Cantor, C.R. Lynch, M.E. Hildesheim, M. Dosemeci, J. Lubin, M. Alavanja, G. Craun, J. Epidemiol. 9 (1998) 21.

[74] J.C. Loper, D.R. Lang, R.S. Schoeny, B.B. Richmond, P.M. Gallagher, C.C. Smith, (1978) Toxicol. Environ. Health 4 (1978) 919.

[75] J. Wu, L. Zhang, Z. Yang, Critical Reviews in Anal. Chem. 40 (2010) 234.

[76] T. Kosjek, E. Heath, M. Petrovíc, D. Barceló, Trends Anal. Chem. 26 (2007) 1076.

[77] Y. Chen, Z. Guo, X. Wang, C. Qiu, J. Chromatogr. A 1184 (2008) 191.

[78] L. Chimuka, E. Cukrowska, J. A. Jonsson, Pure Appl. Chem.76 (2004) 707.

[79] A. Lajeunesse, C. Gagnon, and S. Sauve, Anal. Chem. 80 (2008) 5325.

[80] A. L. Batt, M. S. Kostich, J. M. Lazorchak, Anal. Chem. 80 (2008) 5021.

[81] Y.F. Cheng, D. J. Phillips, U. Neue, Chromatographia 44 (1997) 187.

[82] C. H. Galdiga, T. Greibrokk, J. Chromatogr. A 793 (1998) 297.

[83] D. M. Pavlovíc, S. Babíc, A. J. M. Horvat, M. Kastelan- Macan, Trends Anal. Chem. 26 (2007) 1062.

[84] H. Lord, J. Pawliszyn, J. Chromatogr. A 885 (2000) 153.

[85] F. Sanchez-Rojas, C. Bosch-Ojeda, J. M. Cano–Pavon, Chromatographia 69 (2009) 79.

[86] H. F. Fang, Z. R. Zeng, L. Liu, D. W. Pang, Anal. Chem. 78 (2006) 1257.

[87] L. M. Zhao, H. K. Lee, Anal. Chem. 74 (2002) 2486.

[88] Y.Wang,Y. C.Kwok,Y. He, H.K. Lee, Anal. Chem. 70 (1998) 4610.

[89] J. Pawliszyn, (1997) Solid phase microextraction: theory and practice. Wiley- VCH, New York.

[90] S.L. Chong, D.X. Wang, J.D. Hayes, B.W. Wilhite, A. Malik, Anal. Chem. 69 (1997) 3889.

[91] K. Alhooshani, T.Y. Kim, A. Kabir, A. Malik, J. Chromatogr. A 1062 (2005) 1.

[92] S. Bigham, J. Medlar, A. Kabir, C. Shende, A. Alli, A. Malik, Anal. Chem. 74 2002) 752.

[93] M.M. Liu, Z.R. Zeng, C.L. Wang, Y.J. Tan, H. Liu, Chromatographia 58 (2003) 597.

[94] V.G. Zuin, A.L. Lopes, J.H. Yariwake, F. Augusto, J. Chromatogr. A 1056 (2004) 21.

[95] A. Kabir, C. Hamlet, A. Malik, J. Chromatogr. A 1047 (2004) 1.

[96] T.Y. Kim, K. Alhooshani, A. Kabir, D.P. Fries, A. Malik. J. Chromatogr. A 1047 (2004) 165.

[97] J. Pawliszyn, (2002) Solid phase microextraction. Elsevier, Amsterdam, pp 389-477.

[98] H. Prosen, L. Zupanèiè-Kralj, Trends Anal. Chem. 18 (1999) 272.

[99] A.J. Matich, D.D. Rowan, N.H. Banks, Anal. Chem. 68 (1996) 4114.

[100] L.K. Ng, M. Hupe, J. Harnois, D. Moccia, J. Sci. Food Agric. 70 (1996) 380.

[101] R. Young, V. Lopez-Avila, W.F. Beckert, J. High Resolut. Chromatogr. 19 (1996) 247.

[102] D.W. Potter, J. Pawliszyn, Environ. Sci. Technol. 28 (1994) 298.

[103] P. Kuran, L. Sojak, J. Chromatogr. A 733 (1996) 119.

[104] J. Dewulf, H.V. Langenhove, J. Chromatogr. A 843 (1999) 163.

[105] S. Nakamura, S. Daishina, Anal. Chim. Acta 548 (2005) 79.

[106] E. Becerril, J. P. Lamas, L. Sanchez-Prado, M. Llompart, M. Lores, C. Garcia-Jares, Talanta 83 (2010) 464.

[107] M.S. Dunn, N. Vulic, R.A. Shellie, S. Whitehead, P. Morrison, P.J. Marriott, J. Chromatogr. A 1130 (2006) 122.

[108] L. Mondello, A. Casilli, P.Q. Tranchida, D. Sciarrone, P. Dugo, G. Dugo, LC-GC Europe 21 (2008) 130.

[109] K.K. Kleeberg, Y. Liu, M. Jans, M. Schlegelmilch, J. Streese, R. Stegmann, Waste Manage. 25 (2005) 872.

[110] A. Godayol, M. Alonso, E. Besalú, J.M. Sanchez, E. Anticó, J. Chromatogr. A 1218 (2011) 4863-4868.

[111] L. Hong-Ping, L. Gwo-Chen, J. Jen-Fon, J. Chromatogr. A 1012 (2003) 129.

[112] R.J. Miltner, T.F. Speth, S.D. Richardson, S.W. Krasner, H.S. Weinberg, J.E. Simmons, J. Toxicol. Environ. Health A 71 (2008) 1133.

[113] I. Kristiana, C. Joll, A. Heitz, J. Chromatogr. A 1225 (2012) 45.

[114] P. Gostelow, S.A. Parsons, R.M. Stuetz, Water Res. 35 (2001) 579.

[115] M.J. Sclimenti, S.W. Krasner, S.D. Richardson, The determination of DBPs using a solid-phase microextraction (SPME)- GC/ECD technique, Proceedings of the 2002 AWWA WQTC; AWWA: Denver, CO, 2002.

[116] H.S. Weinberg, S.W. Krasner, S.D. Richardson, A.D. Jr. Thruston, The Occurrence of Disinfection By-Products (DBPs) of Health Concern in Drinking Water: Results of a Nationwide DBP Occurrence Study; EPA/600/R-02/068; U.S. EPA: Athens, GA, 2002. www.epa.gov/Athens/publications/reports/ EPA_600_R02_068.pdf.

[117] S.D. Richardson, Anal. Chem. 79 (2007) 4295.

[118] C.J. Koester, A. Moulik, Anal. Chem. 77 (2005) 3737.

[119] S. Lacorte, I. Guiffard, D. Fraisse, D. Barceló, Anal. Chem. 72 (2000) 1430.

[120] H.B. Lee, T.E. Peart, M.L. Svoboda, J. Chromatogr. A 1094 (2005) 122.

[121] E. Pitarch, C. Medina, T. Portoles, F.J. López, F. Hernández, Anal. Chim. Acta 583 (2007) 246.

[122] S.Y. Zhang, Q.A. Zhang, S. Darisaw, O. Ehie, G.D.Wang, Chemosphere 66 (2007) 1057.

[123] R.A. Trenholm, B.J. Vanderford, J.C. Holady, D.J. Rexing, S.A. Snyder, Chemosphere 65 (2006) 1990.

[124] T.A. Ternes, M. Bonerz, N. Herrmann, D. Loffler, E. Keller, B.B. Lacida, A.C. Alder, J. Chromatogr. A 1067 (2005) 213.

[125] C. Huertas, J. Morillo, J. Usero, I. Gracia-Manarillo, Talanta 72 (2007) 1149.

[126] J.B. Baugros, B. Giroud, G. Dessalces, C. Cren-Olivé, M.F. Grenier-Loustalot, Anal. Chim. Acta 607 (2008) 191.

[127] B.J. Vanderford, R.A. Pearson, D.J. Rexing, S.A. Snyder, Anal. Chem. 75 (2003) 6265.

[128] Directive 2000/60/EC, Off. J. Eur. Commun., October 23, L327 (2000).

[129] Y. Hwang, T. Matsuo, K. Hanaki, N. Suzuki, Water Res. 29 (1995) 711.

[130] F. Dincer, A. Muezzinoglu, Environ. Sci. Health, Part A 43 (2008) 1569.

[131] P. Gostelow, S.A. Parsons, R.M. Stuetz, Water Res. 35 (2001) 579.

[132] K.K. Kleeberg, Y. Liu, M. Jans, M. Schlegelmilch, J. Streese, R. Stegmann, Waste Management 25 (2005) 872.

[133] R. Liu, J. L. Zhou, A. Wilding, J. Chromatogr. A 1022 (2004) 179.

[134] C. G. Campbell, S. E. Borglin, B. Green, A. Grayson, E. Wozei, W. T. Stringfellow, Chemosphere 65 (2006) 1265.

[135] M. Petrovic, E. Eljarrat, M. J. Lopez de Alda, D. Barceló, Anal. Bioanal. Chem. 378 (2004) 549.

[136] S.W. Krasner, S. Pastor, R. Chinn, M.J. Sclimenti, H.S. Weinberg, S.D. Richardson, A.D. Jr. Thruston, The occurrence of a new generation of DBPs (beyond the ICR), Proceedings of the 2001 AWWA WQTC; AWWA: Denver, CO, 2001.

[137] G.D. Onstad, H.S. Weinberg, Anal. Chim. Acta 534 (2005) 281.

[138] D.J. Munch, J.W. Munch, A.M. Pawlecki, Method 552.2: Determination of haloacetic acids and dalapon in drinking water by liquid-liquid extraction, derivatization and gas chromatography with electron capture detection. In Methods for the Determination of Organic Compounds in Drinking Water, Supplement III; EPA/600/R-95/131; U.S. EPA: Cincinnati, OH, 1995.

[139] K.S. Brophy, H.S. Weinberg, P.C. Singer; Quantification of nine haloacetic acids using gas chromatography with electron capture detection. In Natural Organic Matter and Disinfection By-Products: Characterization and Control in Drinking Water; Barrett, S. E., Krasner, S. W., Amy, G. L., Eds.; ACS Symposium Series 761; American Chemical Society: Washington, DC, 2000; pp 343-355.

[140] T.F. Speth, R.S. Summers, A.M. Gusses, Environ. Sci. Technol. 32 (1998) 3612.

[141] M.T. Khan, C.L.D. Manes, C. Aubry, L. Gutierrez, J.P. Croue, Environ. Sci. Technol. 47 (2013) 10884.

[142] M. Luo, Z. Wang, Desalination 141 (2001) 15.

[143] Y. Ding, Y. Tian, Z.P. Li, H.Y. Wang, L. Chen, Chem. Eng. Sci. 104 (2013) 1028.

[144] G. Fernandez-Alvarez, G. Garralon, F. Plaza, A. Garralon, J. Perez, M.A. Gomez, Desalination, 263 (2010) 264.

[145] P. Xu, C. Bellona, J.E. Drewes, J. Membr. Sci., 353 (2010) 111.

[146] J.S. Vrouwenvelder, S.A. Manolarakis, J.P. Van der Hoek, J.A.M. Van Paassen, W.G.J. Van der Meer, J.M.C. Van Agtmaal, H.D.M. Prummel, J.C. Kruithof, M.C.M. Van Loosdrecht, Water Res. 42 (2008) 4856.

[147] S. Velten, F. Hammes, M. Boller, T. Egli, Water Res. 41 (2007) 1973.

[148] C. Nuengjamnong, J. Kweon, J. Cho, C. Polprasert, K. Ahn, Desalination 179 (2005) 117.

[149] S. Jeong, S.J. Kim, L.H. Kim, M.S. Shin, S. Vigneswaran, T.V. Nguyen, I.S. Kim, J. Membr. Sci. 428 (2013) 434.

[150] Y. Zhao, L.F. Song, S.L. Ong, SL., J. Membr. Sci 349 (2010) 65.

[151] J.J. Wu, A.E. Contretas, Q.L. Li, J. Membr. Sci 458 (2014) 120.

[152] S. Hong, M. Elimelech, J. Membr. Sci 132 (1997) 159.

[153] L. Fan, J.L. Harris, F.A. Roddick, N.A. Booker, Water Res. 35 (2001) 4455.

[154] M. Khayet, A. Velázquez, J.I. Mengual, J. Membr. Sci 240 (2004) 123.

[155] C. Jucker, M.M. Clark, J. Membr. Sci 97 (1994) 37.

[156] K. Chon, S. Sarp, S. Lee, J.H. Lee, J.A. Lopez-Ramirez, J. Cho, Desalination 272 (2011) 128.

[157] K. Chon, S. Lee, K. Chon, A.A. Hussain, J. Cho, Desalin. Water Treat. 18 (2010) 61.

[158] S. Lee, W.S. Ang, M. Elimelech, Desalination 287 (2006) 313.

[159] C. Jarusutthirak, G. Amy, J.P. Croué, Desalination 145 (2002) 247.

[160] S. Lee, M. Elimelech, Environ. Sci. Technol. 40 (2006) 980.

[161] H.K. Shon, S. Vigneswaran, I.S. Kim, J. Cho, H.H. Ngo, Water Res. 38 (2004) 1933.

[162] N. Park, S. Lee, S.R. Yoon, Y.H. Kim, J. Cho, Desalination 202 (2007) 231.

[163] M. Elimelech, Z. Xiaohua, A.E. Childress, S. Hong, J. Membr. Sci. 127 (1997) 101.

[164] A.C. Fonseca, R.S. Summers, A.R. Greenberg, M.T. Hernandez, Environ. Sci. Technol. 41 (2007) 2491.

[165] C.Y. Tang, Q.S. Fu, C.S. Criddle, J.O. Leckie, Environ. Sci. Technol. 41 (2007) 2008.

[166] K. Boussu, C. Vandecasteele, B. Van der Bruggen, J. Membr. Sci. 310 (2008) 51.

[167] Y. Zhao, L. Song, S.L. Ong, J. Membr. Sci. 349 (2010) 65.

[168] N. Her, G. Amy, J. Chung, J. Yoon, Y. Yoon, Chemosphere 70 (2008) 495.

[169] M.R. Collins, G.L. Amy, C. Steelink, Environ. Sci. Technol. 20 (1985) 1028.

[170] D.M. Owen, G. Amy, Z.K. Chowdhury, R. Paode, G. McCoy, K. Viscosil, J. Ambient Water Works Association 87 (1995) 46.

[171] R. Fabris, C.W.K. Chow, M. Drikas, B. Eikebrokk, Water Res. 42 (2008) 4188.

[172] E.L. Sharp, P. Jarvis, S.A. Parsons, B. Jefferson, 286 (2006) 104.

[173] K. Chon, J. Cho, HK. Shon, K. Chon, Desalination 301 (2012) 59.

[174] S. Alzahrani, A.W. Mohammad, N. Hilal, P. Abdullah, O. Jaafar, Sep. Pur. Technol. 118 (2013) 324.

[175] X.L. Zeng, L. Han, J.D. Liu, W.C. Ding, Q. Zhang, A. Jiang, Spectrosc. Spect. Anal. 33 (2013) 3312.

[176] C. Ayache, M. Pidou, J.P. Croue, J. Labanowski, Y. Poussade, A. Tazi-Pain, J. Keller, W. Gernjak, Water Res., 47 (2013) 2633.

[177] N. Cortés-Francisco, J. Caixach, Environ. Sci. Technol. 47 (2013) 9619.

CHAPTER 2

OBJECTIVES

The main objective is to evaluate the efficiency of reverse osmosis membranes for micropollutants removal in brackish water, sea water and waste water samples, developing analytical methodologies based on HS-SMPE and GC-MS. The micropollutant families studied in this Thesis include VOCs, fragrance allergens, odours, pesticides, EDC and DBPs.

Another objective of this Thesis is the study of the organic fouling in reverse osmosis membrane surfaces as well as the identification of some potential organic foulants in the influent water of a tertiary waste water treatment and the relationship between basic parameters and fouling.

CHAPTER 3

EXPERIMENTAL, RESULTS AND DISCUSSION

This chapter includes the experimental part and the results obtained in the different studies done during the present Doctoral Thesis, in order to study the micropollutants presence and rejection by advance membrane treatments. The studies have been published or submitted in different international scientific journals, which are shown in the publications list included in the Annex II. Before each group of studies, it is included a brief introduction were the main objectives of the research are detailed. Furthermore, a discussion of the most relevant results is also presented.

The first section focuses on the development of new analytical methodologies for organic micropollutants determination by headspace solid phase microextraction (HS-SPME) and gas chromatography-mass spectrometry (GC-MS) determination. As discussed in the Thesis introduction, the main pathway of organic micropollutants into the global environment is through emissions into environmental waters. Therefore, the determination of water quality is of increasing concern because of the recognized adverse effects of some organic contaminants on human health and the environment. To this end, the development of highly sensitive and selective methods for the determination of different organic contaminants in environmental waters is of major importance within the scientific community. For this reason, one of the main objectives of this Thesis was to develop analytical methods to determine organic micropollutants covering together a wide range of families including volatile organic compounds, fragrance allergens, endocrine disrupting compounds, odours, pesticides and disinfection by-products in water samples. The analytical methods proposed minimized the use of organic solvents in the entire analytical process. Furthermore, the ubiquitous presence of some of these organic micropollutants leads to the inherent exposure of humans to them.

The second section refers to the application of the GC-MS methodologies developed. The study was done in order to evaluate and monitor the presence of the organic micropollutants to assess the effectiveness of a conventional waste water treatment plant (WWTP) using thin film composite polyamide reverse osmosis (RO) membranes as a tertiary treatment. In addition, the micropollutants rejection was also related to their physico-chemical properties. Limited data exist in the literature for meaningful comparison of solute properties and rejection. Therefore, the results obtained in this study can contribute to an improved understanding of micropollutants rejection by RO membranes.

The third section in divided in two complementary studies in order to characterize the organic foulants found in the influent water as well as the organic compounds in the RO membrane surface. The first study allows the characterization of organic foulants in water samples by HS-SPME and GC-MS. Furthermore, typical water parameters, such as the total organic carbon (TOC), chemical oxygen demand (COD), biological oxygen demand (BOD) and specific ultraviolet light absorbance (SUVA) have been determined. All of the influent water analyses have been done in order to correlate the results with the organic fouling presence on the membrane surface and to have complementary information. Therefore, the second study has been done in order to provide valuable information for characterizing specific organic compounds present in the fouling layer by GC-MS, as well as classify them into different families, studying the applicability of different polarity SPME fibres directly into the fouling for the first time.

3.1. Development of methods

As mentioned before in the last chapter, the studies performed in this Thesis have been done due to the occurrence of trace organic micropollutants in treated and untreated water, which has been identified as a significant environmental health concern. Currently, treated municipal waste water is discharged to the environment and generally considered as a waste. However, municipal wastewater effluent should be a resource from which high quality water for reuse can be produced [1].

This section focuses on the development of two analytical methods based on the simultaneously determination of different families of micropollutants by HS-SPME and GC-MS in different types of water samples. The water samples belong to different advanced tertiary RO membrane water treatments, including waste water, sea water and brackish water, coming from different research units located in the North-East of Spain.

As commented in previous sections, the scope of the RO membrane treatments application has been continually expanding. Increased demands on the industry to conserve water, reduce energy consumption, control pollution and reclaim useful materials from waste streams have made new applications economically attractive. In general, RO membranes now offer the possibility of higher rejection of inorganic and organic compounds, including micropollutants [2].

However, the low levels of micropollutants in waters and the high complexity of water samples require the development of high sensitive and selective analytical methods that can simultaneously determine a broad range of these pollutants. Moreover, the efficiency of the RO membrane treatments can be evaluated.

The compounds selected have been previously detected in environmental waters. In this respect, volatile organic compounds (VOCs) are one of the chief issues in the environment. VOCs have neurotoxic and genotoxic effects on human health and can cause respiratory and reproductive disorders [3].

For instance VOCs, which represent approximately a 10% of the total dissolved organic carbon of unpolluted waters and the concentrations, are much higher in raw waters from different anthropogenic sources [6]. In addition, for decades municipalities have utilized chlorine as a primary disinfectant for surface water sources to inactive microbial pathogen. A side effect of chlorination is that residual chlorine can react with naturally occurring organics in water, oxidizing it to form disinfection by-products [4-6]. These byproducts may lead to increased health risks if present at high $ng{\cdot}mL^{-1}$ levels, being some of them classified as carcinogens, such as the trihalomethanes (THMs) [7-8].

The SPME extraction procedures have been optimized with different polarity fibres tested, including polyacrilate (PA), polyethylenglicol (PEG), polydimethylsiloxane/ divinylbenzene (PDMS/DVB), polydimethylsiloxane/divinylbenzene/carboxen (PDMS/

DVB/CAR), polydimethylsiloxane (PDMS). The main parameters that have been optimized are: type of fibre, extraction temperature, ionic strength, extraction time and sample volume. The optimization has been carried out by comparing the chromatographic areas of the compounds analyzed at different conditions.

In the studies, HS-SPME has been selected because it allows complete elimination of organic solvents in the pre-treatment step and decreases the number of steps needed for sample preparation becoming an accepted technique for the determination of volatile and semi-volatile substances, as well as it could be a totally automated technique. Another advantage of HS techniques when volatile compounds are analyzed is that the extraction is highly selective and the matrix effect becomes lower than submerged techniques [9].

The results of these studies have been published in Talanta 116 (2013) 937–945 and Analytical and Bioanalytical Chemistry Research 1 (2014) 38-49.

References

[1] L. Prieto, S. Miralles-Cuevas, I. Oller, A. Agüera, G. Li Puma, S. Malato, J. Hazard. Mater. 211 (2012) 131.

[2] S. C. Monteiro, A. B. A. Boxall, Reviews in Environmental Contamination and Toxicology, 202 (2010) 153.

[3] USEPA, EPA-450/1-90-004a, Cancer Risk from Outdoor Exposure to Air Toxics, Office of Air Quality Planning and Standards, 1990.

[4] R. J. Miltner, T.F. Speth, S.D. Richardson, S.W. Krasner, H.S. Weinberg, J.E. Simmons, J. Toxicol. Environ. Health A 71 (2008) 1133.

[5] S.W. Krasner, H.S. Weinberg, S.D. Richardson, S.J. Pastor, R. Chinn M.J. Sclimenti, G.D. Onstad, A.D. Thurston, Environ. Sci. Technol. 40 (2006) 7175.

[6] J.C. Pressman, S.D. Richardson, T.F. Speth, R.J. Miltner, M.G. Narotsky, Munter, G.E. Rice, L.K. Teuschler, T.A. McDonald, Environ. Sci. Technol. 44 (2010) 7184.

[7] K. Cantor, C.R. Lynch, M.E. Hildesheim, M. Dosemeci, J. Lubin, M. Alavanj, G. Craun, J. Epidemiol. 9 (1998) 21.

[8] J.C. Loper , D.R. Lang, R.S. Schoeny, B.B. Richmond, P.M. Gallagher, C.C. Smith, J. Toxicol. Environ. Health 4 (1978) 919.

[9] Z. Mester, R. Sturgeon, J. Pawliszyn, Spectrochim. Acta Part B 56 (2001) 233.

3.1.1. Simultaneous determination of 76 micropollutants in water samples by headspace solid phase microextraction and gas chromatography-mass spectrometry

SIMULTANEOUS DETERMINATION OF 76 MICROPOLLUTANTS IN WATER SAMPLES BY HEADSPACE SOLID PHASE MICROEXTRACTION AND GAS CHROMATOGRAPHY-MASS SPECTROMETRY

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Abstract

This study focuses on the development of an analytical method based on headspace solid phase microextraction (HS-SPME) and gas chromatography-mass spectrometry (GC-MS) for the simultaneous determination of 76 micropollutants in water samples. The selected micropollutants include volatile organic compounds (VOCs) (e.g. chlorobenzenes, chloroalkanes), endocrine disrupting compounds (EDCs) (e.g. bisphenol A and tributyl phosphate), odour compounds (e.g. limonene, phenol), fragrance allergens (e.g. geraniol, eugenol) and some pesticides (e.g. heptachlor, terbutryn). The experimental conditions affecting their extraction, such as the type of fibre, temperature and time of extraction, sample volume and ionic strength of the samples were optimized using HS-SPME. The method showed good linear range, reproducibility between days, repeatability and low detection limits (at ng·L^{-1} levels). The validated method has been applied to determine the target organic micropollutants in aqueous samples from different experimental research units of surface water, sea water, waste water and those effluents of advance membrane treatments. The optimized method showed good performance in the different types of samples studied. The analysis revealed the presence of several micropollutants at concentrations between 20-5000 µg·L^{-1}, such as ethylbenzene, o-xylene, p-isopropilbenzene, D-limonene, citral and isoeugenol, due to the fact that these species are commonly used in domestic and industrial applications.

Keywords: *gas chromatography-mass spectrometry, organic micropollutants, solid phase microextraction, water samples, water treatment.*

Talanta 116 (2013) 937–945

1. INTRODUCTION

Contamination of environmental waters by trace levels of organic substances, called organic micropollutants, is a subject of increasing concern in the majority of countries. The organic micropollutants includes any organic compounds that may be found at microgram per litre concentrations or lower in water, such as pesticides, pharmaceutical residues, hormones, flame-retardants, plasticizers, perfluorinated compounds, among others [1].

Water quality is currently controlled by several legislations. For instance, the United States Environmental Protection Agency (U.S. EPA) has developed classification systems and Environmental Quality Standards (EQS) for assessing the quality of surface waters [2]. Moreover, in the European Union, the Water Framework Directive, Directive 2008/105/CE control the river, lake, ground and coastal waters and also heavily modified and artificial water bodies [3]. These regulations limit some of the micropollutants studied at low levels of concentration ($\mu g \cdot L^{-1}$) in order to prevent further deterioration and protect, enhance and restore the status of all bodies of water with the aim of achieving at least good status by 2015. Nevertheless, occurrences in groundwater and drinking waters of some other unregulated substances have also been reported in the literature [4].

However, the low levels of micropollutants in waters and the high complexity of water samples require the development of highly sensitive and selective analytical methods that can simultaneously determine a broad range of these pollutants. For the present work, different families of micropollutants were selected and described below.

Volatile organic compounds are one of the chief issues in the environment. VOCs have neurotoxic and genotoxic effects on human health and can cause respiratory and reproductive disorders [5]. Moreover, they represent approximately 10% of the total dissolved organic carbon of unpolluted waters and the concentrations are much higher in raw waters from different anthropogenic sources [6]. In this study 52 VOCs have been selected and some of them are regulated by the Directive 2008/105/CE.

Endocrine disrupting compounds (EDCs) are chemicals which have the potential to disturb hormonal equilibrium in living organisms [7]. These compounds, mistakenly recognized by estrogenic receptors, are treated the same as those naturally present in the organisms. Many EDCs are not regulated yet. However, with the collection of sufficient data to prove their toxic effects on human health, they may be the most probable target compounds for future regulation [8]. The U.S. EPA tried to establish the Endocrine Disruptor Screening Program (EDSP) to develop official screening methods and toxicity testing strategies for approximately 87.000 compounds [9]. In this study 3 EDCs have been selected.

Odour emissions affect quality of life, leading to psychological stress and symptoms such as insomnia, loss of appetite and irrational behaviour [10,11]. Therefore, waste water professionals have found the need to address odours as a primary concern in the design and operation of collection and treatment facilities in order to control odour emissions. However, there is no any European legislation that controls odour compounds in waters. For that reason eight odour compounds were selected to be analyzed, moreover they are the most commonly detected in these waters.

Fragrance allergens are a group of chemicals incorporated in most cosmetic and other personal care products including baby care ones. Some of the suspected allergens can cause systemic effects. Legal restrictions only limit the use of 26 fragrance ingredients suspected of causing skin reactions [12-14]. In this study, ten of these fragrances have been selected, which are reported as the most allergens.

The last group of selected compounds has been some pesticides which were proposed for regulation by the European Commission, on the 31th of June of 2012 [15]. They are generally toxic for living organisms and are difficult to degrade, being toxic agents with persistent bioaccumulative effects [16]. In this study three of these pesticides have been selected.

As the demand for high-quality water is constantly increasing through the world, many studies have given considerable attention aimed at establishing the removal efficiency of organic solutes. Some studies are based on advanced membrane treatments, such as reverse osmosis (RO). Since the development of reverse osmosis and ultrafiltration (UF) as a practical unit operation in the late 1950's, the scope for their application has been continually expanding. In general, RO membranes now offer the possibility of higher rejection of inorganic and organic compounds, including micropollutants. Moreover, UF processes are used as a pretreatment of the reverse osmosis, improving the efficiency of these advance treatments. A few real studies can be found evaluating the elimination of drugs of abuse, endocrine disrupting compounds, pharmaceuticals and personal care products [17-20].

Several extraction techniques can be used for the extraction of organic micropollutants from water samples, whereas solid phase microextraction has been used as the best option for these compounds, while it can selectively extract selected compounds and no solvents are required [21-23].

SPME allows complete elimination of organic solvents in the pretreatment step and decreasing the steps for sample preparation and has become an accepted method for the determination of volatile and semi-volatile substances.

Therefore, in this study headspace solid phase microextraction (HS-SPME) has been used for the determination of the organic micropollutants in water, due to the high volatility of the target compounds. The advantage of HS techniques when volatile compounds are analyzed is that the extraction is more selective and the matrix influence becomes lower [24].

In this study a method based on HS-SPME and GC-MS for the characterization of 76 compounds belonging to different chemical families has been developed. The method has been applied for determine the micropollutants in water samples, which are natural water samples coming from river, wastewater treatment plant and sea. To allow the study of removal of priority compounds by membrane systems, a cost-effective screening technique was developed, which does not use solvent and allows characterization of a large variety of compounds simultaneously.

2. EXPERIMENTAL

2.1 Chemicals and reagents

The 54 volatile organic compounds were obtained from a mixture of 592/524 Volatile Organics Calibration Mix, EPA 524.2 provided by Sigma-Aldrich, Supelco (Madrid, Spain), all of them in a concentration of 2000 mgL^{-1} in methanol. Standard solution of Geosmin (100 mg·L^{-1} in methanol), was also supplied by Sigma-Aldrich.

Individual standards of fragrance allergens: benzyl alcohol, citral, geraniol, hydroxycitronellal, cinnamyl alcohol, eugenol, amyl cinnamaldehid and benzyl salicycate were supplied by Sigma-Aldrich. Moreover, coumarin and isoeugenol analytical standards were provided by Dr. Ehrenstorfer (Augsburg, Germany). Individual standards of odours compounds: dimethyl disulfide, limone, carvone and skatole were supplied by Sigma-Aldrich. Furthermore, 3-methylphenol, phenol and indole analytical standards were supplied from Dr. Ehrenstorfer. Individual standards of pesticide compounds: heptachlor, terbutryn and dicofol were provided by Sigma-Aldrich. Individual standards of EDCs compounds: bisphenol A, tris(2-chloroethyl) phosphate and tributyl phosphate were also supplied from Sigma-Aldrich.

Four solution mixtures of the different families of compounds (odours, allergens, EDCs and pesticides) were prepared at 2000 mg·L^{-1} in methanol from the individual standards. A standard mixture solution of 75 compounds was prepared from the solutions described above (100 mg·L^{-1} in methanol), except for geosmin which was purchased directly at 100 mg·L^{-1}. Working solutions were prepared daily in methanol GC grade with purity >99.9% (from Prolabo, Barcelona, Spain) and stored under refrigeration (2-6ºC). The minimal purity of the standards was 98%.

Sodium chloride (NaCl) (ACS reagent ≥ 99 %) was supplied by Sigma-Aldrich. Helium gas 99,999% was supplied from Praxair, Barcelona, Spain.

Three commercial extraction fibres including 100μm Polydimethylsiloxane (PDMS), 65 μm Polydimethylsiloxane /Divinylbenzene (PDMS/DVB) and 50/30 μm Polydimethylsiloxane/ Divinylbenzene/Carboxen (PDMS/DVB /CAR) were purchased from Supelco.

2.2 Sample collection

The analytical method has been developed to analyse different types of water samples. Studied samples belong to the inlet and outlet of tertiary advanced membrane treatments. The inlet is called influent and the outlet, effluent. These treatments are applied using research units, which are big pilot plants of ultrafiltration and reverse osmosis processes, located in real installations. The water treated ranged from surface water (Llobregat River, Barcelona, Spain), effluents of secondary treatment of an urban waste water treatment plant (Vila-Seca, Spain) and sea water (Mediterranean Sea, Tarragona, Spain). Seawater and river water are treated with a plant according to Figure 1a while wastewater is treated with a plant according to Figure 1b. The process and sampling points (stars) are shown schematically, also in Figure 1; sea water and surface water application research units with ultrafiltration and reverse osmosis processes, waste water treatment plant with a water application research unit of reverse osmosis membranes as a tertiary treatment. Samples were taken on

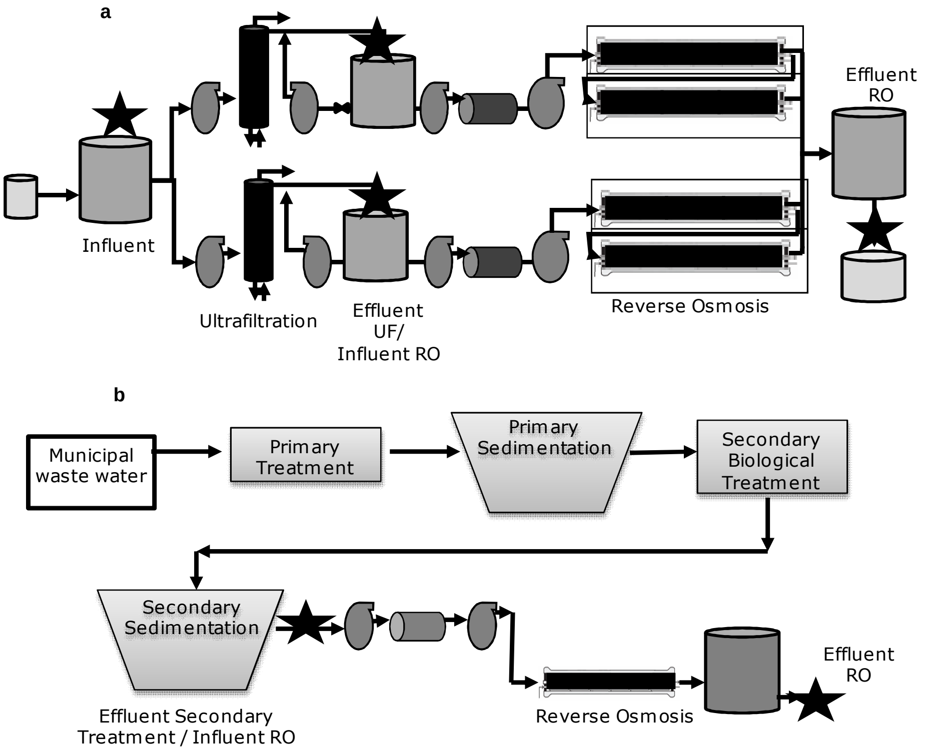


Figure 1. a) Sea water and surface water application research units with ultrafiltration and reverse osmosis processes with stars as a sample points in black, b) Waste water treatment plant from Vila-Seca with application research units of reverse osmosis membranes as a tertiary treatment with stars as a sample points in black.

Talanta 116 (2013) 937-945

August of 2012. Water samples were collected in amber glass containers and were stored in the dark at 4ºC until analysis, within two days.

2.3 Headspace-solid phase microextraction equipment

For the extraction procedure, 30 mL of sample were introduced into a 50 mL PTFE/silicone screw-cap glass vial. Then, 0.4 g·mL^{-1} of NaCl (saturated solution) was added, the vial was closed and put over a magnetic stirrer in a water thermostatic bath at 50ºC.

The magnetic stirring was applied at 1000 rpm during the 30 minutes of extraction and the fibre of PDMS/DVB was exposed to the headspace above the aqueous solution. After the extraction, the fibre was inserted into the injection port of the gas chromatograph for the thermal desorption and analysis. Fibre was desorbed at 270ºC during the chromatographic analysis in the splitless mode, in order to allow the total desorption of compounds and the fibre conditioning. Blanks of the fibres needed to be analyzed before a sample gets extracted.

2.4 Gas chromatography-mass spectrometry equipment and experimental conditions

The gas chromatography analysis was performed with a GCMS-QP2010 Ultra/ GCMS-QP2010 SE from Shimadzu, equipped with a split/splitless injector and coupled to a mass spectrometer detector. Helium was employed as a carrier gas at constant column flow of 1 mL·min^{-1}. Analytes were separated with TRB-5MS column (60m x 0.32 mm i.d., 1 μm film thickness) from Tecknokroma, Barcelona, Spain. The split/splitless injection port was equipped with a 0.75 mm ID liner from Supelco, and operated at 270ºC, allowing direct injection or SPME. The oven temperature program was started at 40ºC, held for 2 min; then increased by 6ºC·min^{-1} up to 150ºC and by 20ºC·min^{-1} up to 300Cº, and held for 12 min. The total run was 39 min. The MS analyses were conducted in full-scan mode with a single quadrupole and monitored masses between 40 and 280 m/z. Ionization was carried out in the electron impact (EI) mode at 70 eV. The transfer line temperature was maintained at 300ºC and the ion source temperature at 250ºC.

3. RESULTS AND DISCUSSION

3.1 GC-MS optimization

A method for the simultaneous determination of 76 micropollutants has been developed. The chromatographic separation takes 39 minutes. To optimize the chromatographic separation, individual mixtures of the different families of the micropollutants were injected in order to separate each compound appropriately. Then, 1 μL of 10 mg·L^{-1} mixture of all micropollutants was directly injected in the splitless injector in Full-scan mode. After the optimization of the temperature gradient, the retention time of every compound was determined.

Moreover, the quantification ion of each compound was selected, which are summarised in Table 1.

Table 1. Target compounds, quantification and identification ions and main validation data obtained by analyzing effluents of reverse osmosis of surface water spiked at 1 ng·mL^{-1} (n=5).

Family	Compound	t_R (min)	Quantification ions	Identification ions	LOD (ng·mL^{-1})	LOQ (ng·mL^{-1})	r^2	RSD^A (%)	RSD^B (%)
	1.1-dichloroethene	5.17	61	96, 98	0.100	0.333	0.989	4.7	8.2
VOCs	**(Z)-1.2-dichloroethene**	6.35	61	96, 63	0.033	0.100	0.990	5.2	6.1
	1.1-dichloroethane	6.40	63	65, 83	0.033	0.333	0.997	3.6	5.6
	2.2-dichloropropane	6.60	77	79, 97	0.033	0.100	0.990	7.8	7.5
	trichloromethane (*)	6.67	83	85, 47	0.001	0.003	0.989	4.5	8.2
	(E)-1.2-dichloroethene	7.16	61	96, 63	0.033	0.333	0.988	9.8	8.7
	bromochloromethane	7.41	130	128, 93	0.100	0.333	0.988	20.3	18.3
	1.1.1-trichloroethane	7.69	97	99, 61	0.033	0.333	0.993	5.3	6.9
	1.2-dichloroethane	7.74	62	64, 49	0.033	0.333	0.993	4.2	7.3
	1.1-dichloro-1-propene	8.05	75	39, 110	0.017	0.033	0.992	5.6	8.3
	benzene	8.26	78	51, 52	0.001	0.003	0.997	4.3	8.7
	carbon tetrachloride	8.38	117	119, 121	0.003	0.033	0.993	6.4	10.1
	1.2-dichloropropane	9.44	63	62, 76	0.017	0.033	0.998	4.3	5.2
	trichloroethene	9.59	130	95, 132	0.003	0.033	0.991	5.2	11.3
	dibromomethane (*)	9.78	174	172, 93	0.003	0.033	0.992	3.2	5.2
	bromodichloromethane (*)	10.11	83	85, 129	0.100	0.333	0.987	18.9	20.5
	(E)- 1.3-dichloro-1-propene	11.14	75	39, 110	0.001	0.003	0.999	5.5	10.1
	(Z)- 1.3-dichloro-1-propene	11.65	75	39, 110	0.003	0.010	0.993	6.1	10.9
	toluene	12.13	91	92	0.0005	0.002	0.991	7.5	12.3
	1.1.2-trichloroethane	12.23	97	83, 61	0.100	0.333	0.988	17.3	15.7
	1.3-dichloropropane	12.64	76	41, 78	0.010	0.033	0.994	4.7	8.3
	dibromochloromethane (*)	13.12	129	127, 131	0.001	0.003	0.992	7.8	9.2
	1.2-dibromoethane	13.49	107	109	0.017	0.033	0.997	10.2	13.6
	tetrachloroethene	13.62	166	164, 129, 131	0.033	0.333	0.992	2.8	5.1
	chlorobenzene (*)	14.85	112	77, 114, 51	0.001	0.033	0.992	3.1	4.2
	1.1.1.2-tetrachloroethane	14.92	131	133, 117, 119	0.010	0.033	0.999	8.2	9.8
	ethylbenzene (*)	15.31	91	106	0.0005	0.002	0.993	6.9	12.6
	o-xylene (*)	15.56	91	106, 105, 77	0.001	0.003	0.994	8.7	11.3
	tribromomethane (*)	16.17	173	93, 81	0.100	0.333	0.978	21.2	20.8
	styrene	16.27	104	78, 103	0.0005	0.002	0.998	5.7	7.7
	p-xylene/ m-xylene (*)	16.38	91	106, 105	0.0005	0.002	0.994	5.8	8.0
	1.1.2.2-tetrachloroethane	16.83	83	85, 95, 131	0.010	0.033	0.998	6.2	7.2
	1.2.3-trichloropropane	17.10	75	97, 110	0.010	0.033	0.996	5.1	6.3
	isopropilbenzene (*)	17.35	105	120, 79	0.001	0.003	0.999	8.2	12.5
	bromobenzene	17.71	77	156, 158, 51	0.0005	0.003	0.999	9.1	10.4
	1-chloro-2-methylbenzene	18.32	126	125, 128	0.001	0.003	0.998	8.3	10.2
	1-chloro-4-methylbenzene	18.47	91	126, 125	0.010	0.033	0.996	6.2	8.8
	1.2.4-trimethylbenzene	18.72	105	120	0.0005	0.002	0.998	11.3	13.2
	1.3.5-trimethylbenzene	18.95	105	120	0.010	0.033	0.998	11.6	6.2
	tert-butylbenzene	19.52	119	91, 134	0.0005	0.002	0.999	5.2	7.3
	sec-Butylbenzene	20.07	105	134	0.0005	0.002	0.999	3.9	6.8
	1.3-dichlorobenzene	20.20	146	148, 111, 75	0.010	0.033	0.991	7.3	11.8
	p-isopropilbenzene	20.43	119	91, 134	0.0005	0.002	0.998	7.8	9.8
	1.2-dichlorobenzene	20.92	146	148, 111	0.001	0.003	0.993	7.2	9.8

Table 1. Continued.

	1.4-dichlorobenzene	21.02	146	148, 111, 75	0.010	0.033	0.993	10.3	10.5
	butylbenzene	21.30	91	92, 134	0.0005	0.002	0.997	5.6	11.7
	1.2-dibromo-3-chloropropane	22.05	157	155, 75	0.001	0.003	0.997	6.2	7.3
	1.2.4-trichlorobenzene	23.95	180	182, 145	0.001	0.003	0.991	4.2	8.9
	naphthalene	24.14	128	127, 129	0.0005	0.003	0.998	7.8	12.1
	hexachlorobutadiene	24.52	225	227, 223	0.010	0.033	0.991	8.5	7.1
	1.2.3-trichlorobenzene	24.55	180	182, 145	0.010	0.033	0.990	12.3	8.9
Odours	**dimethyl disulfide**	11.40	94	79, 45	0.017	0.033	0.998	5.9	11.5
	phenol	18.62	94	66	0.001	0.333	0.989	25.3	10.1
	D-limonene (*)	20.60	68	93	0.001	0.003	0.999	9.2	10.3
	3-methyl-phenol	21.40	108	107, 79	0.100	0.333	0.991	6.3	14.8
	carvone (*)	24.81	82	54, 108	0.001	0.003	0.993	11.8	13.6
	indole	25.48	117	90	0.100	0.333	0.991	9.7	9.3
	skatole	26.56	130	131, 77	0.010	0.033	0.993	4.4	10.4
	geosmin	26.98	112	125, 97	0.0005	0.002	0.997	2.8	8.6
Allergens	**benzyl alcohol**	20.54	79	108	0.001	0.003	0.989	9.8	12.4
	citral	24.62	41	69	0.010	0.033	0.993	8.2	10.2
	geraniol	24.72	69	41	0.033	0.100	0.990	13.1	15.2
	hidroxicitronellal	25.16	59	43, 71	0.100	0.333	0.992	5.2	7.9
	cinnamyl alcohol	25.84	92	78, 134	0.100	0.333	0.997	18.8	19.6
	eugenol	26.12	164	103	0.010	0.033	0.993	3.7	7.7
	isoeugenol	27.04	164	149	0.100	0.333	0.991	15.6	12.3
	coumarin (*)	27.18	118	146, 90	0.0005	0.002	0.988	14.2	18.9
	ammylcinamaldehid	28.67	129	91, 117	0.0005	0.002	0.996	15.1	11.6
	benzil salizicate	30.49	91	65	0.017	0.060	0.990	12.9	11.2
Pesticides	**terbutryn**	30.87	226	241, 170	0.010	0.033	0.995	10.1	13.8
	heptachlor	31.17	100	272	0.017	0.060	0.991	9.9	6.3
	dicofol	31.64	139	111, 251	0.017	0.060	0.995	8.3	14.3
EDCs	**tributyl phosphate (*)**	28.37	99	155, 211	0.001	0.003	0.999	5.3	7.2
	tri(2-chloroethyl) phosphate	29.35	63	249	0.001	0.003	0.993	21.2	22.8
	bisphenol A	33.23	213	119, 228	0.001	0.003	0.986	13.5	18.2

Then, two qualification ions were selected for each compound, presented in Table 1 and compound confirmation was done with whole mass spectrum.

3.2 HS-SPME optimization

Optimization of solid-phase microextraction conditions for the 76 micropollutants selected was accomplished using aliquots of effluents of application research units of reverse osmosis of surface water spiked with the analytes at 0.33 μg·L^{-1} level. According to recent literature [25-26], the parameters predicted to affect the extraction are: type of fibre, extraction temperature, ionic strength, extraction time and sample volume. The optimization was carried out by comparing the chromatographic areas of the compounds analyzed at different conditions.

Initial extraction conditions were: 20 mL of sample (described above) were introduced into a 50 mL PTFE/silicone screw-cap glass vial. Then, 0.4 g·mL^{-1} of NaCl (saturated solution) was added, the vial was closed and put over a magnetic stirrer in a water thermostatic bath at 50ºC. The magnetic stirring was applied at 1000 rpm during the 30 minutes of extraction and the fibre was exposed to the headspace above the aqueous solution. After the extraction, the fibre was inserted into the injection port of the gas chromatograph for the thermal desorption and analysis. Fibre was desorbed at 270ºC during the chromatographic analysis in the splitless mode. Under these conditions, three replicates were done (n=3).

Due to the different properties of the compounds studied, three fibre coatings (PDMS, PDMS/DVB and PDMS/DVB/CAR) were selected for evaluation. In this study, differences between the three coatings in terms of area were observed. Figure 2 (A), shows the behaviour of the different families of the compounds selected. PDMS/DVB gave higher increased area for the majority of the target micropollutants, so it was selected as the best coating for the extraction of the micropollutants from the water.

Once the fibre coating was chosen, the best extraction temperature was studied. Higher extraction temperatures increase vapour pressure for volatile analytes in the headspace. However, higher temperatures might also create a less favourable coating-headspace (air) partition. To optimize the responses, extraction temperature was examined at these three different levels: 30ºC, 50ºC and 70ºC. Initial conditions were the same as above using the selected PDMS/DVB fibre. Figure 2 (B) shows the effect of temperature on the areas of the

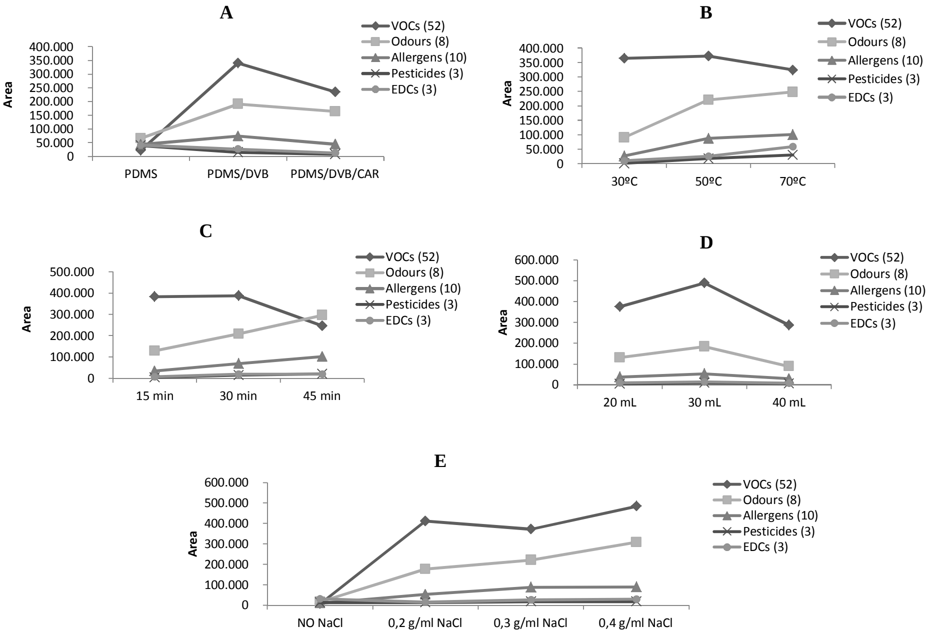


Figure 2. Effects of fibre coatings (A), extraction temperature (B), extraction time (C), sample volume (D) and salting out effect (E) on the HS-SPME of different families (number of compounds in parenthesis) of micropollutants studied in effluents of RO water (n=3).

representative families of the compounds selected. Extraction efficiency for most of the target VOCs was higher at 30ºC whereas the rest of other families presented higher areas at 70ºC because of the chemical properties of the different micropollutants studied. An extraction temperature of 50ºC was selected for this study as a compromise between the results. Responses of the micropollutants were also checked for 15, 30 and 45 minutes of extraction time. Initial conditions were described above. Figure 2 (C) shows the effect of extraction time on the responses of the representative families of compounds chosen above. The figure shows a trend where some components still increased their area after 45 minutes, however 30 minutes was the extraction time chosen because of the degradation by temperature of the target VOCs, which is the bigger group in terms of number of compounds. Moreover, the extraction time chosen was 30 minutes in order to use a reasonable extraction time while obtaining a good compromise between sensitivity and time of analysis.

The effect of sample volume was evaluated using 20, 30 and 40 mL of sample in a 50 mL glass vial. Results of the sample volume influence are shown in Figure 2 (D). As observed, the preferred sample volume for the different families of compounds was 30 mL of water sample. This volume allows enough vapour and liquid phase equilibrium.

The ionic strength of the sample had a positive effect on the extraction of all the studied compounds. The suitability of the HS-SPME technique for the extraction compounds from water depends on the transfer of the analyte from the aqueous phase to the gaseous phase. Salt addition could considerably decrease the solubility of these compounds in water, resulting in a higher concentration of these compounds in the headspace. This effect depends on the polarity of the analyte, the concentration of salt and the sample matrix. The ionic strength test was performed using the initial conditions and the PDMS/DVB fibre at an extraction temperature of 50ºC. The effect of ionic strength was evaluated with the addition of 0; 0.2; 0.3; 0.4 $g \cdot mL^{-1}$ of NaCl. Figure 2 (E) shows the salting out effect on the areas of the representative families of the micropollutants selected. The responses for most target micropollutants increased with the addition of NaCl. Therefore, a concentration of 0.4 $g \cdot mL^{-1}$ of NaCl (saturated solution) has been selected because the results showed highest response.

For the compounds evaluated in this study, the addition of salt enhanced the extraction. Therefore, sampling was carried out at the highest salt level.

To summarize, optimized extraction conditions in this study were: headspace in a 50 mL vial, PDMS/DVB fibre, temperature 50ºC, 0.4 $g \cdot mL^{-1}$ of NaCl addition, 30 minutes of extraction time, 30 mL sample volume, stirring at 1000 rpm and finally desorption of the fibres at 270ºC during the whole time of analysis. An exception occurs on sea water samples because of its content of salt.

In this case, the addition of the sodium chloride was 10 g in 30 mL.

3.3 Method validation

The method has been validated with effluents of reverse osmosis of surface water samples. Previous to the validation parameters, a sample of effluent was analyzed and some of the target compounds were identified (these compounds are marked with an asterisk in Table 1). Therefore, the responses of the target compounds identified in the samples for validation were considered when calculating sample concentrations. The signals of the compounds in these waters obtained were taken into account when constructing the calibration curves. The average of every compound (n=5) in the samples for validation was done and subtracted of each point in the calibration curve.

Linear range of SPME procedure was investigated with increasing concentrations of the analytes at six different concentration levels from 0.002 to 5.000 μg·L^{-1}. Each concentration level was analysed in triplicate. An acceptable linear range, with determination coefficients (r^2) higher than 0.991, was obtained for the majority of compounds within this interval. Table 1 also shows the validation data. No saturation effect of the fibre has been observed at the described concentration range.
The limits of detection (LODs) of the compounds that did not appear in the samples were defined as the concentrations giving a response corresponding to a signal-to-noise ratio 3:1. The LODs of the compounds that appeared in the samples were defined as those whose average signal levels are three times the standard deviation.
LODs ranged from 0.0005 μg·L^{-1} up to 0.100 μg·L^{-1}, which are in agreement with those papers found in the literature [6,16, 28] for VOCs, pesticides and allergens but are slightly lower for endocrine disruptor and odour compounds [11,27].

Limits of quantification (LOQs) were defined as the concentrations giving a response corresponding to a signal-to-noise ratio 10:1 but they were fixed as the lowest calibration level in order to assure correct quantification. LOQ ranged from 0.002 μg·L^{-1} up to 0.333 μg·L^{-1}.

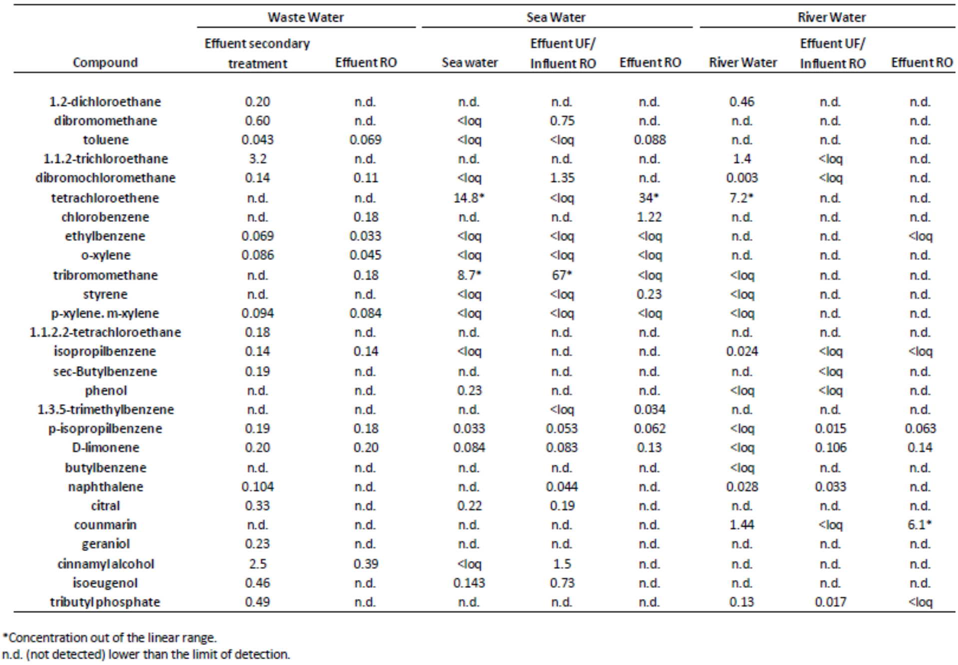
The precision of the method was evaluated by spiking three replicates of a sample at 1μg·L^{-1} levels. Repeatability and reproducibility between 5 days were calculated as the percentage of the relative standard deviation (n=5), and were mostly lower than 20%.

In order to evaluate an estimated the accuracy, the different water were also spiked at three different concentration levels (at 0.3 μg·L^{-1}, 1 μg·L^{-1} and 5μg·L^{-1}). For these three levels, the calculated concentrations of the target micropollutants were in agreement with those obtained with reverse osmosis effluents, taking into account the repeatability of the method used. Quantification of the samples was performed by external calibration using the calibration curves obtained by spiking the standards in reverse osmosis effluent water. Exceptionally, waste water influent and effluent samples of reverse osmosis treatment presented matrix effect and were quantified with matrix match calibration line. Therefore, the quantification of these samples was performed using calibration curves obtained by spiking the standards in those waste water influent and effluent samples of reverse osmosis. Suspended matter or solids can have a significant influence on response at trace level analysis, in particular for influent samples.

3.4 Application of the method

By the proposed method, a total of 27 of the 76 micropollutants were detected and quantified in the different samples. As expected, the levels found in the influents of application research units of river water and seawater samples were considerably lower than those found in the influents of application research units of reverse osmosis of waste water. However, some of the influents contained higher values of micropollutants than their effluents because the hydraulic residence time has not been taken into account. Table 2 shows the concentration of the micropollutants found in all studied samples, influents and effluents of the plants that use a tertiary treatment with advanced membrane treatments such as UF and RO. The relative standard deviations were less than 15% for the concentrations up to 0.05 μg·L^{-1} (n=5). Those target compounds not found in any type of samples studied are not included in Table 2.

Table 2. Concentrations of the micropollutants found in different pilot plants of water samples studied, expressed in ng·mL^{-1} (n=5; RSD<15% at concentrations > 0.05 ng·mL^{-1}).



	Waste Water		Sea Water			River Water		
Compound	Effuent secondary treatment	Effuent RO	Sea water	Effuent UF/ Influent RO	Effuent RO	River Water	Effuent UF/ Influent RO	Effuent RO
1.2-dichloroethane	0.20	n.d.	n.d.	n.d.	n.d.	0.46	n.d.	n.d.
dibromomethane	0.60	n.d.	<loq	0.75	n.d.	n.d.	n.d.	n.d.
toluene	0.043	0.069	<loq	<loq	0.088	n.d.	n.d.	n.d.
1.1.2-trichloroethane	3.2	n.d.	n.d.	n.d.	n.d.	1.4	<loq	n.d.
dibromochloromethane	0.14	0.11	<loq	1.35	n.d.	0.003	<loq	n.d.
tetrachloroethene	n.d.	n.d.	14.8*	<loq	34*	7.2*	n.d.	n.d.
chlorobenzene	n.d.	0.18	n.d.	n.d.	1.22	n.d.	n.d.	n.d.
ethylbenzene	0.069	0.033	<loq	<loq	<loq	n.d.	n.d.	<loq
o-xylene	0.086	0.045	<loq	<loq	<loq	n.d.	n.d.	n.d.
tribromomethane	n.d.	0.18	8.7*	67*	<loq	<loq	n.d.	n.d.
styrene	n.d.	n.d.	<loq	<loq	0.23	<loq	n.d.	n.d.
p-xylene. m-xylene	0.094	0.084	<loq	<loq	<loq	<loq	n.d.	n.d.
1.1.2.2-tetrachloroethane	0.18	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
isopropilbenzene	0.14	0.14	<loq	n.d.	n.d.	0.024	<loq	<loq
sec-Butylbenzene	0.19	n.d.	n.d.	n.d.	n.d.	n.d.	<loq	n.d.
phenol	n.d.	n.d.	0.23	n.d.	n.d.	<loq	<loq	n.d.
1.3.5-trimethylbenzene	n.d.	n.d.	n.d.	<loq	0.034	n.d.	n.d.	n.d.
p-isopropilbenzene	0.19	0.18	0.033	0.053	0.062	<loq	0.015	0.063
D-limonene	0.20	0.20	0.084	0.083	0.13	<loq	0.106	0.14
butylbenzene	n.d.	n.d.	n.d.	n.d.	n.d.	<loq	n.d.	n.d.
naphthalene	0.104	n.d.	n.d.	0.044	n.d.	0.028	0.033	n.d.
citral	0.33	n.d.	0.22	0.19	n.d.	n.d.	n.d.	n.d.
counmarin	n.d.	n.d.	n.d.	n.d.	n.d.	1.44	<loq	6.1*
geraniol	0.23	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
cinnamyl alcohol	2.5	0.39	<loq	1.5	n.d.	n.d.	n.d.	n.d.
isoeugenol	0.46	n.d.	0.143	0.73	n.d.	n.d.	n.d.	n.d.
tributyl phosphate	0.49	n.d.	n.d.	n.d.	n.d.	0.13	0.017	<loq

*Concentration out of the linear range.
n.d. (not detected) lower than the limit of detection.

The presence of 14 volatile organic compounds has been observed in effluents of secondary treatment of waste water samples. Eleven of them were also found in RO effluents of the application research units. Figure 3 shows a chromatogram of two samples of the application research units of reverse osmosis membranes in the waste water treatment plant (WWTP), one of them is from the influent of RO and the other belongs to the effluent of RO. As expected, the influent sample contains more compounds than the effluent sample and it was seen that the majority of the compounds were reduced by using RO membrane treatments due to the capacity of these advance tertiary treatments to eliminate the organic compounds.

Moreover, some of the VOCs have been found in the influents of the application research units of sea water and surface water, at higher concentrations than in waste water secondary effluents. For instance, concentrations of tetrachloroethene, chlorobenzene and tribromomethane exceeded the linear range. Sea water and surface water analyzed in the application research units contained chlorine as a prevention of biofouling. Therefore, some disinfection by products could be formed in these types of water samples.

Some fragrance allergens like citral, coumarin, cinnamyl alcohol, isoeugenol and geraniol were detected in effluents of secondary treatment of waste water samples due to the use of these compounds in personal care products. These results also confirmed those reported in some articles [27-31]. In the application research units of seawater and surface water fewer fragrance allergens were found, only citral and coumarin.

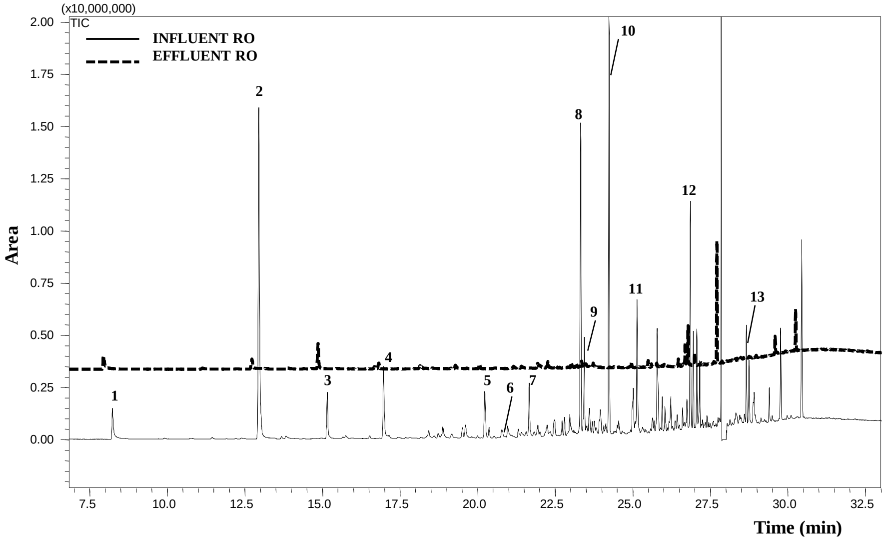


Figure 3. GC Chromatograms of influent and effluent samples belonging to the waste water treatment plant. Peak numbers refer to (1) 1,2-dichloroethane, (2) 1,1,2-trichloroethane, (3) ethylbenzene, (4) isopropilbenzene, (5) sec-butylbenzene, (6) p-isopropilbenzene, (7) D-limonene, (8) naphthalene, (9) citral, (10) geraniol, (11) cinnamyl alcohol, (12) isoeugenol, (13) tributyl phosphate.

Limonene and phenol as odours were detected in the influents of application research units of sea water. Furthermore, limonene was also detected in effluents of secondary treatment of waste water samples. These odour compounds could be present in the air and then precipitated into the waters.

Finally, tributyl phosphate, an endocrine disrupting compound, was also detected in effluents of secondary treatment of waste water samples and in the influent of the application research units of seawater. This organophosphorus compound is used as a solvent in inks, synthetic resins, gums, adhesives and herbicide and fungicide concentrates.

As a general trend, it was observed that the majority of the micropollutants were reduced by using reverse osmosis membrane treatments.

4. CONCLUSIONS

In this present study, headspace solid phase microextraction with a PDMS/DVB fibre combined with gas chromatography-mass spectrometry was used to determine 76 micropollutants in water including volatile organic compounds as described in the introduction, endocrine disrupting compounds, odour compounds, fragrance allergens and some pesticides.

The method developed is sensible, shows good linear range, reproducibility, repeatability and low detection limits (at low ng·L^{-1} levels). The validated method has been used for the determination of the target organic micropollutants in aqueous samples belonging different water treatment of application research units. The optimized method showed good performance in the different types of waters studied. The results indicated that the proposed method could be used to analyze the 76 micropollutants in water samples.

Some micropollutants were found in the samples, due to the fact that these species are commonly used in domestic and industrial applications. The tendency of most of them indicates a possible removal by the membrane reverse osmosis treatment. A cost-effective screening technique was developed to allow the study of removal of priority compounds by membrane systems, which does not use solvent and allows characterization of a large variety of compounds simultaneously.

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5. REFERENCES

[1] S. C. Monteiro, A. B. A. Boxall, Rev. Environ. Contam. T. 202 (2010) 53-154.

[2] Environmental quality standards of surface waters, (http://europa.eu/legislation_summaries/environment/water_protection_management/l28180_e.htm, accessed 3th April 2012).

[3] Directive 2008/105/EC of the european parliament and of the council of 16 December 2008. (http://eurlexeuropa.eu/,accessed 3th April 2012).

[4] S. D. Richardson, Anal. Chem. 84 (2012) 747-778.

[5] USEPA, EPA-450/1-90-004a, Cancer Risk from Outdoor Exposure to Air Toxics, Office of Air Quality Planning and Standards, 1990.

[6] N. Sadao, D. Shigeki, Anal. Chim. Acta 548 (2005) 79-85.

[7] C. Hyun-Shik, C. Kwang-Ho, L. Byungwhan, C. Sang-June, J. Hazard. Mater. 172 (2009) 1-12.

[8] R.V. Kuiper, R.F. Canton, P.E.G. Leonards, B.M. Jenssen, M.P.W. Dubbeldam, M. Wester, J.G. Vos, A.D. Vethaak, Ecotoxicol. Environ. Saf. 67 (2007) 349-360.

[9] USEPA, EPA/630/R-36/012, Special Report on Environmental Endocrine Disruption: An Effects Assessment and Analysis, Office of Research and Development,1997.

[10] C. Hort, S. Gracy, V. Platel, L. Moynault, Chem. Eng. J. 152 (2009) 44-53.

[11] P. Gostelow, S.A. Parsons, R.M. Stuetz, Water Res. 35 (2001) 579-597.

[12] SCCNFP/0017/98 Final fragrance allergy in consumers 1999.

[13] Regulation (EC) No 1223/2009 of the european parliament and of the council of 30 November 2009 on cosmetic products (recast), Official Journal of European Union L342 2009, 59.

[14] C.P. Weisel, S.D. Richardson, B. Nemery, G. Aggazzotti, E. Baraldi, E.R. Blatchley III, B.C. Blount, K.H. Carlsen, P.A. Eggleston, F.H. Frimmel, M. Goodman, G. Gordon, S.A. Grinshpun, D. Heederik, M. Kogevinas, J.S. LaKind, M.J. Nieuwenhuijsen, F.C. Piper, S.A. Sattar, Environ Health Persp. 117 (2009) 500-507.

[15] European commission-Environment.http://ec.europa.eu/environment/water/waterdangerousub/pri_substances.htm, accessed 3th April 2012.

[16] M.P. Ormad, N. Miguel, A. Claver, J.M. Matesanz, J.L. Ovelleiro, Chemosphere 71 (2008) 97–106.

[17] A. Llop, F. Borrull, E. Pocurull, Water Sci. Technol. 60 (2009) 2425-2437.

[18] T. U. Kim, G. Amy, J.E. Drewers, Water Sci. Technol. 51 (2005) 335-344.

[19] M.R. Boleda, K. Majamaa, P. Aerts, V. Gómez, M. T. Galceran, F. Ventura, Desalination and Water Treatment 21 (2010)122-130.

[20] V. Gómez, K. Majamaa, E. Pocurull, F. Borrull, Water Sci. Technol. 66 (2012) 61-71.

[21] C. Yi, G. Zhenpeng, W. Xiaoyu, Q. Changgui, J. Chromatogr. A 1184 (2008) 191-219.

[22] C. Nerin, Anal. Bioanal. Chem. 388 (2007) 1001-1002.

[23] W.W. Buchberger, J. Chromatogr. A 1218 (2011) 603-618.

[24] P. Gostelow, S.A. Parsons, R.M. Stuetz, Water Res. 35 (2001) 579-597.

[25] D. A. Lambropoulou, I.K. Konstantinou, T.A. Albanis, J. Chromatogr. A 1152 (2007) 70-96.

[26] A. Godayol, M. Alonso, E. Besalú, J.M. Sanchez, E. Anticó, J. Chromatogr. A 1218 (2011) 4863-4868.

[27] I. Rodriguez, F. Calvo, J.B. Quintana, E. Rubí, R. Rodi, R. Cela, J. Chromatogr. A 1108 (2006) 158-165.

[28] E. Becerril, J. P. Lamas, L. Sánchez-Prado, M. Llompard, Talanta 83 (2010) 464-474.

[29] S.D. Kim, J. Cho, I.S. Kim, B.J. Vanderford, S.A. Snyder, Water Res. 41 (2007) 1013-1021.

[30] B.C. Blount, R.J. Kobelski, D.O. McElprang, D.L. Ashley, J.C. Morrow, D.M. Chambers, F.L. Cardinali, J. Chromatogr *B* 832 (2006) 292–301.

[31] K. Bester, J. Chromatogr. A 1216 (2009) 470-480.

Talanta 116 (2013) 937–945

3.1.2. Simultaneous determination of 20 disinfection by-products in water from advanced membrane treatments by headspace solid phase microextraction and gas chromatography-mass spectrometry

SIMULTANEOUS DETERMINATION OF 20 DISINFECTION BY-PRODUCTS IN WATER SAMPLES FROM ADVANCED MEMBRANE TREATMENTS BY HEADSPACE SOLID PHASE MICROEXTRACTION AND GAS CHROMATOGRAPHY-MASS SPECTROMETRY

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Abstract

A headspace-solid phase microextraction (HS-SPME) and gas chromatography-mass spectrometry (GC-MS) method has been developed for the simultaneously determination of 20 disinfection by-products (DBPs) in water samples from reverse osmosis (RO) membranes. Selected compounds belong to different families including: trihalomethanes (THMs), halogenated acetonitriles (HANs), halogenated nitromethanes (HNMs), halogenated ketones (HKs) and other halogenated DBPs. Four commercial fibres with different polarities were tested for the extraction of the compounds and the main variables affecting HS-SPME such as extraction time, extraction temperature and pH of the samples were optimized by applying a central composite design.

The method showed good detection limits in the range of 0.003 μg L^{-1} up to 0.010 μg L^{-1} for most of the compounds with reasonable linearity with r^2 higher than 0.991. Moreover, the repeatability of the method, expressed as relative standard deviation (RSD) was lower than 13% (n=5, 1μg L^{-1}) in brackish and wastewater samples.

The validated method has been applied for the determination of the target DBPs in RO water samples from application research units, which treated water from various origins (wastewater, brackish water and sea water), showing good performance in the different types of studied samples. The analysis revealed the presence of several DBPs regarding different families, such as trichloromethane (with concentrations up to 0.36 μg L^{-1}), chloroiodomethane (0.5-1.44 μg L^{-1}), dibromochloromethane (found at concentrations up to 0.76 μg L^{-1}) and tribromoacetaldehyde (at concentrations up to 11 μg L^{-1} in the influent samples). The tendency of most of them indicated a trend of removal by reverse osmosis treatments, especially the total concentration of THMs which decreased below the limit of detection.

Keywords: *advanced membrane water treatment, disinfection by-products, gas chromatography-mass spectrometry, solid-phase microextraction, trihalomethanes, water samples.*

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1. INTRODUCTION

Water is a scarce commodity and a fundamental resource for the human being since it plays a decisive role in health. Its scarcity is driving the increased use of recycled water and removal of contaminants from treated wastewater that is now an important research issue, particularly for potable reuse. Nowadays, a combination of advanced treatments, such as ultrafiltration (UF), nanofiltration (NF) or reverse osmosis (RO), ultraviolet irradiation or advanced oxidation processes, are applied prior to reuse [1-2]. Since the development of ultrafiltration and reverse osmosis as a practical unit operation in the late 1950's, the scope for their application has been continually expanding. In general, RO membranes offer the possibility of high rejection of inorganic and organic compounds, including micropollutants. Moreover, UF membrane processes are used as a pretreatment of the reverse osmosis, improving the efficiency of these advance membrane treatments becoming into an overall increase in the efficiency of the process [3].

For decades, municipalities have used chlorine as a primary disinfectant for brackish water sources in order to inactive microbial pathogens. While the benefits of chlorination are well documented [4], a side effect of chlorination is that the residual chlorine can react with naturally occurring organics in water, oxidizing them to form disinfection by-products (DBPs) [5-7]. These by-products may lead to increased health risks if present at μgL^{-1} levels. A generation ago, when these contaminants were first discovered in drinking water [8-9], concentrations of several hundred $\mu g \cdot L^{-1}$ were common. Nowadays, after many years of actively avoiding trihalomethanes (THM) production, most water-works supply tap water with less than 20 $\mu g \cdot L^{-1}$. THMs have been considered probable human carcinogens (kidney, liver, bladder cancers) [10] and have been regulated in drinking water by the United States Environmental Protection Agency (EPA or sometimes USEPA) with a mandatory Maximum Contaminant Level (MCL) of 100 $\mu g\ L^{-1}$ of total THM [11]. However, recently a new level of 80 $\mu g\ L^{-1}$ has been proposed by the government as a cause of miscarriages. In the actual European and therefore Spanish Legislation [12] the limit of the total THM concentration is 100 $\mu g\ L^{-1}$.

Next in prominence after THMs are the halogenated acetonitriles (HANs) [13], the halogenated nitromethanes (HNMs) [14] and the halogenated ketones (HKs) [15]. Most of these compounds are made from two-carbon fragments. They are found in chlorinated waters at levels one-third to one-half of the THM levels. When they are eventually regulated explicitly, it is expected that they will receive MCLs in the 30-80 $\mu g\ L^{-1}$ range. Epidemiological studies have suggested a link between consumption of drinking waters containing elevated levels of DBPs and adverse human health outcomes, particularly bladder cancer and reproductive effects [16-17].

One goal of the water treatment processes is to control these compounds produced when a disinfectant reacts with ubiquitous dissolved organic matter (DOM), chemicals in water which may be of natural origin such as bromide and iodide and anthropogenic pollutants. Therefore, the development of a highly sensitive method for their simultaneously determination has become a priority. Several extraction techniques can be used for the extraction of disinfection by-products from water samples such as liquid-liquid extraction (LLE), headspace solid phase microextraction (HS-SPME) and headspace single drop microextraction (HS-SDME) [5, 13, 18]. In this study HS-SPME has been selected because it allows complete elimination of organic solvents in the pretreatment step and decreases the number of steps needed for sample preparation becoming an accepted technique for the determination of volatile and semi-volatile substances, as well as it could be a totally automated technique. Another advantage of HS techniques when volatile compounds are analyzed is that the extraction is highly selective and the matrix effect becomes lower than submerged techniques [19].

In this study a method based on HS-SPME and GC-MS for the simultaneous characterization of 20 disinfection by-products belonged to different families with various chemical properties has been developed. The DBPs studied included trihalomethanes, haloacetonitriles, halonitromethanes, haloketones, haloaldehydes and other chlorine, bromine and iodinated disinfection by-products. Table 1 lists the different compounds. The method has been applied to determine these DBPs in aqueous samples from different application research units using RO membranes which treated water from secondary effluents of wastewater, sea and brackish water.

2. EXPERIMENTAL

2.1 Solvents and reagents

The 4 THMs (chloroform, bromodichloromethane, dibromochloromethane and bromoform) were obtained from a mixture of EPA 501/601 Trihalomethanes Calibration Mix provided by Sigma-Aldrich (Supelco, Madrid, Spain), all of them in a concentration of 2000 $mg \cdot L^{-1}$ in methanol (MeOH).

A mixture of 7 disinfection by-products of different groups (bromochloroacetonitrile, trichloronitromethane, dichloroacetonitrile, dibromoacetonitrile, trichloroacetonitrile, 1,1-dichloropropanone and 1,1,1-trichloropropanone) was obtained from EPA 551B Halogenated Volatiles Mix provided by Sigma-Aldrich, all of them in a concentration of 2000 $mg \cdot L^{-1}$ in acetone.

1,2-dibromo-3-chloropropane (90-95%) bromonitromethane (90%), tribromoacetaldehyde (97%), 2-chloro-2-methylpropane (>99%), 2-bromo-2-methylpropane (98%), 2-chloro-2nitropropane (95%), 1-iodo-2-methylpropane (97%), chloroiodomethane (97%) and iodoform (99%) were purchased from Sigma-Aldrich.

Table 1. Target compounds, quantification and identification ions and main validation data obtained by analyzing effluents of reverse osmosis of brackish water (BW) and waste water (WW) advance membrane treatments spiked at 1 μg·L^{-1} (n=5).

Compounds	t_R (min)	Q_1	Q_2	LOD (μg·L^{-1}) WW	LOD (μg·L^{-1}) BW	BW Linear Range* (μg·L^{-1})	BW r^2	BW RSD^A (%)	BW RSD^B (%)
Propane, 2-chloro-2-methyl-	5.38	57	41, 77	0.010	0.010	0.030-10	0.991	10	14
Propane, 2-bromo-2-methyl-	5.85	57	41	0.010	0.010	0.030-10	0.998	6	12
Trichloromethane	7.00	83	85, 47	0.030	0.010	0.030-10	0.999	4	12
Acetonitrile, trichloro-	8.65	108	110	0.50	0.30	1.0-10	0.991	6	15
Bromonitromethane	8.91	91	45, 43	0.50	0.50	1.0-10	0.994	8	10
Methane, bromodichloro-	9.45	83	85, 129	0.010	0.003	0.010-10	0.999	4	5
Acetonitrile, dichloro-	9.60	74	82, 76, 47	0.010	0.010	0.030-10	0.994	4	5
Chloroiodomethane	9.90	49	176, 127	0.010	0.010	0.030-10	0.995	4	7
2-Propanone, 1,1-dichloro-	10.17	43	83, 63	0.010	0.010	0.030-10	0.994	7	13
2-chloro-2-nitropropane	11.40	41	77, 79	0.030	0.010	0.030-10	0.995	13	15
Trichloronitromethane	11.55	119	117, 82	0.010	0.010	0.030-10	0.999	2	8
Propane, 1-iodo-2-methyl-	11.63	57	184, 127, 41	0.003	0.003	0.010-10	0.992	10	14
Methane, dibromochloro-	11.89	129	127, 48	0.010	0.003	0.010-10	0.999	2	14
Acetonitrile, bromochloro-	12.15	74	155, 118	0.050	0.030	0.10-10	0.991	13	17
2-Propanone, 1,1,1-trichloro-	13.24	43	125, 82	0.010	0.010	0.030-10	0.996	6	18
Methane, tribromo-	14.50	173	91, 79, 252	0.030	0.010	0.030-10	0.999	4	15
Acetonitrile, dibromo-	14.93	118	79, 81	0.100	0.100	0.50-10	0.995	6	12
Acetaldehyde, tribromo-	17.38	173	93, 91	0.100	0.100	0.50-10	0.999	7	11
Propane, 1,2-dibromo-3-chloro-	18.64	75	157, 41	0.010	0.003	0.010-10	0.999	13	16
Methane, triiodo-	21.22	127	394, 267	0.300	0.100	0.50-10	0.991	7	9

*LOQ lower concentration point of the linear range
A: Repeatability
B: Reproducibility between days
Q_1: Quantifier ion
Q_2: Qualifier ions

A working solution of all compounds (except tribromoacetal-dehyde) was prepared at 10 mg L^{-1} in GC grade methanol with purity >99.9% (from Prolabo, Barcelona, Spain) from the individual standards or mixtures. Moreover, tribromoacetaldehyde was prepared individually at 10 mg L^{-1} in acetone because of its low stability in MeOH [20]. Solutions were prepared daily in brackish water samples for the calibration curves and stored under refrigeration (2-6ºC).

Sodium chloride (NaCl) (ACS reagent ≥99 %) was supplied by Sigma-Aldrich. GC grade acetone with purity 99.8% and sulphuric acid (H_2SO_4) with purity 98% were supplied by Merck (Darmstadt, Germany). Helium gas with 99,999% purity was supplied from Praxair (Barcelona, Spain).

2.2 Instrumentation and procedures

HS-SPME

The four commercial extraction fibres including, 65 μm Polydimethylsiloxane/ Divinylbenzene (PDMS/DVB), 50/30 μm Polydimethylsiloxane/ Divinylbenzene /Carboxen (PDMS/DVB/CAR), 85 μm Polyacrylate (PA) and 60 μm Polyethylene Glycol (PEG), were purchased from Supelco (Madrid, Spain).

For the extraction procedure, 30 mL of sample was introduced into a 50 mL PTFE/silicone screw-cap glass vial. Then, 12 g of NaCl was added as a solid salt to obtain the stated concentration (saturated solution, 0.4 Kg L^{-1}); the vial was closed and put over a magnetic stirrer (of 1 cm) in a water thermostatic bath at 45ºC.

The fibre of PDMS/DVB/CAR was exposed to the headspace above the aqueous solution and the magnetic stirring was applied at 1000 rpm during the 15 minutes of extraction. After the extraction, the fibre was inserted into the injection port of the gas chromatograph for the thermal desorption and analysis. Fibre was desorbed at 250ºC during the chromatographic analysis in splitless mode. Although the analytes desorption occurred within the first five minutes of the desorption process, leaving the fibre in the injector prevent it from the contamination and carryover effects. Blanks of the fibres were analyzed daily in order to verify the absence of interfering compounds. The fibres were used at least 50 times for sample analysis.

GC-MS

The gas chromatography analysis was performed with a GCMS-QP2010 Ultra/ GCMS-QP2010 SE from Shimadzu (Kyoto, Japan), equipped with a split/splitless injector and coupled to a mass spectrometer detector. Helium was employed as a carrier gas at constant column flow of 1 mL·min^{-1}. Analytes were separated with TRB-5MS column (60m x 0.32 mm i.d., 1 μm) from Tecknokroma (Barcelona, Spain). The split/splitless injection port was equipped with a 0.75 mm ID liner from Supelco and operated at 250ºC, allowing direct injection of the fibre. The oven temperature program was started at 35ºC, maintained for 5 min; then increased by 10ºC·min^{-1} up to 100ºC, maintained for 2 min; and then increased by 15ºC·min^{-1} up to 260ºC, and maintained for 3 min. The total run time was 27 min. The MS analyses were conducted in SIM mode with a single quadrupole.

Table 1 shows the quantifier and the qualifier selected ions for the SIM mode. Ionization was carried out in the electron impact (EI) mode at 70 eV. The transfer line temperature was maintained at 300ºC and the ion source temperature at 280ºC.

2.3 Sample collection

The analytical method has been developed to analyse different types of water samples belonging to the influent and effluent of tertiary advanced RO membrane treatments. These treatments have been applied using application research units, which were pilot plants of reverse osmosis processes, connected to the effluent of conventional treatment plants which treat water from brackish water (Ebro River, Tarragona, Spain), effluents of secondary treatment of an urban waste water treatment plant (Vila-Seca, Spain) and sea water (Mediterranean Sea, Tarragona, Spain).

Water samples were collected in 100 mL amber glass containers, they were acidified at pH 2 with sulphuric acid, filtered through 0.45μm filter, and stored in the dark at 4ºC until analysis, within 48 hours.

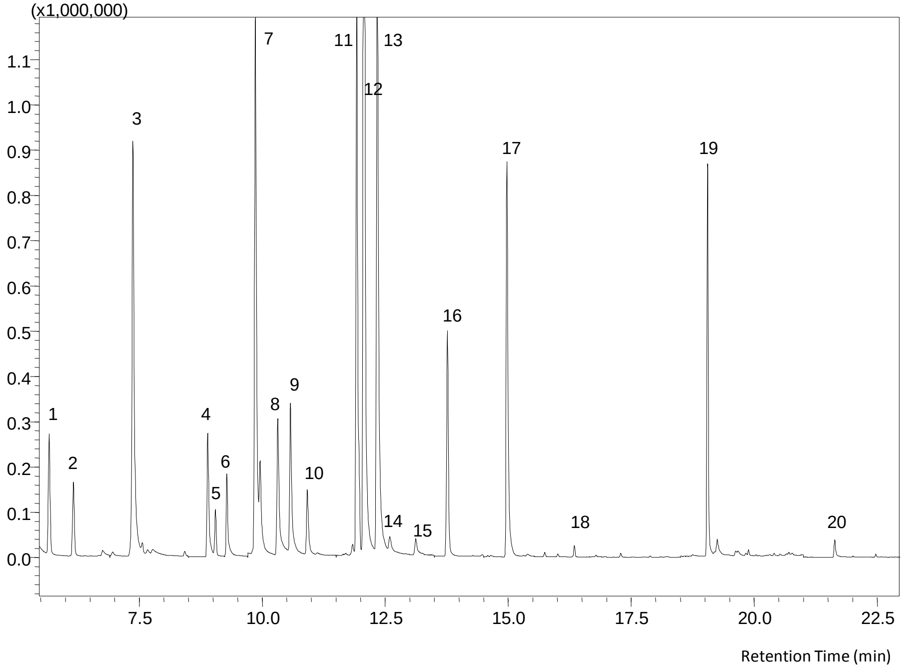


Figure 1. GC-MS chromatogram of standard solution at 5 μg L^{-1}. Peak numbers refer to (1) 2-chloro-2-methylpropane, (2) 2-bromo-2-methylpropane, (3) trichloromethane, (4) trichloroacetonitrile, (5) bromonitromethane, (6) bromodichloromethane, (7) dichloroacetonitrile, (8) chloroiodomethane, (9) 1,1-dichloro-2-propanone, (10) 2-chloro-2-nitropropane, (11) trichloronitromethane, (12) 1-iodo-2-methylpropane, (13) dibromochloromethane, (14) bromochloroacetonitrile, (15) 1,1,1-trichloro-2-propanone, (16) tribromomethane, (17) dibromoacetonitrile, (18) tribromoacetaldehyde, (19) 1,2-dibromo-3-chloro-propane and (20) triiodomethane.

3. RESULTS AND DISCUSSION

In this study a method based on HS-SPME and GC-MS for the determination of 4 THMs, 4 HANs, 2 HNMs, 2 HKs, 3 iodinated DBPs, 2 chlorinated DBPs and 3 brominated DBPs has been developed. The 20 disinfection by-products pertain into different families and have different chemical properties.
After obtaining the GC column temperature programming, good resolution was obtained for all compounds in less than 27 minutes and the 20 DBPs showed good responses. A chromatogram related to injection of standard solution at 5 μg L^{-1} is depicted in Figure 1. Moreover, the most abundant ion of each compound, the quantification ion, was selected as well as the two or three qualification ions which are summarised in Table 1.

3.1 Optimization of HS-SPME

Factors which influence extraction efficiency should be established, such as the type of fibre, the sample pH, the extraction time and the extraction temperature. Other factors such as the

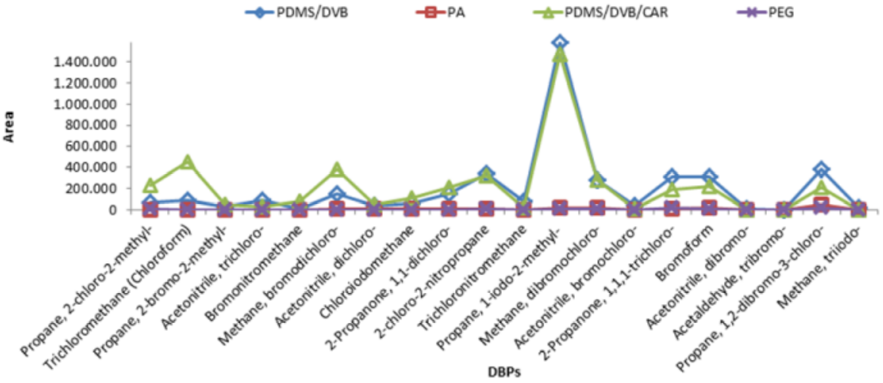


Figure 2. Response signal obtained using four different fibres type (other parameters can be seen in the text).

salt addition, the headspace, the vial and the sample volumes, the magnetic stirring speed, the temperature of desorption and the time of desorption were selected according to the literature [21-23].

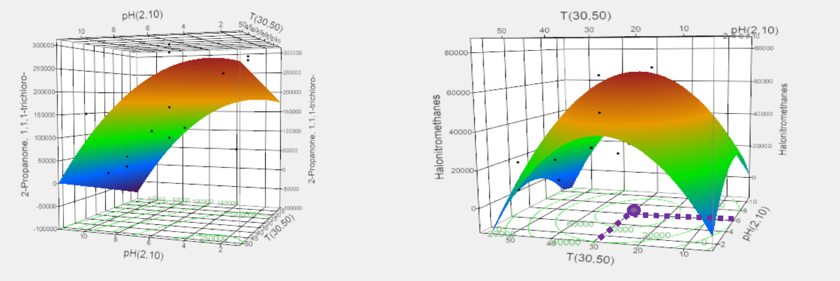
Optimization of solid-phase micro-extraction conditions for the selected DBPs was accomplished analyzing aliquots of the brackish water application research unit at 1 µg L^{-1} level. The optimization was carried out at different extraction conditions using the chromatographic areas of the compounds analysed.

Initial extraction conditions were selected according to the literature for some families of DBPs [21-23]. Thus, 30 mL of sample was introduced into a 50 mL PTFE/silicone screw-cap glass vial. Then, 0.4 Kg L^{-1} of NaCl (saturated solution) was added; the vial was closed and put over a magnetic stirrer in a thermostatic water bath at 40ºC. The magnetic stirring was applied at 1000 rpm during the 20 minutes of extraction and the fibre was exposed to the headspace above the aqueous solution. After the extraction, the fibre was inserted into the injection port of the gas chromatograph for the thermal desorption and analysis. Fibre was desorbed at 250ºC during the chromatographic analysis in the splitless mode.

Due to the different properties of the compounds studied, four fibre coatings (PDMS/DVB, PDMS/DVB/CAR, PA and PEG) were selected for evaluation. Differences between the coatings in terms of peak area were observed.

Figure 2 shows the peak areas of the different selected compounds for the four fibres coatings. Although PDMS/DVB and PDMS/DVB/CAR (the less polar fibres) gave higher areas for all the studied target DBPs, PDMS/DVB/CAR was selected as the best coating for the extraction of these micro-pollutants from the water because the regulated compounds (the THMs group) such as chloroform and bromo-

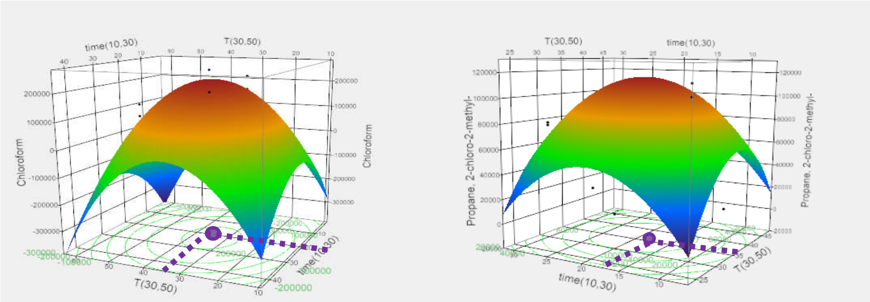
2a) Extraction Temperature: Representative Examples



1,1,1-trichloro-2-propanone (Haloketona)

Halonitromethanes

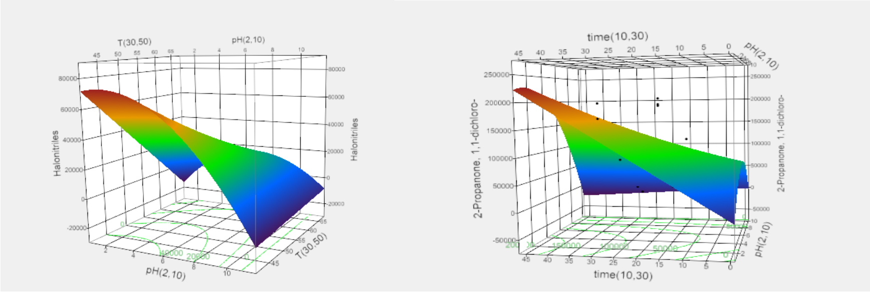
2b) Extraction Time: Representative Examples



Chloroform (Trihalomethane)

2-chloro-2-methyl-propane

2c) Extraction pH: Representative Examples



Haloacetonitriles

1,1-dichloro-2-propanone (Haloketona)

Figure 3. Response surface for the most representative target compounds: a) Extraction temperature, b) Extraction time, c) Extraction pH.

dichloromethane had high peak areas with this type of fibre.

Once the fibre coating was chosen, the best extraction temperature, extraction time and pH were optimized applying a central composite design for each compound. The software used for the central composite design was SAS JMP 10.0.2 (SAS Institute Inc.).

The variables assessed in the experiment were extraction temperature, extraction time and pH. Solution temperature was studied in the range of 30ºC to 50ºC, extraction time was evaluated from 10 to 30 minutes and pH was studied from 2 to 10.

In Figure 3a it could be observed the response surface of some representative groups of DBPs. HKs present higher areas at higher temperatures and HNMs manifest higher areas at temperatures between 35-40ºC. Higher extraction tempera-tures increase vapour pressure for volatile analytes in the headspace. However, higher temperatures might also have created a less favourable coating-headspace (air) partition. Therefore, 45ºC has been selected as the best extraction temperature as a compromise between all the families studied.

The areas of the DBPs were also checked for extraction times defined in the design. Figure 3b shows the behaviour of one of the representative THMs group, chloroform, with 20 minutes as the best extraction time. Moreover, the trend of another compound, the 2-chloro-2-methyl-propane as a representative DBP, is also shown. This compound showed higher areas at extraction times between 15-20 minutes. As agreement between the different disinfection by-products, 15 minutes was selected as the best extraction time, considering that responses were sensible enough and time of analysis was acceptable.

As a part of the central composite design, the pH was also studied in the range between 2-10. Most compounds were preferably extracted at pH 2, being presented in Figure 3c, where the highest areas of the HANs and the HKs are at pH 2.

To summarize, optimized extraction conditions concluded from this study were: headspace in a 50 mL vial, 30 mL sample volume, PDMS/DVB/CAR fibre, temperature 45ºC, 0.4 Kg L^{-1} of NaCl addition, 15 minutes of extraction time, stirring at 1000 rpm and finally desorption of the analytes at 250ºC throughout the entire analysis time. An exception occurs on sea water samples because of their high salt content. In this case, the addition of sodium chloride was 0.3 Kg L^{-1}.

3.2 Method validation

The method has been validated with the effluent of reverse osmosis from the brackish water application research unit. Previous to the validation parameters, a sample of effluent was analyzed and three of the target compounds were identified: 2-chloro-2-methyl-propane, 2-bromo-2-methyl-propane and trichloromethane. Therefore, the average responses (n=5) of these compounds were considered when validation parameters were calculated.

Linear range was investigated with increasing concentrations of the analytes at six different concentration levels from 0.03 to 10.0 μg L^{-1}. An acceptable linear range, with determination coefficients (r^2) higher than 0.991, was obtained for all compounds. Table 1 also shows the validation data. No saturation effect of the fibre has been observed at the described concentration range.

The limits of detection (LODs) of the compounds which did not appear in the samples were defined as the concentrations giving a response corresponding to a signal-to-noise ratio 3:1. The LODs of the compounds found in the samples were estimated as the concentration which gave a signal average plus three times the standard deviation of the sample signal. LODs ranged from 0.003 μg L^{-1} to 0.50 μg L^{-1}, being slightly lower than those found in the literature [14, 24, 25] related to those which have been using other analytical methods were based on liquid-liquid extraction (LLE) followed by GC-MS, LLE followed by gas chromatography electron capture detection (GC-ECD) and headspace single drop microextraction (HS-SDME) prior to GC-MS. On the other hand, some papers have reported slightly lower LODs for the specific halonitriles group [13, 21], due to using higher extraction volumes of samples and higher extraction times.

Limits of quantification (LOQs) were defined based on the concentrations giving a response corresponding to a signal-to-noise ratio 10:1 and they correspond to the lowest calibration level. LOQ ranged from 0.010 μg L^{-1} up to 1.00 μg L^{-1}.

The precision of the method was evaluated by spiking replicates of a sample at 1 μg L^{-1} level. Repeatability and reproducibility between days were calculated as the percentage of the relative standard deviation (RSD) and were mostly lower than 13% and 18% respectively (n=5).

In order to evaluate the accuracy, the different water samples were also spiked at two different concentration levels (0.5 μg L^{-1} and 5 μg L^{-1}) to check the recovery. For these two levels, the calculated concentrations of the target DBPs were in agreement with those obtained with the water used for the validation, taking into account the repeatability of the method used. Quantification of the samples was performed by external calibration using the calibration curves obtained by spiking the standards in reverse osmosis effluent of brackish water. Exceptionally, waste water samples presented matrix effect and were quantified with the matrix match calibration curve. Method validation parameters of waste water samples, as the LODs are also shown in the Table 1 while the linear range, the repeatability and reproducibility between days were similar to the brackish water effluents.

3.3 Application of the method

By the proposed method, a total of 14 of the 20 disinfection by-products were detected and quantified in the different analyzed samples. Due to the previous chlorination by the distributors in the sea and brackish water lines, the concentration of the compounds found in the influents of the application research unit of brackish water and seawater samples were higher than those found in the influents of application research units of waste water. In both water application research units, the level of total THMs in the influent is higher than 100 µg L^{-1}, which is the maximum concentration regulated in Europe for drinking water applications. However, after the reverse osmosis processes, the concentration of the total THMs decreases below the limit, which is indicating that RO is decreasing them.

Table 2 shows the concentration of the DBPs found in all studied samples, influents and effluents of the studied application research units having a tertiary treatment with RO membranes. Dibromoacetonitrile, bromonitromethane, triiodomethane, 1-iodo-2-methylpropane, 2-chloro-2-nitropropane and 1,2-dibromo-3-chloropropane did not appear in the table because their concentration was lower than the limit of detection in all analyzed samples. On the other hand, trichloromethane, bromodichloromethane, dibromochloromethane, tribromomethane and tribromoacetaldehyde were giving signals out of the calibration curve, showing an estimated concentration.

Regarding the waste water application research unit, the presence of 8 disinfection by-products has been detected in effluents of the secondary treatment. These compounds found belong to different families: trihalomethanes, haloacetonitriles, and iodine, chlorine and bromine disinfection by-products. It is worth mention that the THMs group, which is the regulated one, the concentration

Table 2. Concentrations of the DBPs found in different water application research units treating different types of water, expressed in μg L-1 (n=5; RSD <15%).

Compound	Family	Sea Water Influent RO	Sea Water Effluent RO	Waste Water Influent RO	Waste Water Effluent RO	Brackish Water Influent RO	Brackish Water Effluent RO
Trichloromethane		0.36	0.066	4.95	2.50	59*	33*
Methane, bromodichloro-		0.72	0.34	<LOQ	<LOQ	77*	38*
Methane, dibromochloro-		5.5	1.55	<LOQ	<LOQ	40*	15.9*
Methane, tribromo-		95*	16.3*	<LOQ	<LOQ	4.2	1.18
Regulated Total THMs	THMs	102	18.3	4.95	2.5	176	88
Acetonitrile, trichloro-		n.d.	n.d.	n.d.	n.d.	<loq	n.d.
Acetonitrile, dichloro-		0.23	n.d.	0.095	0.090	2.07	0.59
Acetonitrile, bromochloro-	HANs	n.d.	n.d.	n.d.	n.d.	2.49	0.59
Trichloronitromethane	HNMs	n.d.	n.d.	n.d.	n.d.	0.12	n.d.
2-Propanone, 1,1-dichloro-		n.d.	n.d.	n.d.	n.d.	0.52	n.d.
2-Propanone, 1,1,1-trichloro-	HKs	n.d.	n.d.	n.d.	n.d.	0.37	n.d.
Chloroiodomethane	I-DBPs	1.44	1.06	0.077	0.076	0.20	0.18
Propane, 2-chloro-2-methyl-	Cl-DBPs	0.11	0.11	<LOQ	<LOQ	0.11	0.11
Propane, 2-bromo-2-methyl-		0.18	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Acetaldehyde, tribromo-	Br-DBPs	59*	8.3	n.d.	n.d.	11.8	n.d.

*Concentration estimated out of the linear range.
n.d. (not detected) lower than the limit of detection.
<LOQ below quantification limit

was 95% lower than the regulated.

In the sea water application research unit, the DBPs found were from same families as those found in the waste water. 9 DBPs have been found in the influent of the application research unit of sea water with higher concentrations than in waste water secondary effluents, mainly because of the chlorine addition to the distribution lines from the supplier. Tribromomethane and tribromoacetaldehyde exceeded the linear range, indicating an estimated concentration. However, their concentration is lower in the effluent of the RO demonstrating reverse osmosis could decrease their level.

In the brackish water application research unit, the seven families of the DBPs studied were found including the halonitromethanes and the haloketones. 14 DBPs have been found in the influent. Concentrations of trichloromethane, bromodichloromethane and dibromochloromethane exceeded the linear range, being detected at concentrations higher than 40 µg L^{-1}. Figure 4 shows a chromatogram of two samples of the application research unit of reverse osmosis membranes treating brackish water, one of them is from the influent of RO and the other belongs to the effluent of RO. As expected, the influent sample contained higher concentration than the effluent sample and it was observed that the majority of the compounds were reduced more than the 70% by the RO membrane treatments due to the capacity of these advance tertiary treatments to

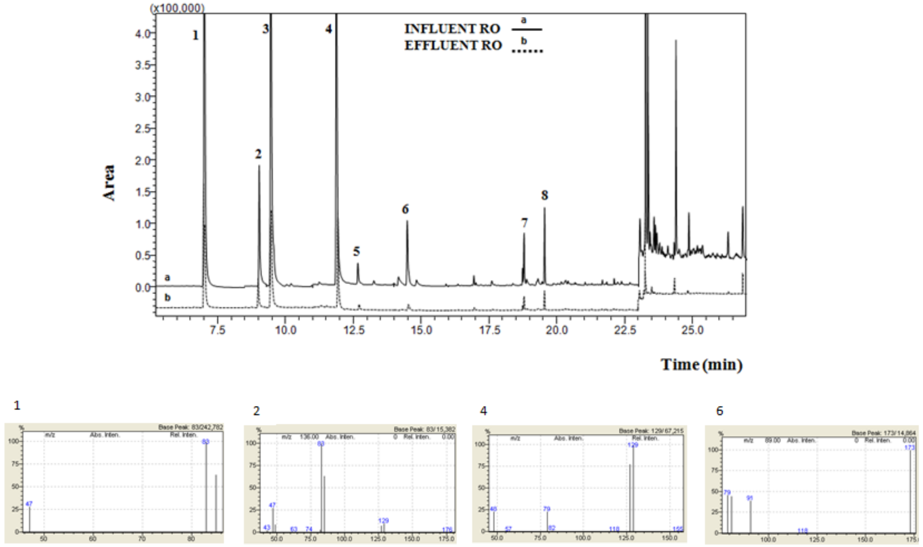


Figure 4. GC-MS Chromatograms of influent and effluent samples belonging to the brackish water application research unit. Peak numbers refer to (1) trichloromethane, (2) bromodichloromethane, (3) dichloroacetonitrile, (4) dibromochloromethane, (5) bromochloroacetonitrile, (6)tribromomethane, (7) tribromoacetaldehyde, (8) 1,2-dibromo-3-chloro-propane. Inserts show the spectra of the regulated DBPs present in the effluent (1, 2, 4, 6).

eliminate organic compounds. These results also confirmed those reported in some other papers [22-23].

As a general trend, it seemed the majority of the disinfection by-products were removed by using reverse osmosis membrane treatments. There are few references focused on the determination of DBPs during advanced membrane treatments [2, 9, 22, 23]. Some of those specifically applied to drinking water applications in which the concentrations of the DBPs are in agreement with our current methodology.

4. CONCLUSIONS

In the present study, headspace solid phase microextraction with a PDMS/DVB/CAR fibre combined with gas chromatography-mass spectrometry was used to determine simultaneously 20 disinfection by-products in water including trihalomethanes, haloacetonitriles, halonitromethanes, haloketones and other iodine, chlorine and bromine DBPs.

The method developed is sensible, shows good linear range, reproducibility, repeatability and low detection limits (at low ng L^{-1} levels). The validated method has been used for the determination of the target organic DBPs in aqueous samples belonging to influents and effluents of membrane treatments (sea water, waste water and brackish water) from different application research units. The results indicated the proposed method could be used to analyze the 20 DBPs in water samples, which does not use solvent and allows characterization of a large variety of compounds simultaneously, showing a good performance.

Some DBPs were found in the samples, due to the fact that sea water and brackish water is constantly being chlorinated for pipe disinfection by the suppliers. The tendency of most of them indicates a trend of removal by reverse osmosis treatments.

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5. REFERENCES

[1] Gómez V, Majamaa K, Pocurull E, Borrull F (2012) Water Sci Technol 66:61-71.

[2] Lyon B, Dotson A, Linden K, Weinberg H (2012) Water Res 45:4653-4664.

[3] Bellona C, Drewes J E, Xu P, Amy G (2004) Water Res 38:2795-2809.

[4] Yang X, Shang C, Huang JC (2005) Water Res 39:4755-4767.

[5] Miltner R J, Speth TF, Richardson SD, Krasner SW, Weinberg HS, Simmons JE (2008) J Toxicol Environ Health A 71:1133-1148.

[6] Krasner SW, Weinberg HS, Richardson SD, Pastor SJ, Chinn R, Sclimenti MJ, Onstad GD, Thurston A D (2006) Environ Sci Technol 40:7175-7185.

[7] Pressman JC, Richardson SD, Speth TF, Miltner RJ, Narotsky MG, Hunter, Rice GE, Teuschler LK, McDonald TA (2010) Environ Sci Technol 44:7184-7192.

[8] Gasia-Bruch E, Sehn P, García-Molina V, Busch M, Raize O, Negrin M (2011) Desal and Water Treat 31:178-189.

[9] Uyak V, Koyuncu I, Oktem I, Toroz I (2008) J Hazard Mater 152:789-794.

[10] Villanueva M, Cantor KP, Grimalt JO, Malats N, Silverman D, Tardon A, Garcia-Closas R, Serra C, Carrato A, Castaño-Vinyals G, Marcos R, Rothman N, Real X, Dosemeci M, Kogevinas M (2007) J Epidemiol 165:148-156.

[11] U.S. Environmental Protection Agency. 2006. National primary drinking water regulations: Statge 2 disinfectants and disinfection byproducts rule. *Fed. Reg.* 71 (2): 387-493.

[12] (REAL Decreto 1400/2003) *(Directive 2008/105/ec of the european parliament and of the council of 16 December 2008. (http://eurlex.europa.eu/, accessed 3th April 2012).*

[13] Kristiana I, Joll C, Heitz A (2012) J Chromatogr A 1225:45-54.

[14] Montesinos I, Cardador MJ, Gallego M (2011) J Chromatogr. 1218:2497-2504.

[15] Serrano M, Silva M, Gallego M (2011) J Chromatogr A 1218:8295-8302.

[16] Cantor K, Lynch CR, Hildesheim ME, Dosemeci M, Lubin J, Alavanja M, Craun G (1998) J Epidemiol 9:21-28.

[17] Loper JC, Lang DR, Schoeny RS, Richmond BB, Gallagher PM, Smith CC (1978) Toxicol Environ Health 4:919-938.

[18] Gostelow P, Parsons SA, Stuetz RM (2001) Water Res 35:579-597.

[19] Mester Z, Sturgeon R, Pawliszyn J (2001) Spectrochim. Acta Part B 56:233-260.

[20] Koudjonou BK, Lebel GL (2006) Chemosphere 64:795-802.

[21] Antoniou CV, Koukouraki EE, Diamadopoulos E (2006) J Chromatogr A 1132:310-314.

[22] Martínez C, Ramírez N, Gómez V, Pocurull E, Borrull F (2013) Talanta 116:937-945.

[23] Sadao N, Shigeki D (2005) Anal Chim Acta 548:79-85.

[24] Liew D, Linge KL, Joll CA, Heith A, Charrois JWA (2012) J Chromatogr A 1241:117-122.

[25] Bougeard CMM, Goslan EH, Jefferson B, Parsons SA (2010) Water Res 44:729-740.

3.1.3. Discussion of results

Although the results of the experimental part of the studies included in this section have been already discussed in their respective papers, the current section presents and discusses the most important aspects of these.

The results presented in this section demonstrate the applicability of the HS-SPME followed by GC-MS methodology for the simultaneously determination of a wide range of volatile organic compounds, odour compounds, fragrance allergens, pesticides, endocrine disrupting compounds and disinfection by-products. Those families of compounds have different chemical properties including different levels of volatility and polarity. It was challenging to optimize the whole chromatographic separation for the different compounds studied in 39 minutes. Therefore, optimization of the separation was performed firstly individually for each family in full scan mode. After the quantification and qualification ions of each compound were selected. Compound confirmation was done with the whole mass spectrum. For the 76 micropollutants determination, the quantification was finally done by full scan mode. For the 20 DBPs determination, the quantification was done by Selected Ion Monitoring due to it was easier for their detection being a low number of compounds.

As mentioned before, for the SPME optimization, different variables were evaluated by comparing the chromatographic separation for the different compounds studied. In some occasions, it was difficult to achieve this optimization due to the different chemical properties of the compounds studied and finally some properties have been selected as a compromise between them. The SPME was performed in the headspace of the sample due to the volatility of the substances as well as the matrix interference which could occur when the fibre is immersed.

Quantification of the samples was performed by external calibration using the calibration curves obtained by spiking the standards in reverse osmosis effluent water. In the case of waste water influent and effluent samples of reverse osmosis treatment, they presented matrix effect and therefore they were quantified with matrix match calibration line. The quantification of these samples was performed using calibration curves obtained by spiking the standards in those waste water influent and effluent samples of reverse osmosis. It should be mention that suspended matter or solids can have a significant influence on response at trace level analysis, in particular for influent samples.

For the micropollutants method, the compounds determined were: tributyl phosphate, coumarin, carvone, limonene, isopropilbenzene, o-xylene, p/m-xylene, ethylbenzene, chlorobenzene, dibromochloromethane, bromodichloromethane and dibromomethane. For the DBPs method, the target compounds were determined: 2-chloro-2-methyl-propane, 2-bromo-2-methyl-propane and trichloromethane.

Another important conclusion derived from both methodologies is that the validated method has been used for the determination of the target organic compounds in aqueous samples belonging different water treatment of application research units, showing good performance in the different types of waters studied. Some compounds were found in the samples, due to the fact that these species are commonly used in domestic and industrial applications. The tendency of most of them indicates a possible removal by the membrane reverse osmosis treatment, which is in agreement with some previous studies [1-2]. Therefore, in the following chapter is presented the study of reverse osmosis treatment for micropollutants rejection in advanced water reuse applications.

References

[1] K. Kimura, G. Amy, J. E. Drewes, T. Heberer, T. Kim, Y. Watanabe, J. Membr. Sci. 227 (2003) 113.

[2] V. Gómez, K. Majamaa, E. Pocurull, F. Borrull, Water Sci. Technol. 66.1 (2012) 61.

3.2. Application of the developed methods

In the last chapter, two methodologies based on headspace solid phase microextraction (HS-SPME) and gas chromatography-mass spectrometry (GC-MS) has been described for simultaneously characterization of different families of micropollutants in water samples. In order to study the applicability of the methods developed, waste water was selected for micropollutants monitoring. The study was carried out in an urban WWTP located in the NE of Spain that treats about 16.500 m^3/day of water. It consists of a primary treatment, a secondary biological treatment and a tertiary treatment including chlorination, coagulation/foculation, lamellar clarification and sand filtration. The effluent of the secondary treatment was connected to a research unit comprising UF system (as a RO pretreatment) followed by RO treatment.

The main objective was to study the micropollutants rejection by reverse osmosis membranes. Furthermore, the relation between the rejection of the micropollutants, the molecular weight and the octanol-water partition coefficients was also evaluated. There are some studies in the literature referring to micropollutants monitoring [1-4], but not comparing them with the chemical properties between the membranes and analytes.

As it is known, the higher to octanol-water partition coefficient is, the more non-polar the compound, being better rejected by RO membranes the less polar compounds. The log Kow partition coefficients are generally inversely related to aqueous solubility and directly proportional to molecular weight.

In addition, complementary organic water analyses were performed such as total organic carbon (TOC), chemical oxygen demand (COD), biological oxygen demand (BOD), ultraviolet absorbance at 254 nm (UV254) and color, following their standard methods [5].

Samples analyzed belong to the influent and effluent of RO membrane treatment as well as the influent of the WWTP. A total of 30 samples were analysed in the full study.

The study presented in this chapter has been presented in the European Desalination Conference (EDS) in Cyprus in 2014. Moreover, the study has been published in the scientific journal of Desalination and Water Treatment, (July 2014) 1-10, DOI: 10. 1080/19443994.2014.940208.

References

[1] J.E. Drewes, Heberer, T. Rauch, K. Reddersen, 23 Ground Water Monitoring & Remediation (2003) 64.

[2] K. Kimura, G. Amy, J. E. Drewes, T. Heberer, T. Kim, Y. Watanabe, J. Mem. Sci. 227 (2003) 113.

[3] A.A Alturki, N. Tadkae, J. A. McDonals, S.J. Khan, W.E. Price, L.D. Nghiem, J. Mem. Sci. 365 (2010) 206.

[4] B. Van der Bruggen, C. Van de casteele, Environmental Pollution 122 (2003) 435.

[5] Standard Methods for the Examination of Water and Waste water, Published by the American Public Health Association, Water Environment Federation, and the American Water Works Association 21st Edition 2005.

3.2.1. Study of reverse osmosis treatment for micropollutants rejection in advanced water reuse applications

STUDY OF REVERSE OSMOSIS TREATMENT FOR MICROPOLLUTANTS REJECTION IN ADVANCED WATER REUSE APPLICATIONS

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Abstract

Reverse osmosis (RO) membranes have made a breakthrough in waste water reclamation for the rejection of micropollutants in multiple applications such as reuse. Since these compounds are not completely eliminated using conventional treatments. This paper offers an overview of a waste water treatment plant using RO membrane treatment to study the rejection of 75 micropollutants from different families. The 75 selected micropollutants include some emerging and persistent compounds like volatile organic compounds (52), endocrine disrupting compounds (2), odour compounds (8), fragrance allergens (10) and some pesticides (3). Experimental results indicated that secondary effluents from conventional treatments contained most of the micropollutants studied; showing that conventional treatments such as activated sludge are not able to completely eliminate them. The rejection of these organic compounds was studied after the reverse osmosis system. In addition, the relation between the micropollutant's rejection, the molecular weight and the octanol-water partition coefficients was also evaluated.

Keywords: *advanced waste water treatment, GC-MS, organic micropollutants, reverse osmosis.*

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1. INTRODUCTION

The occurrence of trace organic contaminants in treated and untreated domestic waste water has been identified as a significant environmental health concern.

Currently, treated industrial and municipal waste water is discharged to the environment and generally considered as a waste. However, municipal waste water effluent should be considered a resource from which high quality water could be produced [1].

It is recognized that current waste water treatment technologies are very often unable to entirely degrade such persistent micropollutants. Consequently, some of the micropollutants and/or their metabolites are being accumulated in the aquatic environment where they may result in an ecological risk [2]. Therefore, alternative advanced technologies for tertiary treatment of waste water treatment plant (WWTP) effluents are necessary. At present, these micropollutants are not routinely monitored by water treatment companies due to the lack of regulatory requirements. Furthermore, there is an extreme cost involved in monitoring thousands of potential contaminants that are expected to be removed after the treatment, although in reality they are not included in the literature. The most common families of micropollutants studied include volatile organic compounds, disinfection by-products, steroids and hormones, antiseptics, personal care products (sun creams, fragrances, odors, etc.), petrol additives, drugs, heavy metals and metalloids, pesticides, surfactants and endocrine disruptors [3-4]. Therefore, few studies either have looked at the occurrence of these compounds in groundwater or have evaluated their rejection in waste water treatment plants [5-7]. However, some experimental flat sheet and pilot plant studies have been reporting other types of organic compounds, such as organic colloidal particles which are classified as contaminants and could cause performance problems in the reverse osmosis (RO) membranes [8-9]. Viable solutions for improving the removal of these micropollutants from water are pressurized membrane processes. The WWTP effluents can be then further treated with an array of advanced treatment processes, including microfiltration (MF), ultrafiltration (UF), RO or nanofiltration (NF) [10]. Recent developments in membrane bioreactor (MBR) systems have led to the availability of these systems as an alternative to conventional activated sludge treatment processes [11].

This article presents a study where the presence of 75 organic micropollutants was evaluated and monitored to assess the effectiveness of a conventional WWTP using a thin film composite polyamide RO membrane as a tertiary treatment. In addition, the micropollutants rejection was also related to their physico-chemical properties. Since limited data exist in the literature for meaningful comparison of solute properties and rejection, the results obtained in this study can contribute to

Desalin. Water Treat. (2014) 1-10 DOI: 10.1080/19443994.2014.940208

an improved understanding of micropollutants rejection by RO membranes. The 75 target compounds monitored ranged in variets from volatile organic compounds (VOCs) (e.g. chlorobenzenes, chloroalkanes), endocrine disruptting compounds (EDCs) (e.g. tri(2-chloroethyl) phosphate and tributyl phosphate), odour compounds (e.g. limonene, phenol), fragrance allergens (e.g. geraniol, eugenol) and some pesticides (e.g. heptachlor, terbutryn).

2. METHODS

2.1 STUDIED COMPOUNDS

The different compounds selected have physico-chemical properties that are representative of a wide range of organic compounds present in impaired water sources. The 75 selected micropollutants, provided by Dr. Ehrenstorfer (Augsburg, Germany) and Sigma-Aldrich, Supelco (Madrid, Spain), included volatile organic compounds (52), endocrine disrupting compounds (2), odour compounds (8), fragrance allergens (10) and some pesticides (3). Table 1 summarizes the physico-chemical properties of the compounds determined in this study.

2.2 ANALYTICAL METHOD

This study was focused on the simultaneous characterization of 75 micropollutants in waste water samples with an analytical method based on headspace solid phase microextraction (HS-SPME) and gas chromatography-mass spectrometry (GC-MS), which was optimised in a previous paper [12].

Analytes were extracted using a volume of 30 mL of waste water, placing it into a 50 mL PTFE/silicone screw-cap glass vial and mixed with 400 g·L^{-1} of sodium chloride (saturated solution). The vial was hermetically closed, heated up to 50 ºC within a thermostatic water bath and put over a magnetic stirrer. A fibre of PDMS/DVB was exposed to the headspace above the aqueous solution and the magnetic stirring was fixed at 1000 rpm during the 30 minutes of extraction. At the end of the extraction, the fibre was inserted into the injection port of the gas chromatograph for the thermal desorption and analysis. Fibre was desorbed at 270 ºC during the chromatographic analysis in the splitless mode to avoid carryover.

Micropollutants were analyzed by using Shimadzu GCMS-QP2010 Ultra/ GCMS-QP2010 SE gas chromatography analysis, equipped with a split/splitless injector and coupled to a mass spectrometer detector. Helium was employed at constant column flow of 1 mL·min^{-1}. Analytes were separated with TRB-5MS column (60m x 0.32 mm i.d., 1μm film thickness) from Tecknokroma, (Barcelona, Spain). The split/splitless injection port was equipped with a 0.75 mm ID liner from Supelco, and operated at 270 ºC, allowing direct injection of SPME. The oven temperature program was started at 40 ºC, held for 2 min; then increased by 6 ºC·min^{-1} up to 150 ºC and by 20 ºC · min^{-1} up to 300 ºC, and held for 12 min. The total run was 39 min.

Table 1. Target compounds and their retention time, log Kow partition coefficients, molecular weight and detection limits [12]

Family	Compound	t_R (min)	log K_{ow}	Molecular Weight ($g \cdot mol^{-1}$)	LOD ($\mu g \cdot L^{-1}$)
VOCs	**1.1-dichloroethene**	5.17	2.13	96	0.100
	(Z)-1.2-dichloroethene	6.35	1.86	96	0.033
	1.1-dichloroethane	6.40	1.79	98	0.033
	2.2-dichloropropane	6.60	2.28	112	0.033
	trichloromethane	6.67	1.97	118	0.001
	(E)-1.2-dichloroethene	7.16	2.09	96	0.033
	bromochloromethane	7.41	1.41	129	0.100
	1.1.1-trichloroethane	7.69	2.48	132	0.033
	1.2-dichloroethane	7.74	1.48	98	0.033
	1.1-dichloro-1-propene	8.05	2.03	110	0.017
	benzene	8.26	2.13	78	0.001
	carbon tetrachloride	8.38	2.73	152	0.003
	1.2-dichloropropane	9.44	1.97	112	0.017
	trichloroethene	9.59	2.71	130	0.003
	dibromomethane	9.78	1.70	172	0.003
	bromodichloromethane	10.11	1.70	162	0.100
	(E)- 1.3-dichloro-1-propene	11.14	2.06	110	0.001
	(Z)- 1.3-dichloro-1-propene	11.65	2.06	110	0.003
	toluene	12.13	2.75	92	0.0005
	1.1.2-trichloroethane	12.23	2.05	132	0.100
	1.3-dichloropropane	12.64	2.00	112	0.010
	dibromochloromethane	13.12	2.04	206	0.001
	1.2-dibromoethane	13.49	1.96	186	0.017
	tetrachloroethene	13.62	2.67	164	0.033
	chlorobenzene	14.85	2.86	112	0.001
	1.1.1.2-tetrachloroethane	14.92	2.62	166	0.010
	ethylbenzene	15.31	3.14	106	0.0005
	o-xylene	15.56	3.13	106	0.001
	tribromomethane	16.17	2.35	250	0.100
	styrene	16.27	2.87	104	0.0005
	p-xylene/ m-xylene	16.38	3.17	106	0.0005
	1.1.2.2-tetrachloroethane	16.83	2.39	166	0.010
	1.2.3-trichloropropane	17.10	2.29	146	0.010
	isopropilbenzene	17.35	3.48	120	0.001
	bromobenzene	17.71	2.71	156	0.0005
	1-chloro-2-methylbenzene	18.32	3.42	126	0.001

Table 1. (Continued)

	1-chloro-4-methylbenzene	18.47	3.33	126	0.010
	1.2.4-trimethylbenzene	18.72	3.65	120	0.0005
	1.3.5-trimethylbenzene	18.95	3.42	120	0.010
	tert-butylbenzene	19.52	4.11	134	0.0005
	sec-Butylbenzene	20.07	4.57	134	0.0005
	1.3-dichlorobenzene	20.20	3.52	146	0.010
	p-isopropilbenzene	20.43	4.38	134	0.0005
	1.2-dichlorobenzene	20.92	3.43	146	0.001
	1.4-dichlorobenzene	21.02	3.42	146	0.010
	butylbenzene	21.30	4.26	134	0.0005
	1.2-dibromo-3-chloropropane	22.05	2.95	234	0.001
	1.2.4-trichlorobenzene	23.95	4.01	180	0.001
	naphthalene	24.14	3.35	128	0.0005
	hexachlorobutadiene	24.52	4.78	258	0.010
	1.2.3-trichlorobenzene	24.55	4.05	180	0.010
Odours	**dimethyl disulfide**	11.40	1.77	94	0.017
	phenol	18.62	1.50	94	0.001
	D-limonene	20.60	4.57	136	0.001
	3-methyl-phenol	21.40	1.98	108	0.100
	carvone	24.81	2.71	150	0.001
	indole	25.48	2.14	117	0.100
	skatole	26.56	2.60	131	0.010
	geosmin	26.98	3.57	182	0.0005
Allergens	**benzyl alcohol**	20.54	1.05	108	0.001
	citral	24.62	3.76	152	0.010
	geraniol	24.72	3.56	154	0.033
	hidroxicitronellal	25.16	1.41	172	0.100
	cinnamyl alcohol	25.84	1.95	134	0.100
	eugenol	26.12	2.49	164	0.010
	isoeugenol	27.04	3.04	164	0.100
	coumarin	27.18	1.39	146	0.0005
	ammylcinamaldehid	28.67	4.16	202	0.0005
	benzil salizicate	30.49	4.67	228	0.017
Pesticides	**terbutryn**	30.87	3.74	241	0.010
	heptachlor	31.17	6.66	370	0.017
	dicofol	31.64	4.28	371	0.017
EDCs	**tributyl phosphate**	28.37	4.00	266	0.001
	tri(2-chloroethyl) phosphate	29.35	0.5	284	0.001

Mass spectrometry was performed in full-scan mode with a single quadrupole and monitored masses were between 40 and 280 m/z. Ionization was carried out in the electron impact (EI) mode at 70 eV. The transfer line temperature was maintained at 300 ºC and the ion source temperature at 250 ºC.

In addition, complementary analysis of some basic organic water parameters was performed such as total organic carbon (TOC), chemical oxygen demand (COD), biological oxygen demand (BOD), absorbance at 254 nm (UV 254) and color, following their standard methods [13].

2.3 Waste water treatment plant overview

The study was carried out in an urban WWTP located in the NE of Spain. Primary and secondary biological treatments were designed to treat 15.000 $m^3 \cdot day^{-1}$ of water during winter time and 47.500 $m^3 \cdot day^{-1}$ during summer time. The effluent of the secondary treatment was connected to a research unit comprising UF system (as a RO pretreatment) followed by RO treatment. Figure 1 depicts the existing treatment scheme.

The plant was operated continuously in once-through mode and was operated for at least one week before water samples were taken. This ensured representative operation conditions for the RO plant with stabilized membrane performance. The tested RO membranes were DOW FILMTEC^{TM} BW30 (A Trademark of the Dow Chemical Company or an affiliated company of Dow). These membranes were industrial standard rejection and high productivity brackish water membranes. The molecular weight cut-off (MWCO) of these membranes was in the range of 100 Dalton.

The process and sampling points (stars)

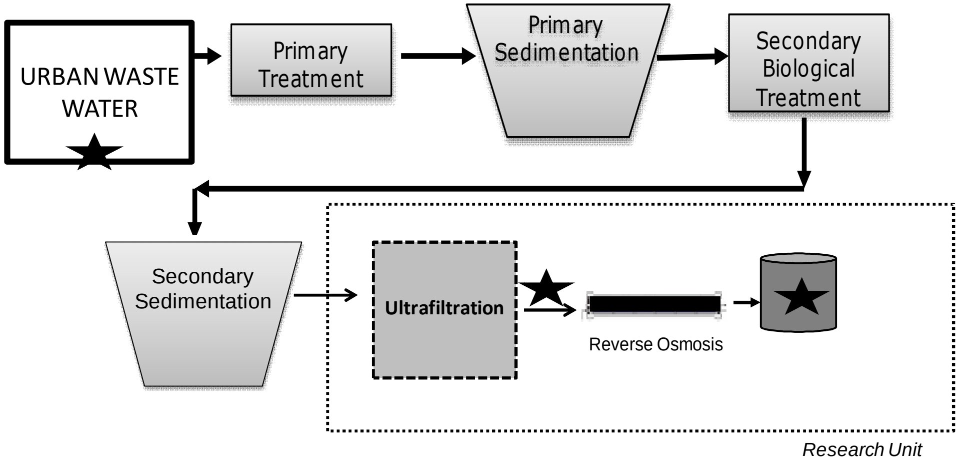

Figure 1. Waste water plant overview. Sampling points are indicated by a star.

are also shown schematically in Figure 1. Samples belong to the influent and effluent of RO membrane treatment as well as the influent of the WWTP. Water samples were collected weekly in amber glass bottles and were stored in the dark at 4 ºC until analysis, within two days. A total of 30 samples were analysed in the full study.

3. RESULTS AND DISCUSSION

3.1 WATER CHARACTERIZATION

When compared to other waters such as river water or sea water, waste water has a higher load of organic content. For this reason, its organic and biological fouling tendency in reverse osmosis is higher. For the present study, the operational flow-rate through the RO membrane, which is the rate of influent water introduced to the RO membrane, was fixed at 900-950 L·h^{-1} and the recovery, which is the percentage of RO influent water that emerges from the system as product water or effluent, was fixed at 50%.

Table 2. RO experimental conditions during the study.

Parameter	Unit	Experimental Range
Temperature	ºC	16-20
pH	-	7.0-7.8
Feed conductivity	mS/cm	2500-3800
Flow-rate	L/h	900-950
Recovery	%	50-51
Feed pressure	Bar	11-14
Salt Rejection	%	98.7-99.1

These selected parameters are worldwide recognized as standard operational conditions for RO systems in waste water application treatments. In addition, based on the flow-rate and recovery, the feed pressure was adjusted. Characteristics of RO influent water and operational parameters are collected in Table 2, where minimum and maximum values through the study period are indicated.

In addition, values of different organic parameters such as COD, TOC, BOD$_5$ and UV254 of the RO influent and effluent were analyzed. As expected, the values in the RO effluent samples were always lower than in the RO influent samples, as shown in Figure 2. In addition, the limit of detection (LOD) of the COD and BOD$_5$ were represented in the figure.

It could be observed that the COD of the RO influent water varied from 24 mg·L^{-1}of O$_2$ the day 1 to 10 mg·L^{-1} of O$_2$ on day 25, while the BOD$_5$ was less than 2.5 mg·L^{-1} of O$_2$ over the entire period. This gives a BOD$_5$/COD ratio of less than 0.2, which indicates that most of the organic compounds in the waste water are poorly biodegradable [14-15].

In addition, the COD and the BOD$_5$ results of the effluent samples were lower than the limit of detection of the method in all cases.

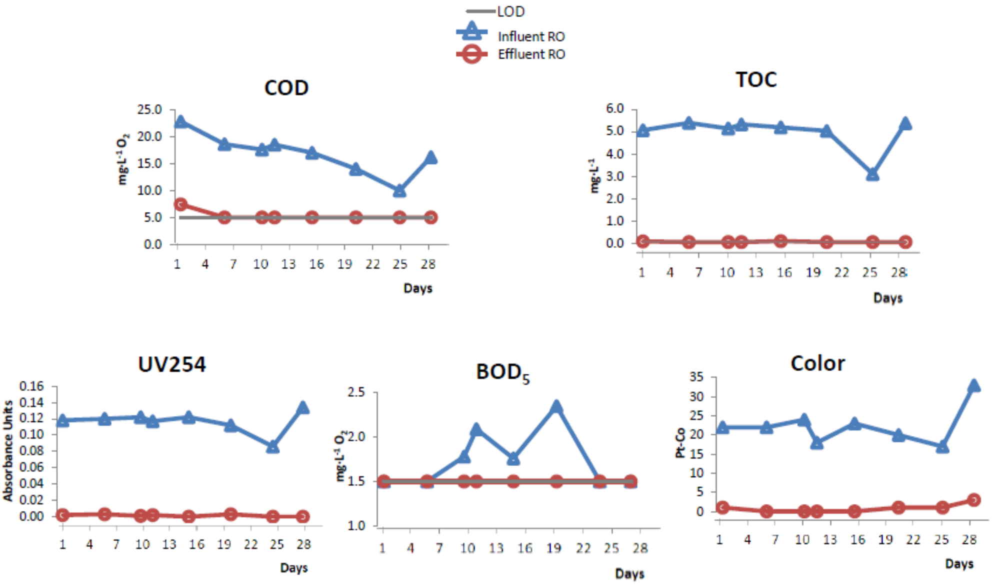

Figure 2. Organic parameters of the RO influent and effluent water.

There was a trend in some of the parameters, such as TOC, COD and UV254, where their concentrations in the RO influent consistently decreased during the study, probably because of some unexpected issues in the conventional treatment, such as rainy days which diluted the organic content in the primary and secondary treatment. Moreover, there was an unexpected shutdown of the RO membrane treatment, which was also reflected on the water analysis showing higher concentrations in the last sampling point (day 28).

3.2 REJECTION OF MICROPOLLUTANTS

The rejection percentage or rejection efficiency of every compound via RO treatment was calculated as presented using Equation 1 below:

$$\text{Rejection} = \left(1-\frac{Ce}{Ci}\right)*100 \qquad (1)$$

where Ce is the concentration of the analyte in the effluent of the RO membrane system and Ci is the concentration of the analyte in the RO influent.

The target micropollutants belong to different families (VOCs, fragrance allergens, odours, EDCs and pesticides), shown previously in Table 1, with different physico-chemical properties which could result in different RO performance. Analyte rejection by RO membranes will be affected by the analyte and membrane properties, RO

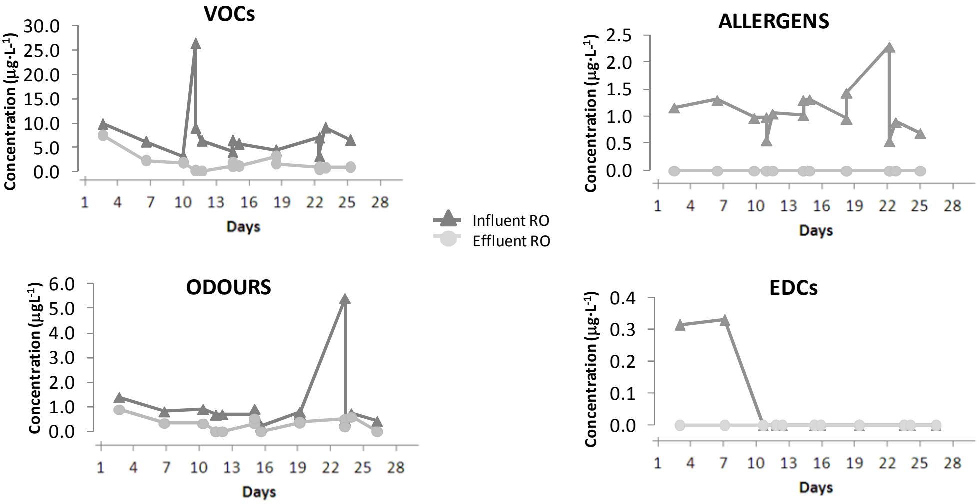

Figure 3. Concentration of the micropollutants found classified by families.

influent composition and operating conditions [16-17].

The micropollutants could be rejected by one of a combination of three basic mechanisms: size exclusion, charge exclusion and physico-chemical interacttions between analyte, solvent and membrane. For organic molecules, especially for uncharged compounds, the most commonly used parameter is the molecular weight because it is assumed that transport through the membrane is mainly related to size exclusion as well as its polarity.

As expected, all RO effluents showed less concentration of micropollutants than the RO influent in all the families studied. Almost all the micropollutants found correspond to VOCs, the biggest group (with 54 compounds). VOCs (77% in the influent and 86% in the effluent of the total micropollutants identified) and odour compounds (10.9% in the influent and 14% in the effluent of the total micropollutants identified) could be properly quantified in the influent and effluent samples. On the other hand, fragrance allergens (11.6% in the influent of the total micropollutants identified) and EDCs (0.5% in the influent of the total micropollutants identified), the concentration in the RO effluents was lower than 1 $\mu g \cdot L^{-1}$ in both families. Figure 3 shows the concentration of the micropollutants found in the RO influent and effluent classified by families. The pesticide group is not shown in the figure, as its concentration was lower than the detection limit in all samples tested.

The micropollutants families with consistently higher rejection were the fragrance allergens and EDCs because of their polarity as well as their molecular weight (see in Table 1).

Table 3. Organic parameters and micropollutants analyzed (in $\mu g\cdot L^{-1}$) found in the WWTP influent, RO influent and effluent samples (n=30).

	ORGANIC PARAMETERS	**AVERAGE INFLUENT WWTP**	**AVERAGE RO INFLUENT**	**AVERAGE RO EFFLUENT**	**AVERAGE Rejection %**
	Color (Pt-Co)	-	23	0.5	98
	UV254 (cm^{-1})	-	0.120	0.002	98
	BOD5 (ppm O_2)	-	1.593	<1.500	53*
	TOC (ppm)	-	5.20	0.07	99
	COD (ppm O_2)	-	19.7	5.8	71
	MICROPOLLUTANTS				
VOCs	Trichloromethane	2.50	2.47	<0.001	99*
	E-1.2-Dichloroethane	0.30	0.13	<0.033	88*
	Carbon tetrachloride	n.d.	0.11	<0.003	99*
	Trichloroethene	0.26	0.12	<0.003	99*
	Methane, bromodichloro-	n.d.	0.80	0.14	83
	Toluene	1.08	0.07	0.06	16
	Ethane, 1,1,2-trichloro-	6.59	2.71	0.47	83
	Methane, dibromochloro-	n.d.	0.28	0.14	49
	Tetrachloroethene	<0.001	0.86	2.27	<5
	Benzene, chloro-	n.d.	0.07	0.19	<5
	Ethylbenzene	0.05	0.05	0.03	25
	o-Xylene	0.09	0.08	<0.001	99*
	Styrene	0.20	0.20	<0.0005	99*
	p-Xylene/m-Xylene	0.09	0.09	<0.0005	99*
	Benzene, (1-methylethyl)-	0.14	0.14	0.14	<5
	Benzene, 1,2,4-trimethyl-	0.17	0.16	0.15	6
	Benzene, 1,3,5-trimethyl-	0.21	0.17	0.16	5
	Benzene, tert-butyl-	0.24	0.23	<0.0005	98*
	Benzene, 1,3-dichloro-	0.18	0.18	<0.010	97*
	Benzene, 1,2-dichloro-	n.d.	0.34	<0.001	99*
	Benzene, 1,4-dichloro-	0.23	0.34	<0.010	99*
	Benzene, 1,2,4-trichloro-	n.d.	0.22	<0.001	98*
	Naphthalene	0.13	0.11	0.10	3
Odours	Disulfide, dimethyl	0.66	0.27	0.18	32
	Phenol	3.00	0.42	0.43	<5
	Phenol, 3-methyl-	0.75	3.27	<0.100	98*
	Geosmin	0.27	0.23	<0.005	99*

Table 3. (Continued).

Allergens	Citral	0.33	0.30	<0.010	98*
	Cinnamyl Alcohol	11.52	1.37	<0.100	96*
	Eugenol	0.51	0.30	<0.010	98*
	Isoeugenol	0.96	0.48	<0.100	90*
	Benzil Salizicate	0.21	0.11	<0.017	93*
EDC	Tributyl phosphate	n.d.	0.32	<0.001	99*

n.d. No detected compound
*Estimated rejection

Two odour compounds (dimethyl disulfide and phenol) were low rejected due to their low log K_{ow} partition coefficient and their low molecular weight.

It needs to be noted that close to the limit of detection, accuracy in detected concentrations might be affected. The target organic parameters as well as the specific micropollutants detected in the WWTP influent, RO influent and effluent samples as an average of all the sampling are presented in Table 3. Moreover, their rejection by RO membranes is also shown in the table. Some of the rejections were estimated in cases where the concentration in the RO effluent was lower than the limit of detection. Those rejections were estimated taking into account the half of the limit of detection. It is worth mentioning the presence of some halogenated VOCs, such as bromodichloromethane, dibromochloromethane and 1,3-dichlorobenzene in the RO influent due to chlorination stages of the conventional treatment. These species were finally reduced by the RO treatment.

In addition, some micropollutants such as trichloromethane, 1,1,2-trichloroethane, phenol and cinnamyl alcohol were present in the WWTP influent and not eliminated by the conventional treatment. The molecular weight, the log K_{ow} and the RO rejections regarding some representative micropollutants found in the RO influents and effluents are represented and compared in Figure 4. The molecular weight of some micropollutants versus their rejections have a similar trend especially for uncharged compounds, because it is assumed that transport through the membrane is mainly related to size exclusion (Figure 4a).

The log K_{ow} partition coefficient compared with the micropollutants rejection is shown in Figure 4b. A similar trend has been observed for the majority of the compounds, especially those which have higher log K_{ow} partition coefficient and higher molecular weight. The higher to K_{ow}, the more non-polar the compound, being better rejected by RO membranes the less polar compounds.

The log K_{ow} partition coefficients are generally inversely related to aqueous solubility and directly proportional to molecular weight. In addition, similar tendency was also observed for the micropollutants rejection by the relation between the molecular weight and the log K_{ow} and it is shown in Figure 4c.

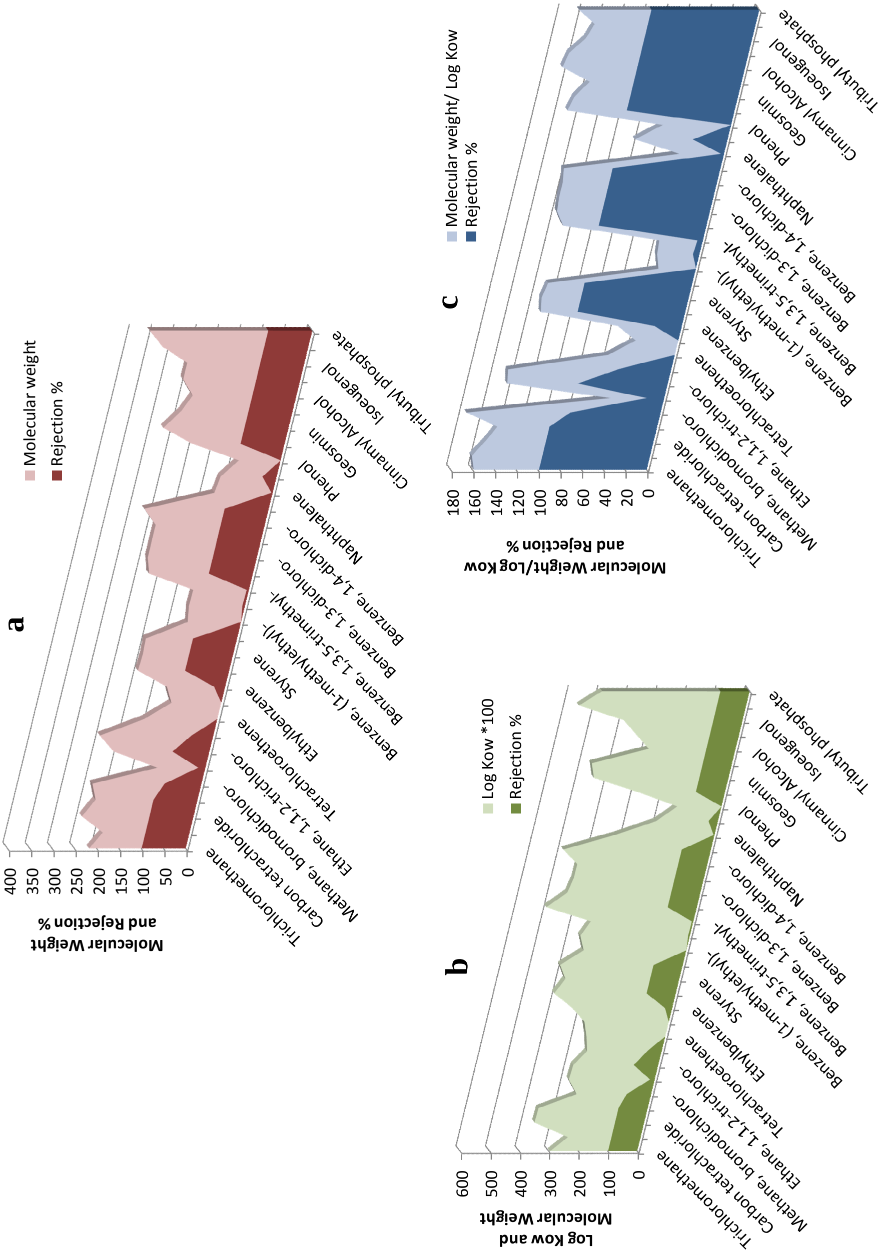

Figure 4. Comparison between the molecular weight, the log K_{ow} and the rejection of some representative micropollutants.

As a general trend, the results reported indicate that RO membrane treatment can achieve an enhanced rejection efficiency of a wide range of trace organic contaminants, over conventional treatment methods, which is in agreement with other authors [18-21].

4. CONCLUSIONS

The presence and behavior of 75 micropollutants during RO membrane treatment has been evaluated in an urban WWTP. Results reported in this study indicate that RO membrane processes can achieve an enhanced rejection efficiency of a wide range of trace organic contaminants, since conventional processes alone are not sufficient to remove these micropollutants.

The majority of the present micropollutants are removed from the waste water using RO membrane treatment, improving the effluent quality in terms of micropollutants concentration. Fragrance allergens and EDCs were the families of the micropollutants with consistently high rejection, being higher than 83% because of their polarity as well as their molecular weight.

It is assumed that transport through the membrane is mainly related to size exclusion. Therefore, as a general trend, higher rejection was observed when increasing molecular weight.

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5. REFERENCES

[1] L. Prieto-Rodriguez, S. Miralles Cuevas, I. Oller, A. Agüera, G. Puma, S. Malato, Treatment of emerging contaminants in waste water treatment plants (WWTP) effluents by solar photocatalysis using low TiO2 concentrations, J. Hard. Materials, 211-212 (2012) 131-137.

[2] P. D. Hansen, Risk assessment of emerging contaminants in aquatic systems, Trends Anal. Chem. 26 (2007) 1095-1099.

[3] C.G. Daughton, T. A. Ternes, Pharmaceuticals and personal care products in the environment: agents of subtle change?, Environ Health Perspect., 107 (1999) 907-938.

[4] C. G. Daughton, Non-regulated water contaminants: emerging research, Environmental Impact Assessment Review 24 (2004) 711– 732.

[5] www.epa.gov/ppcp/lit.html, accessed 5th April 2013.

[6] J.E. Drewes, Heberer, T. Rauch, K. Reddersen, Fate of pharmaceuticals during ground water recharge, Ground Water Monitoring and Remediation 23 (2003) 64-72.

[7] http://ca.water.usgs.gov/gama/, accessed 5th April 2013.

[8] S. Lee, J. Cho, M. Elimelech, Combined influence of natural organic matter (NOM) and colloidal particles on nanofiltration membrane fouling, Journal of Membrane Science, 262 (2005) 27–41.

[9] C. Bellona, M. Marts, J. E. Drewes, The effect of organic membrane fouling on the properties and rejection characteristics of nanofiltration membranes, Separation and Purification Technology, 74 (2010) 44–54.

[10] K. Kimura, G. Amy, J. E. Drewes, T. Heberer, T. Kim, Y. Watanabe, Rejection of organic micropollutants (disinfection by-products, endocrine disrupting compounds, and pharmaceutically active compounds) by NF/RO membranes, J. Mem. Sci. 227 (2003) 113-121.

[11] A.A Alturki, N. Tadkaew, J. A. McDonal, S.J. Khan, W.E. Price, L.D. Nghiem, Combining MBR and NF/RO membrane filtration for the removal of trace organics in direct potable water reuse applications, J. Mem. Sci. 365 (2010) 206-215.

[12] C. Martínez, N. Ramírez, V. Gómez, E. Pocurull, F. Borrull, Simultaneous determination of 76 micropollutants in water samples by headspace solid phase microextraction and gas chromatography-mass spectrometry, Talanta, 116 (2013) 937–945.

[13] Standard Methods for the Examination of Water and Waste water, Published by the American Public Health Association, Water Environment Federation, and the American Water Works Association 21st Edition 2005.

[14] B.Słomczyńska, T.Słomczyński, Physico-Chemical and Toxicological Characteristics of Leachates from MSW Landfills, Polish Journal of Environmental Studies, 13 (2004) 627-637.

[15] N. Park, B. Kwon, S. Kim, J. Cho, Characterizations of the colloidal and microbial organic matters with respect to membrane fouling, J. Mem. Sci. 275 (2006) 29-36.

[16] C. Bellona, J. E. Drewes, P. Xu, G. Amy, Factors affecting the rejection of organic solutes during NF/RO treatment a literature review, Water Research 38 (2004) 2795-2809.

[17] www.dowwaterandprocess.com, accessed 10th April 2013.

[18] V. Gomez, K. Majamaa, E. Pocurull, F. Borrull, Determination and occurrence of organic micropollutants in reverse osmosis treatment for advance water reuse, Water Sci. and Technol. 66.1 (2012) 61-71.

[19] B. Van der Bruggen, C. Van de casteele, Removal of pollutants from surface water and groundwater bynanofiltration: overview of possible applications in the drinking water industry, Environment. Pollution 122 (2003) 435–445.

[20] A.M. Urtiaga, ,G. Pérez, R. Ibáñez, I. Ortiz, Removal of pharmaceuticals from a WWTP secondary effluent by ultrafiltration/reverse osmosis followed by electrochemical oxidation of the RO concentrate, Desal. 331 (2013) 26–34.

[21] P. Cartagena, M. El Kaddouri, V. Cases, Reduction of emerging micropollutants, organic matter, nutrients and salinity from real waste water by combined MBR-NF/RO treatment, Separation and purification technology 110 (2013) 132-143.

3.2.2. Discussion of results

The main achievement of the study was the application of the HS-SPME GC-MS method for the determination of 75 micropollutants, evaluating the rejection and comparing it with the physic-chemical properties of the compounds selected. The results and conclusions have been already discussed in the paper previously. However, the detailed results are described below.

The organic water analysis of the influent water system showed that the water treated has a high load of organic content when compared to other waters such as river water or sea water. Therefore, the organic and biological fouling tendency is higher than the other types of water samples [1-2].

Almost all the micropollutants found were VOCs, which is the biggest group with a number of 54 compounds. VOCs could be properly quantified in the influent as well as in the effluent samples. Odour compounds were also quantified in the influent and effluent samples due to their volatility and low molecular weight of some of them. On the other hand, fragrance allergens and EDCs the concentration in the RO effluents was lower than 1 $\mu g \cdot L^{-1}$ in both families. Therefore they only could be properly quantified in the influent samples. The pesticide family was lower than the detection limit in all samples analyzed.

Figure 11 shows two samples analyzed, one from the RO influent and the other one from the RO effluent. It could be seen that the RO influent had more organic compounds that the RO effluent. Moreover, it can be seen the efficiency of the RO membrane treatment regarding the elimination of the majority of these compounds studied.

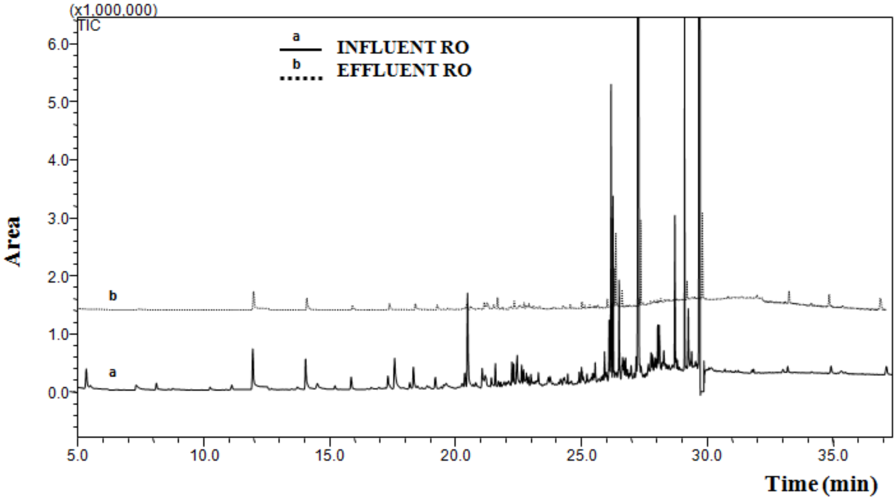

Figure 11. GC-MS chromatogram of RO influent and effluent waste water sample.

Micropollutants rejection by RO membranes is being affected by the analyte and membrane properties, RO influent composition and operating conditions. Therefore, the micropollutants could be rejected by one of a combination of three basic mechanisms: size exclusion, charge exclusion and physic-chemical interactions between analyte, solvent and membrane. For organic molecules, especially for uncharged compounds, the most commonly used parameter is the molecular weight because it is assumed that transport through the membrane is mainly related to size exclusion as well as its polarity. The physic-chemical properties studied and compared include the molecular weight, the log K_{ow} and the RO rejections regarding some representative micropollutants. The molecular weight of some micropollutants versus their rejections has a similar trend especially for uncharged compounds.

The log K_{ow} partition coefficient compared with the micropollutants rejection have a similar trend, being observed for the majority of the compounds. Those compounds which have higher log K_{ow} partition coefficient, being more hydrophobic and less polar compounds, and having higher molecular weight, are better rejected. The higher to K_{ow}, the more non-polar the compound, being better rejected by RO membranes the less polar compounds. The log K_{ow} partition coefficients are generally inversely related to aqueous solubility and directly proportional to molecular weight.

The micropollutants families with consistently higher rejection were the fragrance allergens and EDCs because of their polarity as well as their molecular weight. Two odour compounds (dimethyl-disulfide and phenol) had lower rejection due to their low log K_{ow} partition coefficient (more hydrophilic and more polar) and their low molecular weight.

Reverse osmosis membrane treatments can achieve an enhanced rejection efficiency of a wide range of micropollutants studied, over conventional treatment methods, since conventional processes alone are not sufficient to remove these micropollutants. Therefore, the effluent quality improves in terms of micropollutants concentration.

References

[1] J. Chu, J. Che, C. Wang, P. Fu, Water Res., 38 (2004) 2746.

[2] L.F. Greenlee, D.F. Lawler, B. D. Freeman, B. Marrot, P. Moulin, Water Res. 43 (2009) 2317.

3.3 Characterization of organic fouling

In recent years, advanced membrane treatments such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) membranes, have received a huge attention for water treatment, including waste water reclamation, sea water desalination and drinking water treatment [1]. According to the different applications of membrane processes, numerous researchers have tried to improve membrane properties associated with fouling resistance, developing operational protocols in terms of influent water quality, physical and chemical cleaning conditions, and taking into account the addition of some agents such as anti-fouling and anti-scaling agents [2-4].

However, membrane fouling is still one of the major limitations for practical operations of membrane processes. It is caused by the adsorption, accumulation or precipitation of dissolved constituents on the membrane surfaces and it can reduce effluent flux and increase operating pressure which are related to the energy requirements and cost effectiveness [5]. Membrane fouling could occur in two ways: the formation on a fouling layer and the foulants adsorption. The cake fouling could be decreased after water cleanings, while the adsorption of foulants could only be removed by aggressive chemical cleanings. In addition, fouling can be affected by the interaction between foulants. When the influent water contains a mixture of contaminants, the adsorption of a single foulant decreases by competitive sorption process [6].

Until present, most research studies attempting to relate physico-chemical properties of solutes and membranes to solute rejection were conducted with virgin membranes in laboratory scale plants without taking into account the change of membrane properties as a result of membrane fouling during long-term operation in large plants. One way to try to understand the fouling is to characterize the foulants found in the membranes. As a result, it is possible to understand the fouling mechanism of the filtered water and how the fouling could be reduced or avoided.

Given the limited studies on the role of physico-chemical interactions between fouled membranes and organic micropollutants, one of the aims of this research is the development and improvement of analytical methods to detect and identify membrane fouling in application research units and the reasons of decrease of membrane performance.

In this chapter, two studies are presented. The first one includes the study of organic foulants in a research unit using membrane advanced treatment as a tertiary treatment in a WWTP. The organic foulants were characterized using both conventional and advanced analytical tools in water samples. Gas chromatography-mass spectrometry (GC-MS) analysis was performed after different polarity solid phase microextraction (SPME) fibres and compared with the organic solvent liquid-liquid extraction, with dichloromethane: isopropanol solvents, in order to identify and semi-quantify the organic compounds. In addition, the organic characterization, such as TOC, DQO, BOD_5 and color, of the influent water was performed in order to correlate with the organic fouling results and therefore, to have supplementary information regarding the foulants.

The second study was focused on the membrane organic fouling characterization in the membrane surface. For the analysis of the membrane surface fouling, membrane autopsy was performed. The membrane elements were packed in plastic bags and stored at 2ºC until destructive study, which was performed within 24h after removal of the membrane elements from the installation. Membrane elements were opened lengthwise. The analysis include loss on ignition for determining the tan per cent of organic and inorganic content of the solid residue, the dissolved organic carbon for quantifying the presence of organic compounds and finally the organic fouling characterization by GC-MS in order to correlate those compounds found in the influent water in the previous study, with those found in the membrane surface fouling. GC-MS analysis was also performed after different polarity solvent extraction in order to identify and semi-quantify the organic compounds and compare it with the SPME extraction methodology.

The presence in water of micropollutants and possible organic foulants, as well as the organic membrane fouling were analyzed by different SPME polarity fibers followed by GC-MS determination. SPME technique has been tested for the first time, to provide valuable information regarding the organic fouling. The SPME studied fibres had different chemical polarities which complementary could identify different compounds with different chemical properties. The selected fibres were PDMS for low polarity, PDMS/DVB and PDMS/DVB/CAR for intermediate polarity and PA for high polarity organic compounds. It has been demonstrated that similar families of compounds were found also by organic solvent extraction. In addition, SPME has the advantage of being a solvent free technique, robust and fast.

Furthermore, some compounds were commonly found in the fouling and on membrane surface, as well as in the influent water. They probably could lead to RO membrane organic fouling and consequently membrane flux rate loss.

The studies presented in this chapter have been submitted in two international journals. The first one has been submitted into Desalination and Water Treatment. The second one has been accepted into Water Science and Technology.

References

[1] K. Chon, H.K. Shon, J. Cho, Bioresour. Technol. (2012), http://dx.doi.org/10.1016/j. biortech.2012.04.048.

[2] J.P. Chen, S.L. Kim, Y.P. Ting, J. Membr. Sci. 219 (2003) 27.

[3] P. Xu, C. Bellona, J.E. Drewes, J. Membr. Sci. 353 (2010) 111.

[4] W.S. Ang, A. Tiraferri, K.L. Chen, M. Elimelech, J. Membr. Sci. 376 (2011) 196.

[5] S. Phuntsho, A. Listowski, H.K. Shon, P. Le-Clech, S. Vigneswaran, Desalination 271 (2011) 241.

[6] Li, H., Lin, Y., Luo, Y., Yu, P., Hou, L., J. Hazard. Mater. 192 (2011) 490.

3.3.1. Headspace-solid phase microextraction: useful technique to characterize organic foulants in water reuse applications

HEADSPACE-SOLID PHASE MICROEXTRACTION: USEFUL TECHNIQUE TO CHARACTERIZE ORGANIC FOULANTS IN WATER REUSE APPLICATIONS

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Abstract

Sample preparation is an essential step in analytical science analysis, greatly influencing the reliability and accuracy, the time and cost of analysis. Solid-phase microextraction (SPME) is a very simple and efficient, solventless sample preparation technique, which has been widely used in different fields of analytical chemistry. In this study, four different polarity SPME fibres coupled with gas chromatography-mass spectrometry have been used for the determination of organic substances in the reverse osmosis (RO) influent of a waste water reuse installation. The results have been compared as well with those obtained with conventional liquid-liquid extraction. Adsorption of organic foulants on the membrane surface causes organic and biological fouling which also leads to flow loss and consequently to high influent pressure requirements.

Polyacrilate (PA) and Polydimethylsiloxane/Divinilbenzene/Carboxene (PDSM/DVB/CAR) are complementary fibres which can jointly characterize the organic foulants in the influent water. Organic foulants characterized belong to different families including: aromatic hydrocarbons, linear hydrocarbons, ketones, alcohols, fatty acids, phenols, nitro-containing compounds, phthalates, fragrance allergens, hormones, halogenated compounds, acetate derivates, sulfur-containing compounds, amines and sugars.
In addition, RO influent water values of total organic carbon, chemical oxygen demand, biological oxygen demand and color were analyzed during the study in order to complement the water analysis.

Keywords: *Headspace solid phase microextraction; gas chromatography-mass spectrometry; organic foulant; reverse osmosis; water reuse.*

Desalin. Water Treat. (submitted)

1. INTRODUCTION

In recent years, membrane processes, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) membrane, have received an increasing attention as promising technologies for water treatment, such as drinking water treatment, waste water treatment and sea water desalination, since they can produce water with superior quality at low cost. This effect has been widely studied *(Bellona et al. 2004; Pearce 2007; Bonnelye et al. 2008; Parck et al. 2006).* In spite of great advances in membrane technology, membrane fouling is still one of the major challenges faced by installations dealing with difficult waters. Membrane fouling is caused by the adsorption, accumulation or precipitation of dissolved constituents from the influent water on the membrane surfaces, as *Fang et al. (2010)* mentioned in their paper. In particular, organic matter plays a crucial role in formation of RO fouling, being the organic fouling a serious problem for membrane processes and limiting the widespread use of membranes. Such fouling results in an increase of the energy and reduction of water production, well documented by *(Miltner et al. 2008; Krasner et al. 2006; Pressman et al. 2010)*.

Previous research reported that relatively hydrophilic and non-charged fractions, comprising polysaccharides and protein-like substances, may be responsible for severe fouling formation in a membrane bioreactor (MBR) and a NF membrane system operated in a water reuse installation *(Chon et al. 2010; Chon et al. 2011)*. Some studies have also focused on the relationship between physical and chemical properties of organic matter (OM) and membrane fouling formation *(Jarusutthirak et al. 2002; Lee et al. 2006; Shon et al. 2004; Park et al. 2006)*. Although many studies have been conducted to determine or identify the most relevant factors contributing to fouling formation, understanding of membrane foulants in a large scale water reclamation plant is still incomplete as the majority of previous research has been performed under controlled laboratory conditions.
Previous research has been focused on OM characterization in the influent water by different analytical techniques which were focused on identifying major constituent of organic foulants and determining the natural organic matter (NOM) fraction and functional groups, as well as their molecular weight *(Her et al. 2008).* These analytical techniques included pyrolisis and mass spectroscopy *(Chon et al. 2012)*, high performance size exclusion chromatography with ultraviolet and dissolved organic carbon detections and Fourier transform infrared spectroscopy (FTIR) *(Alzahrani et al. 2013).* Some studies have also applied advanced water characterization techniques, such as excitation emission matrix fluorescence spectroscopy (EEM) and liquid chromatography with organic carbon detection (LC-OCD) for the characterization of foulants *(Ayache et al. 2013)*, as well as high resolution mass spectrometry for molecular characterization of dissolved organic matter *(Cortés et al. 2013).* These studies determined two fouling indexes: the total fouling index and the

hydraulically irreversible fouling index, comparing them with the organic fouling results.

Several sample preparation techniques, such as liquid-liquid extraction (LLE), single drop microextraction and solid phase extraction can be used for the extraction of organic compounds from RO influent water samples, whereas headspace solid phase microextraction (HS-SPME) can selectively extract organic compounds and no solvents are required. SPME has been widely used in different fields of analytical chemistry since its first applications to environmental and food analysis and is ideally suited for coupling with mass spectrometry (MS). The SPME technique can be routinely used in combination with gas chromatography and it reduces the time needed for sample preparation. The organic compounds in the sample are directly extracted to the fibre coating. Some of the studies reported in the literature *(Chen et al. 2008; Nerin et al. 2007; Buchberger et al. 2011; Martinez et al. 2013)* have been analyzed different micropollutants by SPME, including pharmaceuticals and personal care products, which are continuously released into the environment. Therefore, advanced characterization of organic foulants is believed to provide valuable insights into the fouling characteristics in a large scale application of UF and RO systems for municipal water reclamation.

The objective of this study was to evaluate the potential of the headspace HS-SPME technique for water characterization.

The advantage of HS techniques, when volatile or semivolatile compounds are analyzed, is that the extraction is more selective and the matrix influence becomes lower *(Gostelow et al. 2001)*. A study of four different polarity SPME fibres was done in order to sequentially identify individually the organic compounds of the RO influent water. In addition, a comparison with the conventional liquid-liquid extraction was also performed.

Furthermore, classical organic characterization of the influent water, such as chemical oxygen demand (COD), color, UV254, biological oxygen demand (BOD), total organic carbon (TOC), and specific light absorbance (SUVA), was done in order to correlate the results with the organic fouling presence on the membrane surface and to have complementary information.

2. MATERIALS AND METHODS

2.1 Chemicals and materials

Dichloromethane (DCM) and isopropanol (IPA) solvents were GC grade with purity >99.9% from Prolabo, (Barcelona, Spain). Helium gas 99,999% was supplied from Praxair (Barcelona, Spain).

Four commercial extraction fibres including 100μm Polydimethylsiloxane (PDMS), 65 μm Polydimethylsiloxane /Divinylbenzene (PDMS/DVB), 50/30 μm Polydimethylsiloxane/ Divinylbenzene/Carboxen (PDMS/DVB/CAR) and 85 μm Polyacrylate (PA) were purchased from Supelco, (Madrid, Spain).

2.2 Research unit

The study was carried out in a research unit which consists of RO membranes with a UF system used as pretreatment. The research unit was operated using the secondary clarified water coming from a conventional urban WWTP located in the NE of Spain. The pretreatment of the conventional WWTP included: coarse screening (1mm), sand filtration followed by primary sedimentation, secondary biological treatment and secondary sedimentation. Figure 1 depicts the existing treatment scheme with the sampling point. Influent RO water samples were collected weekly in amber glass bottles and were stored at 4ºC until analysis. Maximum storage time was 2 days.

The RO elements tested were operated for 2 months to investigate the organic and biofouling resistance, as well as the removal of organic compounds from the secondary effluent of the WWTP. The tested membranes were DOW FILMTEC^{TM} XLE-440. They are extra low energy reverse osmosis elements designed to deliver high quality water at low operating cost for urban and industrial water applications. The operational flow was fixed between 330-360 L·h^{-1} and the pressure drop was in the range 0.14-0.32 bar. In addition, conductivity, temperature and pH were also monitored. These selected parameters are worldwide recognized as standard operational conditions for RO systems in wastewater application treatments, as it is reflected in the literature *(www.dowwaterandprocess.com).*

2.3 Water analysis

30 mL of water sample was introduced into a 50 mL PTFE/silicone screw-cap glass vial for the HS-SPME extraction.

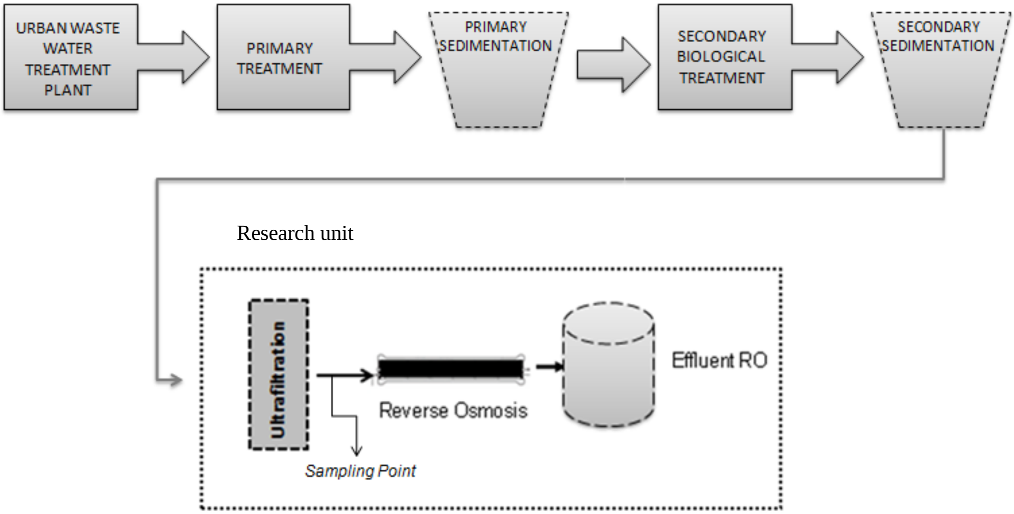

Figure 1. Set-up of WWTP and research unit.

Then, 0.4 g·mL^{-1} of sodium chloride (saturated solution) was added to the water sample, the vial was closed and put over a magnetic stirrer in a water thermostatic bath at 50ºC. The magnetic stirring was applied at 1000 rpm and the SPME fibre was exposed to the headspace for 30 minutes. After the extraction, the fibre was inserted into the injection port of the gas chromatograph for the thermal desorption and analysis. Fibre was desorbed at 270ºC during the chromatographic analysis in the splitless mode.

LLE was also performed to the water samples in order to compare the results with the SPME extraction. The conventional standard method is described elsewhere *(Zapf et al. 1995).* Samples were acidified with 10% hydrochloric acid to pH 2 and extracted with 2 x 100 mL of dichloromethane /isopropanol (90:10 v/v); the extracts were then concentrated in a R-210 Büchi rotavapor (Flawil, Switzerland) down to 250 μL as a final volume. Then, 1μL was injected into the GC injector port.

The gas chromatography analysis of the SPME and LLE extracts were performed with a GCMS-QP2010 Ultra/ GCMS-QP2010 SE from Shimadzu (Kioto, Japan), equipped with a split/splitless injector and coupled to a mass spectrometer detector. Helium was employed as a carrier gas at a constant column flow of 1.4 mL·min^{-1}. Analytes were separated with a TRB-5MS column (60m x 0.32 mm i.d., 1 μm film thickness) from Tecknokroma (Barcelona, Spain). The split/splitless injection port was equipped with a 0.75 mm ID liner from Supelco, and operated at 280ºC, allowing direct injection or SPME desorption. The oven temperature program was started at 80ºC, held for 5 min; and then increased by 10ºC·min^{-1} up to 300ºC and held for 10 min. The total GC-MS analysis run was 42 min. The MS analyses were conducted in full-scan mode with a single quadrupole and monitored masses were between 40 and 280 m/z. Ionization was carried out in the electron impact (EI) mode at 70 eV. The transfer line temperature was maintained at 300ºC and the ion source temperature at 250ºC.

The organic compounds were identified by the mass spectrum library, NIST08.LIB, considering only those compounds with match spectra higher o equal than 95%. Other compounds with match between 85-95% were also tentatively identified. In addition, the performance of the RO membranes was monitored in terms of several operational and organic basic parameters such as TOC, color, UV254, COD and BOD following standard methods *(Standard Methods for the Examination of Water and Wastewater).*

3. RESULTS AND DISCUSSION

3.1 Basic organic water analysis

Organic matter is much more relevant in water reuse applications than in other types of water samples such as river or sea water, having a TOC content approximately three times higher *(Słomczyńska et al. 2004),* which is not being totally eliminated by conventional water treatments.

Table 1. Operational and organic water parameters in the RO study.

Parameters	Values
Flow[L/h]	336-352
Pressure [bar]	6.27-6.30
Pressure drop [bar]	0.14-0.32
Conductivity [µS/cm]	1964-2012
Temperature [°C]	24.5-26.8
pH	7.2-7.3
Total COD (mg·L^{-1} O$_2$)	15.6-32.3
Color (Pt-Co)	28-42
UV 254 (cm^{-1})	0.13-0.15
BOD (mg·L^{-1} O$_2$)	<1.5-3.68
TOC (mg·L^{-1})	5.7-7.7
DOC (mg·L^{-1})	5.7-7.7
SUVA (L·(mg-m)$^{-1}$)	<4

In this study, changes in water characteristics through the RO membranes in terms of organic presence were monitored in order to investigate the RO influent water characteristics. Characteristics of RO influent water and operational parameters can be found in Table 1, showing the variability in terms of water quality measured weekly. The values are presented as the result range of the whole experiment.

The dissolved organic carbon (DOC) was also measured. The combined expression of UV254/DOC as SUVA is a good representation of humic content. Humic substances exhibits relatively high SUVA values and contain relatively large amounts of aromatic carbons. However, microbial by-products, such as acids, polysaccharides, aminosugars

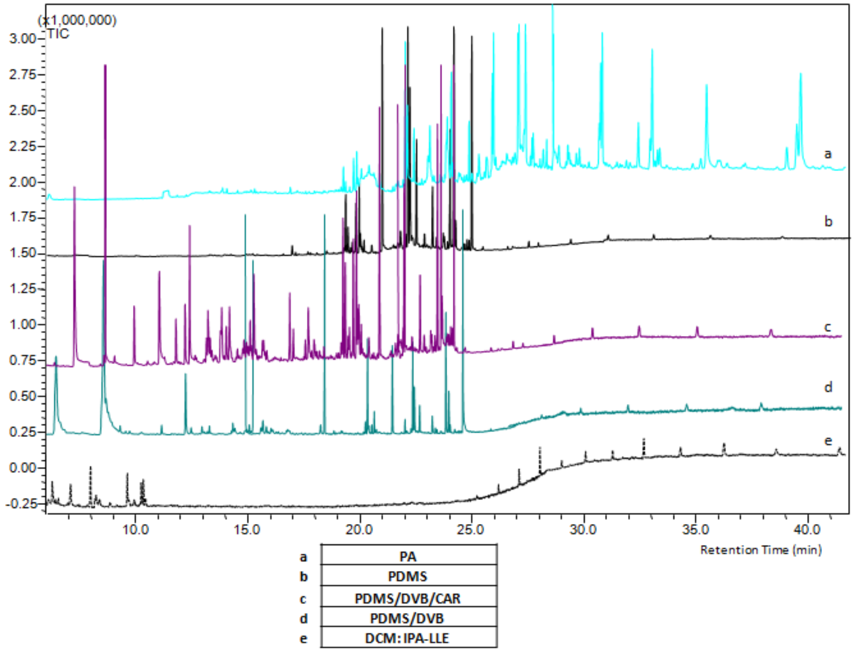

Figure 2. GC-MS chromatograms for the four different SPME fibres and the LLE of the RO influent water.

and proteins, generally have relatively low SUVA values *(Park et al. 2006).* In this study, SUVA on the RO influent water had values less than 4 L·(mg·m)$^{-1}$, therefore, it is expected that the main DOC content is formed by microbial by-products (acids, aminosugars, polysaccharides and sugars).

3.2 Characterisation of potential foulants

The presence of micropollutants and possible organic foulants on the RO influent water were determined by four different SPME polarity fibres and also compared with a conventional LLE, both followed by GC-MS analysis. The tested fibres were PDMS with low polarity, PDMS/DVB and PDMS/DVB/CAR with intermediate polarity and PA with high polarity. Chromatograms of the RO influent water tested with the SPME fibres are depicted in Figure 2.

PA fibre extracted more polar compounds which eluted after the first 20 minutes of the GC analysis such as some fatty acids including butyric acid 3-tetradecyl ester, 2-propenoic acid tridecyl ester and benzoic acid 2-ethoxyethyl ester. PDMS/DVB/CAR fibre extracted a higher number of organic compounds, such as 1,2-benzenedicarboxylic acid, bis(2-methylpropyl) ester (fatty acid),

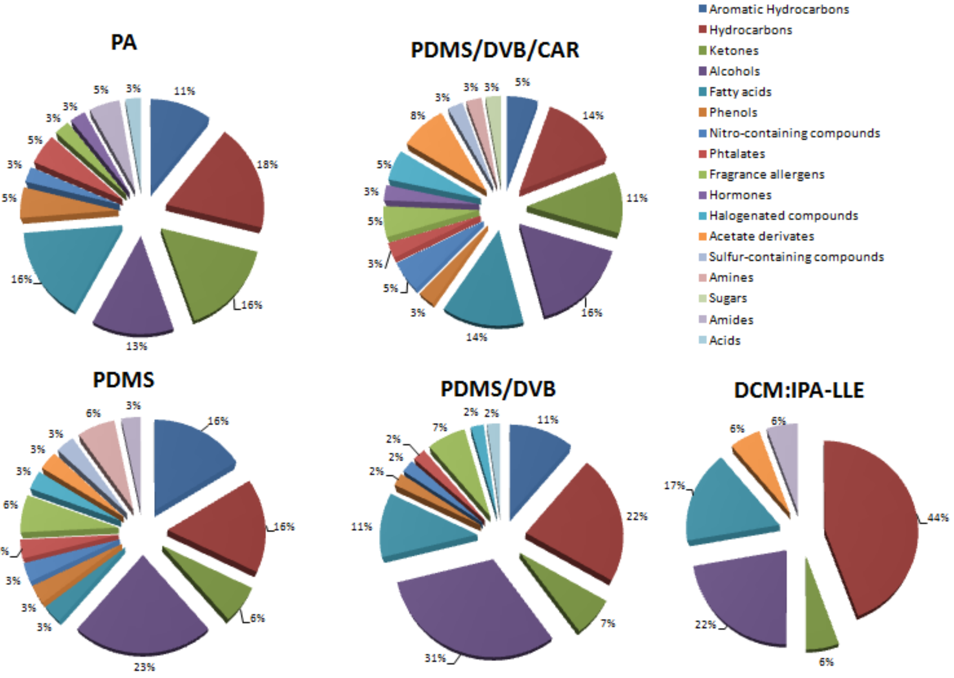

Figure 3. Families of organic compounds found by the different SPME fibres and the LLE.

diazoprogesterone (hormone) and d-glucitol, 4-o-decyl (sugar) compared to the PDMS/DVB fibre. This is due to the fact that the intermediate polarity of PDMS/DVB/CAR fibre can also extract the polar compounds. It can be concluded that PA and PDMS/DVB/CAR can together characterize from very polar compounds such as fatty acids to very apolar compounds such as hydrocarbons.

The organic foulants found by the different fibres were also classified into different families of compounds. All families of organic compounds found by the different fibres are shown in the Figure 3.

In the case of the PA fibre, it could be observed that it extracted more polar compounds such as fatty acids, acids and amides (16%, 3% and 5% of the total organic compounds extracted), than the other types of fibres. For example, only 3% of the extracted compounds by PDMS fibre were fatty acids, (because it is the less polar fibre). A detailed list of identified compounds of the two complementary fibres (PDMS/DVB/CAR and PA) is presented in the Table 2.

Major constituents of the RO influent water can be categorized into different families: aromatic hydrocarbons and linear hydrocarbons (identified by the library with match spectra higher o equal than 90%), ketones and alcohols (with match spectra higher than 85%), fatty acids, phenols and nitro-containing compounds (with match spectra higher than 90%), phthalates, fragrance allergens (d-limonene and tonalide), and hormones (diazoprogesterone) (with match spectra higher than 85%). In addition, there were several specific compounds, including butylated hydroxytoluene, 5,8-decadien-2-one, 5,9-dimethyl-, di-tert-butylphenol, benzonitrile 4-(4-butyl-1-cyclohexen-1-yl)-, dibutyl phthalate and tonalide, which were extracted by both fibres. Benzonitrile is peculiar nitrogen containing aromatic compound, *(Patterson et al. 1973)* and aromatic amino-acid *(Bandurski et al. 1976).* It could also be generated during the desorption of humic material *(Shulten et al. 1997).* Similarly, benzoic acid is a well known fragment of humic-like material and might have more than one origin *(Gillam et al. 1985; Wilson et al. 1983).*

On the other hand, phthalates are compounds present in numerous plastic materials, and also could produce the peak of benzoic acid *(Kusch et al. 2012).* A probable pathway of benzoic acid formation from phthalates could be the release of free phtalic acid, which is decarboxylated to benzoic acid. These findings partly support other previous studies, which took place in the same research unit treating waste water and analyzing the fouling layers of the RO membranes *(Khan et al. 2014).* There were some howover families of compounds extracted by PDMS/DVB/ CAR and not by PA and vice versa. For instance, PDMS/DVB/CAR extracted halogenated hydrocarbons (tetra-chloroethylene), acetate derivates (isopulegol acetate), sulfur-containing compounds (1-propene-1-thiol), amines and sugars (all of them with match spectra higher than 85%). On the other hand, PA fibre extracted amides (propanamide, 2-methyl-) and acids

Table 2. Organic compounds found by using the PDMS/DVB/CAR and PA SPME fibres.

SPME FIBRE	COMPOUNDS	FAMILY	MATCH
PDMS/ DVB/ CAR	p-Benzoquinone, 2,6-di-tert-butyl-; Butylated Hydroxytoluene*	Aromatic Hydrocarbons	>95%
	Decane; Eicosane, 3-methyl; 2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)-; 7-(1,3-Dimethylbuta-1,3-dienyl)-1,6,6-trimethyl-3,8-dioxatricyclo[5.1.0.0(2,4)]octane; 4-(2,2-Dimethyl-6-methylenecyclohexylidene)-3-methylbutan-2-one*	Hydrocarbons	>90%
	Ethanone, 1-(6,6-dimethylbicyclo[3.1.0]hex-2-en-2-yl)-; 5,8-Decadien-2-one, 5,9-dimethyl-*; 1-Hydroxy-6-(3-isopropenyl-cycloprop-1-enyl)-6-methyl-heptan-2-one; 3-Ethyl-4,4-dimethyl-2-(2-methylpropenyl)cyclohex-2-enone	Ketones	>86%
	1-Hexanol, 2-ethyl-; Ethanol, 2-[2-[2-[4-(1,1,3,3-tetramethylbutyl)phenoxy]ethoxy]ethoxy]; 1-Heptanol, 6-methyl-; 5,7-Octadien-3-ol, 2,4,4,7-tetramethyl-; 2,5-Pentadecadien-1-ol; 3-Cyclohexene-1-methanol, .alpha.,.alpha.4-trimethyl-	Alcohols	>89%
	Benzoic acid, 5-acetyl-2-methoxy-, methyl ester; 1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester; 1,4-Benzenedicarboxylic acid, bis(2-methylpropyl) ester; Propanoic acid, 2-methyl-, 2,2-dimethyl-1-(1-methylethyl)-1,3-propanediyl ester; Acetic acid, (1,2,3,4,5,6,7,8-octahydro-3,8,8-trimethylnaphth-2-yl)methyl ester	Fatty acids	>91%
	Di-tert-butylphenol*	Phenols	>95%
	Benzonitrile, 4-(4-butyl-1-cyclohexen-1-yl)-*; Pyrido[2,3-g]indole, 5-methoxy-2,3,7,9-tetramethyl-	Nitro-containing compounds	>90%
	Dibutyl phthalate *	Phtalates	>90%
	Tonalide*; D-Limonene	Fragrance allergens	>90%
	Diazoprogesterone	Hormones	>85%
	Tetrachloroethylene; 4-(2,4-Dichloro-7,8,9,10-tetrahydro-6H-5-oxa-cyclohepta[b]naphthalen-5a-yl)-morpholine	Halogenated compounds	>85%
	4-tert-Butylcyclohexyl acetate; Isopulegol acetate; Acetate, 2-cyclohexenyl-3-[1-(2-oxopropyl)ethenyl]-2,4,4-trimethyl	Acetate derivates	>90%
	1-Propene-1-thiol	Sulfur-containing compounds	>91%
	3,6-Bis(N-dimethylamino)-9-ethylcarbazole	Amines	>85%
	d-Glucitol, 4-O-decyl-	Sugars	>93%
	Butylated Hydroxytoluene*; 1,4-Benzenediol, 2-[(-octahydro-tetramethyl-1-naphthalenyl)methyl]-; Cyclopenta[g]-2-benzopyran, -hexahydro-hexamethyl-; 4-Acetylphenyl 5-acetyl-2-methoxyphenyl ether	Aromatic Hydrocarbons	>90%

Table 2. (Continued).

PA	trans-4,5-Epoxydecane; 4-(2,2-Dimethyl-6-methylenecyclohexylidene)-3-methylbutan-2-one*; Tetrahydrofurfuryl acrylate; Oxirane, 2,2'-[1,4-butanediylbis(oxymethylene)]bis-; 4-Hydroxybutyl acrylate; Butanal, 4-[(tetrahydro-2H-pyran-2-yl)oxy]-; 1,3,5-Trioxane, 2,4,6-tripropyl-	Hydrocarbons	>90%
	5,8-Decadien-2-one, 5,9-dimethyl-*; 4'-Ethoxy-2'-hydroxyoctadecanophenone; 1,3-Dioxolan-4-one, 2-(1,1-dimethylethyl)-5-(1-methylethyl)-; 2,5-Dimethyl-4-hydroxy-3-hexanone; 3-Methyl-hexahydro-pyrano[3,2-b]pyran-2-one; Hexamethylbenzophenone	Ketones	>85%
	1-Butanol, 4-butoxy-; Undecanol-4; Tetraethylene glycol diethyl ether; 3-Nonanol, 3-methyl-; (7a-Isopropenyl-4,5-dimethyloctahydroinden-4-yl)methanol	Alcohols	>90%
	Butyric acid, 3-tetradecyl ester; 2-Propenoic acid, tridecyl ester; Benzoic acid 2-ethoxyethyl ester; 2-Methoxy-3-methyl-butyric acid, methyl ester; 1,3,5-Trioxane, 2,4,6-tripropyl-; Sulfurous acid, pentadecyl 2-pentyl ester	Fatty acids	>95%
	Di-tert-butylphenol*	Phenols	>95%
	Benzonitrile, 4-(4-butyl-1-cyclohexen-1-yl)-*	Nitro-containing compounds	>93%
	Dibutyl phthalate*; Phthalic acid, butyl undecyl ester	Phtalates	>87%
	Tonalide*	Fragrance allergens	>90%
	Pseduosarsasapogenin-5,20-dien	Hormones	>90%
	Propanamide, 2-methyl-; Hexanamide, N-tetrahydrofurfuryl-	Amides	>95%
	Butanoic acid, anhydride	Acids	>89%

*Underlined compounds are found by both fibres.

(butanoic acid) were as well extracted (with match spectra higher than 89%).

LLE with a mixture of DCM:IPA organic solvents was performed for the comparison with the SPME methodology. The GC chromatogram is presented in Figure 2. It could be appreciated that SPME fibres extracted more compounds than the conventional LLE. In addition, the signal areas of the compounds extracted by LLE were always lower than those extracted by the SPME fibres. In Figure 3 the number of families found by the LLE, being lower than with SPME, is also represented. The families of organic compounds found were hydrocarbons (being the 44% of the total organic compounds extracted), ketones, alcohols, fatty acids, phenols and amides.

Therefore, as a general conclusion, the influent water was better characterized by the PDMS/DVB/CAR and PA SPME fibres than the LLE followed by GC-MS.

4. CONCLUSIONS

In the present study, the analysis of the potential organic RO foulants present in the influent water has been performed by different HS-SPME polarity fibres followed by GC-MS analysis. PA and

PDMS/DVB/CAR were complementary fibres which together could mainly characterize the organic compounds in the influent water.

More families of compounds have been found with the powerful technique HS-SPME than LLE. In addition, SPME has the advantage of the no organic solvent needed while decreasing the steps for sample preparation.

However, more experiments are needed, such as flat sheet studies, in order to understand and confirm if these families of compounds could be possible strong organic foulants of RO membranes. In addition, it would be interesting to know their nature and the concentration limit in which they start to act as a foulants.

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REFERENCES

Alzahrani S., Mohammad A.W., Hilal N., Abdullah P. and Jaafar O., (2013) Identification of foulants, fouling mechanisms and cleaning efficiency for NF and RO treatment of produced water. Separation and Purification Technology, 118, 324-341.

Ayache C., Pidou M., Croue J. P., Labanowski J., Poussade Y., Tazi-Pain A., Keller, J. and Gernjak, W. (2013) Impact of effluent organic matter on low-pressure membrane fouling in tertiary treatment. Water Research, 47 (8), 2633-2642.

Bandurski E.L., Nagy B., (1976) The polymer-like organic material in the Orgueil meteorite. Acta, 40, 1397-1406.

Bellona C., Drewes J.E., Xu P., Amy G., (2004). Factors affecting the rejection of organic solutes during NF/RO treatment-a literature review. Water Research, 38, 2795-2809.

Bonnelye V., Guey L., Del Castillo J., (2008). UF/MF as RO pre-treatment: the real benefit. Desalination, 222, 59–65.

Buchberger W.W., (2011) Current approaches to trace analysis of pharmaceuticals and personal care products in the environment. Journal of Chromatography A, 1218, 603-618.

Chen Y., Guo Z., Wang X. and Qiu C., (2008) Sample preparation. Journal of Chromatography A, 1184, 191-219.

Chon K., Sarp S., Lee S., Lee J.H., Lopez-Ramirez J.A., Cho J., (2011). Evaluation of a membrane bioreactor and nanofiltration for municipal wastewater reclamation: Trace contaminant control and fouling mitigation. Desalination, 272, 128–134.

Chon K., Lee S., Chon K., Hussain A.A., Cho J., (2010). Developing organic fouling indices of microfiltration and nanofiltration membranes for wastewater reclamation. Desalination and Water Treatment, 18, 61–70.

Chon K., Cho J., Shon H.K. and Chon K., (2012) Advanced characterization of organic foulants of ultrafiltration and reverse osmosis from water reclamation. Desalination, 301, 59-66.

Cortés-Francisco N. and Caixach J., (2013) Molecular Characterization of Dissolved Organic Matter through a Desalination Process by High Resolution Mass Spectrometry. Environmental Science and Technology, 47, 9619-9627

Fang J., Yang X., Ma J., Shang C., Zhao Q., (2010). Characterization of algal organic matter and formation of DBPs from chlor(am)ination. Water Research, 44, 5897-5906.

Gillam A.H., Wilson M.A., (1985) Pyrolysis GC-MS and NMR studies of dissolved seawater humic substances and isolates of a marine diatom. Organic Geochemistry, 8, 15-25.

Gostelow P., Parsons S.A. and Stuetz R.M., (2001) Odour measurements for sewage treatment works. Water Research, 35, 579-597.

Her N., Amy G., Chung J., Yoon J. and Yoon Y., (2008) Characterizing dissolved organic matter and evaluating associated nanofiltration membrane fouling. Chemosphere, 70, 495-502.

Jarusutthirak C., Amy G., Croué J.P., (2002). Fouling characteristics of wastewater effluent organic matter (EfOM) isolates on NF and UF membranes. Desalination, 145, 247–255.

Khan M.T., Bush M., Garcia Molina V., Emwas A.H., Aubry C., Croue J.P., (2014) How different is the composition of the fouling layer of wastewater reuse and seawater desalination RO membranes?. Water Research, 59, 271-282.

Kusch P., (2012). Pyrolysis-gas chromatography/mass spectrometry of polymeric materials. In: Mohd, M.A. (Ed.), Advanced Gas Chromatography e Progress in Agricultural, Biomedical and Industrial Applications. InTech, Rijeka, Croatia, pp. 333-362. Available from: http://cdn.intechopen.com/pdfs/32828/InTech-Pyrolysis_gas_chromatography_mass_spectrometry_of_polymeric_materials.pdf.

Krasner S.W., Weinberg H.S., Richardson S.D., Pastor S.J., Chinn R., Sclimenti M.J., Onstad G.D., Thurston A.D., (2006). Occurrence of a new generation of disinfection byproducts. Environmental Science and Technology, 40, 7175-7185.

Lee S., Elimelech M., (2006). Relating organic fouling of reverse osmosis membranes to intermolecular adhesion forces. Environmental Science and Technology, 40, 980–987.

Martínez C., Ramírez N., Gómez V., Pocurull E. and Borrull F., (2013) Simultaneous determination of 76 micropollutants in water samples by headspace solid phase microextraction and gas chromatography-mass spectrometry. Talanta, 116, 937-945.

Miltner R.J., Speth T.F., Richardson S.D., Krasner S.W., Weinberg H.S., Simmons J.E., (2008). Integrated Disinfection By-Products Mixtures Research: Comprehensive Characterization of Water Concentrates Prepared from Chlorinated and Ozonated/Postchlorinated Drinking Water. Journal of Toxicology and Environmental Health A. 71, 1133-1148.

Nerin C., (2007) Focus on sample handling. Analytical and Bioanalytical Chemistry, 388, 1001-1002.

Park N., Kwon B., Kim S. and Cho J., (2006) Characterizations of the colloidal and microbial organic matters with respect to membrane foulants. Journal of Membrane Science, 275, 29-36.

Patterson J.M., Shiue C.Y., Smith W.T., (1973) Benzonitrile formation in the pyrolysis of aromatic nitrogen compounds. Journal of Organic Chemistry, 38, 2447-2450.

Pearce G.K., (2007). Effect of coagulation on MF/UF for removal of particles as a pretreatment in seawater desalination. Desalination, 203, 286–295.

Pressman J.C., Richardson S.D., Speth T.F., Miltner R.J., Narotsky M.G., Hunter, G.E, Rice., Teuschler L.K., McDonald T.A., (2010). Concentration, chlorination, and chemical analysis of drinking water for disinfection byproduct mixtures health effects research: US EPA's four lab study. Environmental Science and Technology, 44, 7184-7192.

Schulten H.R., Schnitzer M., (1997) The chemistry of soil organic nitrogen: a review. Biology and Fertility of Soils, 26, 1-15.

Shon H.K., Vigneswaran S., Kim I.S., Cho J., Ngo H.H., (2004). The effect of pretreatment to ultrafiltration of biologically treated sewage effluent: a detailed effluent organic matter (EfOM) characterization. Water Research, 38, 1933–1939.

Słomczyńska B. and Słomczyński T., (2004) Physico-Chemical and Toxicological Characteristics of Leachates from MSW Landfills. Polish Journal Environmental Studies 13, 627-637.

Standard Methods for the Examination of Water and Wastewater, Published by the American Public Health Association, Water Environment Federation, and the American Water Works Association 21st Edition 2005.

Wilson M.A., Philp R.P., Gillam A.H., Gilbert T.D., Tate K.R., (1983) Comparison of the structures of humic substances from aquatic and terrestrial sources by pyrolysis gas chromatography-mass spectrometry. Cosmochimica Acta, 47, 497-502.

www.dowwaterandprocess.com, (Accessed 21th June 2014).

Zapf A., Heyer R. and Stan H.J., (1995) Rapid micro liquid-liquid extraction method for trace analysis of organic contaminants in drinking water. Journal of Chromatography A, 694, 453-461.

Desalin. Water Treat. (submitted)

Desalin. Water Treat. (submitted)

3.3.2. Characterization of organic fouling in reverse osmosis membranes by headspace-solid phase microextraction and gas chromatography-mass spectrometry

CHARACTERIZATION OF ORGANIC FOULING IN REVERSE OSMOSIS MEMBRANES BY HEADSPACE SOLID PHASE MICROEXTRACTION AND GAS CHROMATOGRAPHY-MASS SPECTROMETRY

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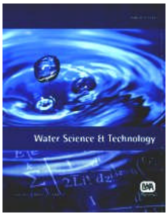

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Abstract

Adsorption of organic substances on reverse osmosis (RO) membrane surfaces may form an organic film on the membrane known as organic fouling and causing flow-rate loss. This problem is mostly unavoidable as no pre-treatment method exists for perfect removal of possible foulants, including organic compounds resulting from undesirable bioactivity. Understanding the characteristics of fouling layers is an essential step towards overall improvement of RO membrane operations.

In this study, the characterization of organic fouling in reverse osmosis membranes treating the effluent of a secondary treatment from an urban waste water treatment plant was performed. Headspace solid phase microextraction (HS-SPME) coupled with gas chromatography-mass spectrometry has been used for the first time, to provide valuable information of organic fouling. Different polarity SPME fibres were tested for this purpose.

In addition, the characterization of the organic fouling obtained by HS-SPME was compared with the results obtained by extraction using several organic solvents. The results indicated that more number of compound families can be identified by HS-SPME than by organic solvent extraction. Moreover, complementary organic analyses were done for better understanding of the organic fouling in RO membranes, such as total organic carbon and loss on ignition.

Keywords: *Gas chromatography-mass spectrometry; organic fouling characterization; reverse osmosis membranes; extraction; headspace solid phase microextraction; water treatment.*

Water Sci. Technol. (accepted)

1. INTRODUCTION

Reverse osmosis (RO) membranes have been applied as an advanced water treatment process for the removal of natural organic matter (NOM) and micropollutants throughout the world (www.dowwaterandprocess.com). Low pressure membrane filtration systems, such as ultrafiltration (UF) have also been widely applied in water treatment as a RO pre-treatment or as a filtration step. RO pre-treatment should be considered when total organic carbon (TOC) exceeds 3 mg·L^{-1} (Pearce 2007). Membrane technologies, including RO and UF, have a wide range of applications, ranging from brackish water and sea water desalination, pure and ultrapure water production, drinking and industrial water production and wastewater treatment (Amy *et al.* 2005).

Despite considerable research efforts undertaken by the scientific community, membrane fouling is still a major technical hurdle that needs to be addressed to enhance the cost effectiveness of operating RO systems for waste water reclamation. Therefore, organics in waste water applications, even at very low concentrations, must be evaluated since they could be precursors of organic fouling (Baudequin *et al.* 2014; Gautam & Menkhaus 2014). Influent water with high organic matter content is the cause of organic fouling deposits. In addition, organic foulants are also the precursors of biological growth which leads to biofouling (Swietlik *et al.* 2004). Biofouling can be considered as a biotic form of organic fouling and has been known as a contributing factor to more than 45 % of all membrane fouling problems in RO (Jin et al. 2009).

Fouling is an inherent phenomenon that reduces membrane performance, resulting in higher energy consumption, and lower removal efficiency. In particular, organic matter plays a crucial role in formation of RO fouling, limiting the widespread use of membranes (Jarusutthirak *et al.* 2002; Xu *et al*. 2006; Jeong *et al.* 2013), increasing adsorption of micropollutants is an advantage of the fouling formation, producing narrower membrane pores and decreasing mass transport through the membrane (Agenson *et al.* 2007). Moreover, the consequences of fouling include a decrease in water production, increased differential pressure (and energy consumption), higher cleaning frequency and a possible decrease in the effluent quality (Peña *et al*. 2013).

One way to find strategies to minimize the fouling is to characterize the foulants found on the membrane surface, because as a result, it would be possible to understand how fouling could be reduced or avoided. To determine the nature of membrane fouling, several analytical techniques have been applied. Most of the major methods typically used, include visual observation, loss on ignition (LOI), heterotrophic plate count (Speth *et al.* 1998), phospholipids, polysaccharides, total organic carbon (TOC), pyrolisis-gas chromatography-mass spectrometry (GC-MS) for some hydrophobic organics characterization (Luo & Wang 2001; Khan *et al.* 2013), scanning electron microscopy (SEM), energy dispersive X-ray (EDX), fourier transform infrared spectroscopy (FTIR) and GC-MS (Fernandez-Alvarez *et al.* 2010; Xu *et al.* 2010; Ding *et al.* 2013). Those methodologies are focused on characterising, as a general trend, the organic fouling identifying specific surface functional groups in RO membrane fouling. In addition, few studies have focused on describing the types of polymers and microorganisms that are associated with membrane biofouling, analyzing also organic and biological compounds (Nuengjamnong *et al.* 2005; Velten *et al.* 2007; Vrouwenvelder *et al.* 2008; Zhao *et al.* 2010; Jeong *et al.* 2013). However, it still remains a basic lack of understanding about which specific foulants, such as microorganism cells and their fragments, NOM, extracellular polymeric substances (EPS), and byproducts of microbial metabolism, govern membrane organic fouling. Despite extensive studies on the relationship between membrane surface properties and membrane fouling, the roles of specific surface functional groups in RO membrane fouling under different solution conditions still needs further understanding (Puro *et al*. 2002).

The aim of the present study was to provide valuable information as well as to gain knowledge characterizing specific organic compounds present in the fouling layer and classifying them into different families. The application of different polarity solid phase microextraction (SPME) fibres directly into the fouling has been studied for the first time.

Several extraction techniques can be used for the extraction of organic micropollutants from the organic fouling, whereas SPME has been studied as the first time, taking into advantage that it can selectively extract compounds and no solvents are required (Nerin 2007; Yi *et al.* 2008; Buchberger 2011). SPME allows complete elimination of organic solvents in the pretreatment step and decreasing the steps for sample preparation and has become an accepted method for the determination of volatile and semi-volatile organic compounds. Therefore, in this study headspace (HS) SPME has been used for the characterization of the organic compounds families in the membrane fouling, due to its advantages. The advantage of HS techniques when volatile compounds are analyzed is that the extraction is more selective and the matrix influence becomes lower (Lambropoulou 2007). To the best knowledge, no studies have evaluated the SPME preconcentration technique for organic compounds extraction from RO membrane fouling.

For better characterization of the organic fouling, different organic solvent extractions of the RO membrane have been performed and analyzed by GC-MS in order to identify specific organic compound families and compared them with the SPME extraction. According to the literature (Wu *et al.* 2014) depending on the solvent, different compounds can be extracted, for example analyzing the organic foulants on membranes fouled by pulp and paper mill effluent using solid-liquid extraction. Additionally, complementary organic analyses were done to the RO membranes for better understanding the organic fouling, including TOC and LOI.

2. MATERIALS AND METHODS

2.1 Materials and solvents

Methanol (MeOH), isopropanol (IPA), hexane (HX), dichloromethane (DCM) and acetonitrile (ACN) solvents were GC grade with purity > 99.9 % from Prolabo (Barcelona, Catalonia, Spain). Helium gas 99,999 % was supplied from Praxair (Barcelona, Catalonia, Spain).

Four commercial extraction fibres including 100 μm polydimethylsiloxane (PDMS), 65 μm polydimethylsiloxane/ divinylbenzene (PDMS/DVB), 50/30 μm polydimethylsiloxane/divinylbenzene/c arboxen (PDMS/DVB/CAR) and 85 μm polyacrylate (PA) were purchased from Supelco (Madrid, Community of Madrid, Spain).

2.2 Waste water treatment plant set-up

The urban waste water conventional treatment plant located in the north-east of Spain, has a first stage consisting of a primary treatment and a secondary biological treatment designed to treat 15.000 $m^3 \cdot d^{-1}$ of water during winter time and 47.500 $m^3 \cdot d^{-1}$ during summer time. The study was carried out in a research unit which consisted of RO membranes with UF system used as a pretreatment. The research unit was operated using the secondary clarified water coming from the conventional waste water treatment plant (WWTP).

The tested RO membranes were Dow Filmtec^{TM} XLE - 4040. They are extra low energy reverse osmosis elements designed to deliver high quality water at low operating costs for urban and industrial water applications. The RO elements tested were operated for 2 months to investigate the organic and biofouling resistance, as well as the removal of organic compounds present in the water from the secondary effluent of the WWTP.

2.3. Membrane autopsy and general parameters

The RO membrane elements were autopsied to determine foulant accumulation onto the membrane surface. Then, they were packed in plastic bags and stored at 4 ºC until the autopsy, which was performed within 24 h after their removal from the installation. RO membrane elements were opened lengthwise to take a representative amount of membrane sample.

In order to analyse the loss on ignition (LOI), approximately 10 g of fouling were removed with small flexible rubber spatula from one side of single membrane leaf. After drying the samples at 110 ºC, they were then ignited at 550 ºC and weighed again to identify inorganic and organic portions of foulant materials. The loss on weight after ignition was taken as the organic portion of the foulant and the residual as the inorganic portion, following the standard method (www.astm.org/ Standards/D7348.htm).

For the analysis of the organic carbon on the membrane surface, a previous extraction is required. A section of 4 cm^2 over the length of the membrane element was cut and placed in a 40 mL sealed vial. The sample included the feed spacer and the membrane. Then, 20 mL of ultrapure water were added and the vial was placed in an ultrasonic cleaning bath from Fisher Scientific (Massachusetts, United States). The ultrasonic treatment (2 min) followed by mixing the vial manually few seconds, was repeated three times. Next, 20 mL of water were collected from the vial to measure the TOC (Shimadzu TOC-L equipment), measuring only the dissolved organic carbon part (Standard Methods for the Examination of Water and Wastewater).

2.4 Organic fouling characterization by GC-MS

For the organic fouling characterization, the potential of the SPME was evaluated and a comparison with liquid extraction using different organic solvents was performed.

Regarding the SPME procedure, the fouling was removed with small flexible rubber spatula from one side of a single membrane leaf. 0.5 g of fouling was analyzed extracting the organic compounds by HS-SPME, using four different polarity fibres, followed by GC-MS determination. The fouling was introduced into a 20 mL vial, which was closed and put in a water thermostatic bath at 50 ºC without agitation. The extraction time was 30 minutes and the SPME fibre was exposed to the headspace. After the extraction, the fibre was inserted into the injection port of the gas chromatograph for the thermal desorption and analysis. Fibre was desorbed at 270 ºC during the chromatographic analysis in the splitless mode.

Five different solvents were tested for the organic solvent membrane extraction: MeOH, IPA, HX, DCM and ACN (Internal procedure of Dow Chemical, DWPS TARR-070.00_Organic membrane extraction). The organic solvents used had different chemical properties which were closely associated the results from charac-terizing the extracted organic fouling. HX was classified as a non-polar solvent with a polarity (given as the dielectric constant) of 1.88. IPA and MeOH were classified as protic solvents with a dielectric constant of 18 and 33 respectively. ACN and DCM were classified as polar aprotic solvents with a dielectric constant of 37.5 and 9.1 respectively.

Four sections of 20×30 cm^2 over the length of the membrane element were cut. First, the membrane sections were dried in the incubator at 35 ºC overnight. Membrane samples were cut into small pieces for easy extraction. Then, the membrane pieces (approximately of 1 cm^2) were placed into 100 mL glass bottle. 50 mL of solvent was added to ensure all the membrane pieces covered. The bottle was introduced in the ultrasonic bath and the extraction was carried out applying temperature, 10 degrees less than the boiling point of each solvent during 1 h. After the extraction, the extract was filtered using a syringe filter of 0.45 μm. The filtrate was placed in a round bottom flask and evaporated to dryness in a rotary evaporator. Finally, it was re-dissolved in 1ml of the tested solvent and 1 μL was injected in the injection port of the GC. New membranes were also evaluated and therefore extracted and analyzed in order to eliminate the organic compounds which could be extracted from the membrane, being first immersed in distilled water overnight to remove excess compounds from manufacturing process.

Gas chromatographic analysis of both extracts were performed with a GCMS-QP2010 Ultra/ GCMS-QP2010 SE from Shimadzu (Kioto, Japan), equipped with a split/splitless injector and coupled to a mass spectrometer detector. Helium was employed as a carrier gas at constant column flow of 1.4 mL·min^{-1}. Analytes were separated with TRB-5MS column (60 m × 0.32 mm i.d., 1 μm film thickness) from Tecknokroma (Barcelona, Spain). The split/splitless injection port was equipped with a 0.75 mm ID liner from Supelco, and operated at 280 ºC, allowing direct injection or SPME fibre.

The oven temperature program was started at 80 ºC, held for 5 min; and then increased by 10 ºC·min^{-1} up to 300 ºC and held for 10 min. The total run was 42 min. The MS analyses were conducted in full-scan mode with a single quadrupole and monitored masses between 40 and 280 m/z. Ionization was carried out in the electron impact (EI) mode at 70 eV. The transfer line temperature was maintained at 300 ºC and the ion source temperature at 250 ºC.

The organic compounds were identified by the mass spectrum library, NIST08, considering only those compounds with match spectra higher than 95 %. Other compounds with match between 85 - 95 % were also tentatively identified.

3. RESULTS AND DISCUSSION

3.1. Loss on ignition and organic carbon determination

LOI was determined by drying and weighing isolated foulant material at 110 ºC. The samples were then ignited at 550 ºC and weighed again to identify inorganic and organic portions of foulant materials. The loss on weight after ignition was taken as the organic portion of the foulant and the residual as the inorganic portion of the foulant.

Fouling distribution was also calculated by the LOI test, which also differentiates between the inorganic and the organic fouling distribution. The membrane fouling distribution was 1.02 g·m^{-2} of membrane, being 3 % dry substance and 97 % water. Therefore, there were approximately 30 mg·m^{-2} of fouling in the membrane surface (3 % of 1.02 g·m^{-2}).

Moreover, the percent contribution of inorganic and organic fouling was estimated. The contribu-tions of organic and inorganic fouling were 91 % and 9 %, respecttively, being a total of 27 mg·m^{-2} of organic fouling in the membrane surface. The results indicated there was a considerable presence of organic fouling in the membrane surface.

Organic carbon concentration on the RO membrane surface was 47 mg·m^{-2}, quantified as the soluble organic carbon part in the water extract.

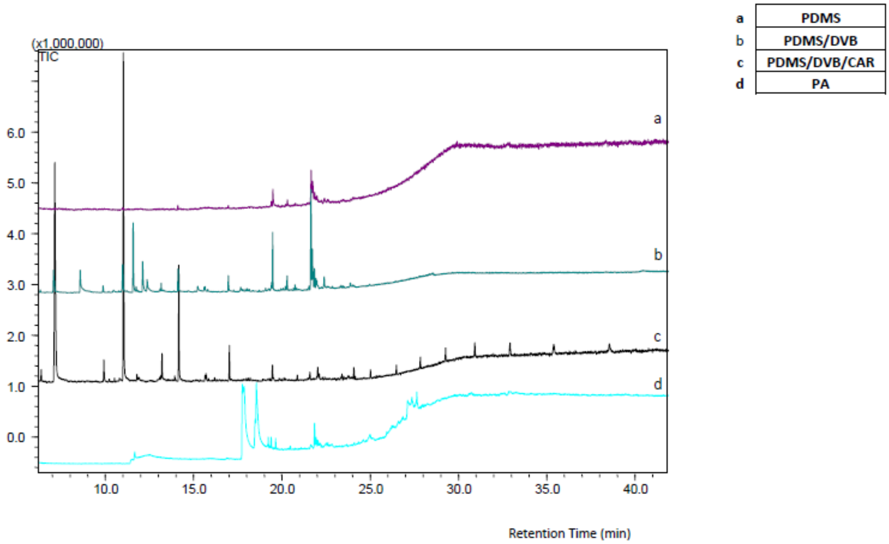

Figure 1. GC-MS chromatograms of the organic fouling extraction using four different SPME fibres.

Visual observations and analysis of the biomass parameters LOI and organic carbon supported the findings from the pressure drop and flow-rate loss operational measurements observed.

3.2. Organic fouling characterization

HS-SPME followed by GC-MS analysis was performed for characterizing the presence of organic species in the RO membrane fouling. The tested fibres were PDMS for low polarity, PDMS/DVB and PDMS/DVB/CAR for intermediate polarity and PA for high polarity. The aim of this analysis was to compare the organic fouling extraction performed by different SPME fibres, comparing the chromatograms, analyzing the compounds individually and classifying them into different families which would be prominent signals of biofouling and microbial activity occurring on all the membranes (Tariq Khan *et al.* 2013). As an example, acetamide could be a mass fragment of amminosugars, while other families such as proteins detected were composed of phenylalanine, tyrosine and tryptophan, with mass fragments of toluene, phenol, and indole.

Chromatograms of the membrane fouling extracted by the different SPME fibres are depicted in Figure 1.

It could be observed that PDMS/DVB/CAR extracted more compounds than the other fibres, including the PDMS and PDMS/DVB fibres due to its intermediate polarity which could extract polar and less polar compounds. In addition, the organic compounds detected after the first 25 minutes of the GC analysis were only extracted by the PDMS/DVB/CAR and PA fibres, having the first one best response areas. PA fibre was not able to extract those compounds eluted at the beginning of the chromatogram, which were extracted by the PDMS/DVB/CAR fibre, such as ketones (2-nonanone), sulphur-containing compounds (dimethyl trisulfide) and amides (4-ethylbenzamide). As mentioned before, all of these compounds families and mass fragments provided evidence of the presence of material originated from microbial cells.

The families of compounds extracted for each type of fibre are also presented in Figure 2. The families were represented as the percentage of the total compounds found by each fibre.

For example, in the PDMS/DVB/CAR extraction, 6 % of the organic compounds extracted were hydrocarbons (i.e. dodecane and tetramethyloctane), 6 % ketones (i.e. 2-nonanone), 13 % acids, 13 % sulphur-containing compounds (i.e. dimethyl trisulfide), 6 % alcohols (i.e. 1-hexanol, 2-ethyl), 6 % fragrance allergens (i.e. tonalid), 13 % aromatic hydrocarbons

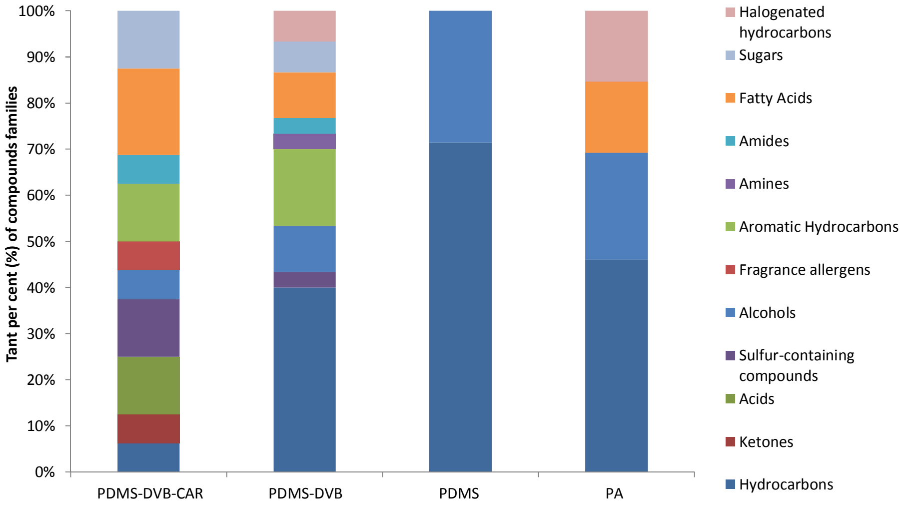

Figure 2. Families of compounds extracted by different SPME fibres from membrane fouling.

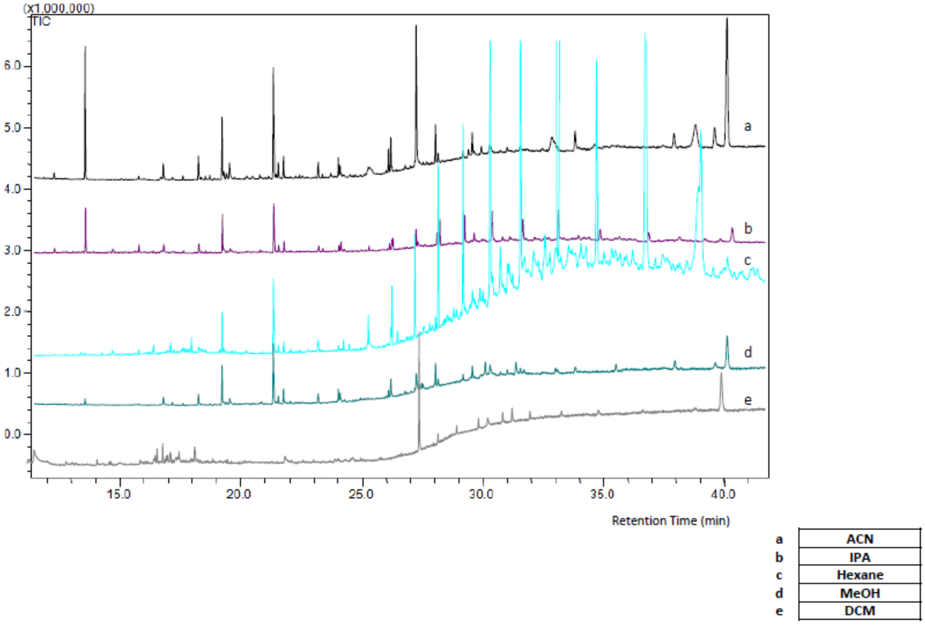

Figure 3. GC-MS chromatograms of the different solvent extractions of membrane fouling.

(i.e. benzene,1-methyl-2-(1-methylethyl)-), 6 % amides (i.e. 4-ethylbenzamide), 19 % fatty acids (i.e. ectadecanoic acid, ethenyl ester and benzoic acid, 5-acetyl-2-methoxy-, methyl ester) and 13 % sugars (i.e. D-arabino-hex-1-enitol, 1,5-anhydro-2-deoxy-). Hydrocarbons (71 %) and alcohols (29 %) are the families of compounds extracted with the PDMS fibre, while the PA fibre extracted hydrocarbons (46 %), alcohols (23 %), fatty acids (15 %) and halogenated hydrocarbons (15 %). PDMS/DVB fibre extracted more families of compounds than PDMS and PA. However, the PDMS/DVB/CAR fibre extracted more families than PDMS/DVB, being the best fibre tested in terms of compound families extracted.

RO processes can either directly or indirectly remove NOM from water, depending on their operational conditions and the specific characteristics of the NOM such as its molecular weight, carboxylic acidity and humic substances content (Collins *et al.* 1985; Owen *et al.* 1995). However, more recent studies have shown that low molecular weight NOM compounds, such as those found in the present study, are considered the most difficult to remove by conventional coagulation (Fabris *et al.* 2008; Sharp *et al.* 2006). In addition, some investigations have found that hydrophilic NOM (non-humic acids, including fatty acids), might be a significant membrane fouling compounds.

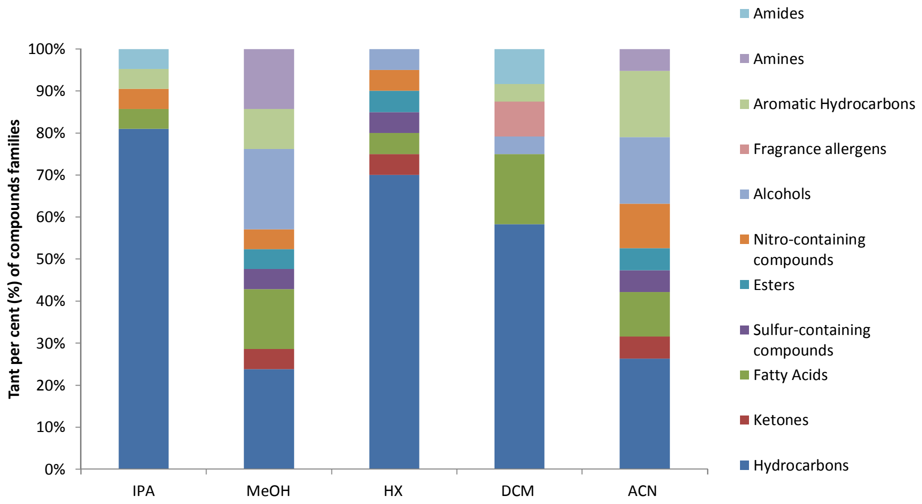

Figure 4. GC-MS chromatograms of the different solvent extractions of membrane fouling.

Regarding the organic solvent extraction, different polarity solvents were tested, including ACN, IPA, HX, MeOH and DCM, whose GC-MS chromatograms are shown in the Figure 3.

The most polar solvent was MeOH, followed by ACN, IPA and DCM, with intermediate polarity. And finally, HX was the less polar organic solvent. It could be observed that the best solvent for the extraction was the hexane, since it could extract the apolar compounds, such as some hydrocarbons (including eicosane, pentadecane and nonadecane), as well as some polar compounds which appeared at the beginning of the GC chromatogram, such as fatty acids (docosanoic acid, docosyl ester), alcohols (tetradecadien-1-ol) and ketones (benzophenone). In addition, it could also be observed that with hexane the extraction was more sensitive than with the other solvents obtaining high responses. In Figure 4 it is shown the different solvents tested and the families of compounds found for each solvent. Linear hydrocarbons (including eicosane, dodecane, 2-methyl-6-propyl-, nonadecane, tricosane, hexacosane, hepdatecane- tetramethyl- and octadecane, 2-methyl-) are the family of compounds most extracted, all of them with match spectra higher than 95 %. In the case of isopropanol, dichloromethane and hexane extractions, the hydrocarbons represented more than the 58 % of organic compounds extracted.

However, in the acetonitrile and methanol extractions more families of compounds were extracted such as aromatic hydrocarbons (benzene, 1,3-

trichloro and indole, 3-methyl-), alcohols (9-decen.2-ol, hexadecen-1-ol, trans-9- and tridecan-1-ol), acids (phtalamic acid), nitro-containing compounds (benzonitrile, 4-(4-butyl-1-cyclohexen-1-yl)-) and sulphur-containing compounds, all of them being identified with match spectra higher than 90 %.

Table 1. Common compounds found in the RO influent waste water and membrane fouling

COMPOUNDS	RET. TIME (min)	FAMILY
Benzoic acid, 5-acetyl-2-methoxy-, methyl ester	9.9	Fatty Acids
3,6-Bis(N-dimethylamino)-9-ethylcarbazole	11.0	Amines
1-Hexanol, 2-ethyl-	11.8	Alcohols
Octadecanoic acid, 1-[(tetradecyloxy)carbonyl] pentadecyl ester	13.1	Fatty Acids
4-(2,4-Dichloro-7,8,9,10-tetrahydro-6H-5-oxa-cyclohepta[b]naphthalen-5a-yl)-morpholine	13.2	Aromatic hydrocarbons
p-Benzoquinone, 2,6-di-tert-butyl-	17.6	Aromatic hydrocarbons
Propanoic acid, 2-methyl-, 2,2-dimethyl-1-(1-methylethyl)-1,3-propanediyl ester	20.9	Fatty Acids
1-Hydroxy-6-(3-isopropenyl-cycloprop-1-enyl)-6-methyl-heptan-2-one	22.0	Aromatic hydrocarbons
7-(1,3-Dimethylbuta-1,3-dienyl)-1,6,6-trimethyl-3,8-dioxatricyclo[5.1.0.0(2,4)]octane	22.2	Hydrocar bons
Tonalide	24.1	Fragance Allergens

When comparing both extraction methodologies, SPME and organic solvent extraction, it has been demonstrated that similar families of compounds were found. As mentioned before, membrane studies have highlighted that NOM rejection is controlled by size exclusion, physicochemical influent water conditions as well as interactions between the organic foulant and the membrane properties. This is particularly important as the hydrophobic membranes have been deemed to be more susceptible to fouling adsorption than hydrophilic membranes (Hong *et al.* 1997; Fan *et al.* 2001; Khayet *et al.* 2004). It has actually been demonstrated that humic compounds adsorbed more favorably onto hydrophobic membranes (Jucker *et al.* 1994). The RO membrane studied in this paper has more hydrophilic behavior than other membranes in the literature. Therefore, the families of compounds found in the membrane fouling were less humic character.

Furthermore, SPME is a fast method which requires a total of 30 minutes for the extraction and allows complete elimination of organic solvents in the pretreatment step decreasing the steps for sample preparation, while the organic solvent extraction needs more time and consumes more solvents. In addition, higher number of compound families has been found with the new tested SPME technique than the organic solvent extraction, providing valuable information of organic fouling.

Currently, SPME technique has been used for the determination of the organic compounds from the RO influent water. Therefore, the organic compounds commonly found in the influent water as well as in the membrane fouling are presented in Table 1. All of them were identified by the mass spectrum library with a match higher than the 95%.

The results indicated that there were several common families of compounds found in the influent water and on the membrane surface fouling being: fatty acids (i.e. benzoic acid, 5-acetyl-2-methoxy-, methyl ester), amines (i.e. 3,6-Bis(N-dimethylamino-9-ethylcarbazole), alcohols (i.e. 1-hexanol, 2-ethyl), aromatic hydrocarbons and fragrance allergens. Those families of organic compounds found are characteristic carboxylic acids (e.g., the derivate compounds of the octadecanoic acid and 1-[(tetradecyloxy) carbonyl] pentadecyl ester), amino acids, proteins and carbohydrates, and they could promote bacterial growth in the aquatic environment and biofilm growth causing operational problems in the RO system (i.e., clogging of the influent channel at very low concentrations) due to the biofouling layer formation (Nguyen *et al.* 2012). The fragrance allergens (such as tonalide) are organic compounds coming from anthropogenic sources (Einsle *et al.* 2006). All these organic fouling compounds could also lead to RO membrane flow-rate loss being adsorbed and taking part of the fouling.

The adsorbed organic foulants could change the membrane surface characteristics which could result in severe flux decline and affect the rejection.

4. CONCLUSIONS

In the present study, SPME technique has been tested for the first time, to provide valuable information regarding the organic fouling. It has been demonstrated that similar families of compounds were found also by organic solvent extraction. In addition, SPME has the advantage of being a solvent free technique, robust and fast. A detailed analysis of the organic membrane fouling has been done by analyzing the specific organic compounds by GC-MS, as well as the loss on ignition and the organic carbon on the membrane surface.

PDMS/DVB/CAR was the best fibre selected, which provided more information regarding the organic compounds extracted. In the case of the organic solvents, hexane gave more information regarding the organic fouling than the other solvents.

Furthermore, some compounds were commonly found in the fouling and on membrane surface, as well as in the influent water. They probably could lead to RO membrane organic fouling and consequently membrane flux rate loss.

Abbreviations: ACN, acetonitrile; DCM, dichloromethane; EI, electron impact; FTIR, fourier transform infra-red spectroscopy; GC-MS, gas chromatography-mass spectrometry; HS-SPME, headspace solid phase microextraction; HX, hexane; IPA, isopropanol; LOI, loss on ignition, MeOH, methanol; NOM, natural organic matter; PA, polyacrilate; PDMS, polydimethylsiloxane; PDMS/DVB, polydimethylsiloxane/divinylbenzene; PDMS/DVB/CAR polydimethylsiloxane/divinilbenzene/carboxene; RO, reverse osmosis; TOC, total organic carbon; UF, ultrafiltration; WWTP, waste water treatment plant.

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5. REFERENCES

Agenson K. O. and Urase T., 2007 Change in membrane performance due to organic fouling in nanofiltration (NF)/reverse osmosis (RO) applications, *Separation and Purification Technology*, **55**, 147-156.

Amy G., Kim T.U., Yoon J., Bellona C., Drewes J.E., Pellegrino J. and Heberer, T., 2005 Removal of micropollutants by NF/RO membranes, *Water Science and Technology*, **5** (5), 25-33.

Baudequin C., Mai Z. and Rakib M., 2014 Removal of fluorinated surface-tants by reverse osmosis- Role of Surfactants in membrane fouling, *Journal of Membrane Science*, **458**, 111-119.

Buchberger W.W., 2011 Current approaches to trace analysis of farmaceuticals and personal care products in the environment, *Journal of Chromatography A,* **1218**, 603-618.

Collins M.R., Amy G.L., Steelink, C., 1985 Molecular weight distribution, carboxylic acidity, and humic substances content of aquatic organic matter: implications for removal during water treatment, Environmental Science and Technology, 20, 1028–1032.

Ding Y., Tian Y., Li ZP., Wang HY. and Chen L., 2013 Interaction energy evaluation of the role of solution chemistry and organic foulant composition on polysaccharide fouling of microfiltration membrane bioreactors, *Chemical Engineering Science,* **104**, 1028-1035.

Einsle T., Paschke H., Bruns K., Schrader S., Popp P., Moeder M., 2006 Membrane-assisted liquid–liquid extraction coupled with gas chromatography–mass spectrometry for determination of selected polycyclic musk compounds and drugs in water samples, *Journal of Chromatography A,* **1124**, 196-204.

Fan L., Harris J.L., Roddick F.A., Booker N.A., 2001 Influence of the characteristics of natural organic matter on the fouling of microfiltration membranes, *Water Research*, **35**, 4455–4463.

Fabris R., Chow C.W.K., Drikas M., Eikebrokk B., 2008 Comparison of NOM character in selected Australian and Norwegian drinking waters, *Water Research*, **42**, 4188–4196.

Fernandez-Alvarez G., Garralon G., Plaza F., Garralon A., Perez J. and Gomez MA., 2010 Autopsy of SWRO membranes from desalination plant in Ceuta after 8 years in operation, *Desalination*, **263**, 264-270.

Gautam A., and Menkhaus T.J. 2014 Performance evaluation and fouling analysis for reverse osmosis and nanofiltration membranes during processing of lignocellulosic biomass hydrolysate, *Journal of Membrane Science*, **451**, 252-265.

Hong S., Elimelech M., 1997 Chemical and physical aspects of natural organic matter (NOM) fouling of nanofiltration membranes, *Journal of Membrane Science*, **132**, 159–181.

Internal procedure of DOW Chemical: DWPS TARR-070.00_Organic membrane extraction.

Jarusutthirak C., Amy G. and Croue J.P., 2002 Fouling characteristics of wastewater effluent organic matter (EfOM) isolates on NF and UF membranes, *Desalination*, **145**, 247–255.

Jeong S., Kim S. J., Kim C.M., Vigneswaran S., Nguyen T.V., Shon H.K., Kandasamy J. and Kim S., 2013 A detailed organic matter characterization of pretreated seawater using low pressure microfiltration hybrid systems, *Journal of Membrane Science*, **428**, 290–300.

Jeong S., Kim S.J., Kim L.H., Shin M.S., Vigneswaran S., Nguyen T.V. and Kim I.S., 2013 Foulant analysis of a reverse osmosis membrane used pretreated seawater, *Journal of Membrane Science,* **428**, 434-444.

Jin X., Huang X.F. and Hoek E.M.V., 2009 Role of specific ion interactions in sea water RO membrane fouling by alginic acid, *Environmental Science and Technology*, **43**, 3580-3587.

Jucker C., Clark M.M., 1994 Adsorption of aquatic humic substances on hydrophobic ultrafiltration membranes, *Journal of Membrane Science*, **97**, 37–52.

Khan MT, Manes C.L.D., Aubry C., Gutierrez, L. and Croue, JP., 2013 Kinetic Study of Seawater Reverse Osmosis Membrane Fouling, *Environmental Science and Technology,* **47**, 10884-10894.

Khayet M., Velázquez A., Mengual J.I., 2004 Direct contact membrane distillation of humic acid solutions, *Journal of Membrane Science*, **240**, 123–128.

Lambropoulou D. A., Konstantinou I.K., Albanis T.A., 2007 Recent developments in headspace microextraction techniques for the analysis of environmental contaminants in different matrices, *Journal of Chromatography A*, **1152**, 70-96.

Luo M. and Wang Z., 2001 Complex fouling and cleaning-in-place of a reverse osmosis desalination system, *Desalination*, **141**, 15-22.

Nerin C., 2007 Focus on sample handling, *Analalytical and Bioanalytical Chemistry*, **388**, 1001-1002.

Nguyen T., Roddick FA. and Fan L., 2012 Biofouling of water treatment membranes: A review of underlying causes, monitoring techniques and control measures, *Membranes,* **2**, 804-840.

Nuengjamnong C., Kweon J., Cho J., Polprasert C. and Ahn K., 2005 Membrane fouling caused by extra-polymeric substances during micro-filtration processes, *Desalination*, **179**, 117-124.

Owen D.M., Amy G., Chowdhury Z.K., Paode R., McCoy G., Viscosil K., 1995 NOM characterization and treatability, *Journal of Ambient Water Works Association*, **87** (1), 46–63.

Pearce G.K., 2007 The case for UF/MF pretreatment to RO in seawater applications, *Desalination*, **203**, 286–295.

Peña N., Gallego S., del Vigo F. and Chesters SP., 2013 Evaluating impact of fouling on reverse osmosis membranes performance, *Desalination,* **55**, 958-968.

Puro L., Tanninen J. and Nystrom M., 2002 Analyses of organic foulants in membranes fouled by pulp and paper mill effluent using solid-liquid extraction, *Desalination,* **143**, 1-9.

Sharp E.L., Jarvis P., Parsons S.A., Jefferson B., 2006 Impact of fractional character on the coagulation of NOM, *Colloids Surface A: Physicochemical Enginyer Aspects*, **286**, 104–111.

Speth TF., Summers RS. and Gusses AM., 1998 Nanofiltration foulants from a treated surface water, *Environmental Science and Technology,* **32**, 3612-3617.

Standard Methods for the Examination of Water and Wastewater, Published by the American Public Health Association, Water Environment Federation, and the American Water Works Association 21st Edition 2005.

Swietlik J., Dabrowska A., Raczyk-Stanislawiak U. and Nawrocki J., 2004 Reactivity of natural organic matter fractions with chlorine dioxide and ozone, *Water Research*, **38**, 547-558.

Tarik Khan M., Laro de O. Manes C., Aubry C., Gutierrez L. Croue J.P., 2013 Kinetic Study of Seawater Reverse Osmosis Membrane Fouling, *Environmental Science and Technology,* **47**, 10884-10894.

Velten S., Hammes F., Boller M., Egli T., 2007 Rapid and direct estimation of active biomass on granular activated carbon through adenosine tri-phosphate (ATP) determination, *Water Research*, **41**, 1973-1983.

Vrouwenvelder J.S., Manolarakis S.A., Van der Hoek J.P., Van Paassen J.A.M., Van der Meer W.G.J., Van Agtmaal J.M.C., Prummel H.D.M., Kruithof J.C. and Van Loosdrecht M.C.M., 2008 Quantitative biofouling diagnosis in full scale nanofiltration and reverse osmosis installations, *Water Research*, **42**, 4856-4868.

Wu J.J., Contretas A.E. and Li Q.L., 2014 Studying the impact of RO membrane surface functional groups on alginate fouling in seawater desalination, *Journal of Membrane Science*, **458**, 120-127.

www.astm.org/Standards/D7348.htm, (accessed 10th June 2014).

www.dowwaterandprocess.com, (accessed 10th June 2014).

Xu P., Bellona C. and Drewes J.E., 2010 Fouling of nanofiltration and reverse osmosis membranes during municipal wastewater reclamation: Membrane autopsy results from pilot-scale investigations, *Journal of Membrane Science,* **353**, 111-121.

Xu P., Drewes J. E., Kim T. U., Bellona C. and Amy G., 2006 Effect of membrane fouling on transport of organic contaminants in NF/RO membrane applications, *Journal of Membrane Science*, **279**, 165–175.

Yi C., Zhenpeng G., Xiaoyu W., Changgui Q., 2008 Sample preparation, *Journal of Chromatography A,* **1184**, 191-219.

Zhao Y., Song L.F. and Ong S.L., 2010 Fouling behavior and foulant characteristics of reverse osmosis membranes for treated secondary effluent reclamation, *Journal of Membrane Science*, **349**, 65-74.

Water Sci. Technol. (accepted)

3.1.3. Discussion of results

ORGANIC MICROPOLLUTANTS IN REVERSE OSMOSIS WATER TREATMENTS, PRESENCE AND REJECTION
Carolina Martínez de Peón

We have demonstrated in this section that the methods presented, based on SPME-GC-MS, are effective at determining organic foulants and organic fouling compounds in water and in RO membrane deposits. The use of different SPME polarity fibres has allowed us to analyze different families of compounds which have been classified afterwards.

However, we have to take into account that these are preliminary studies due it has been the first time that organic fouling has been analyzed by HS-SMPE and GC-MS. Therefore, the chromatographic separation should be improved for each influent water treatment process.

In the first study presented, it was determined the presence of the organic foulants in the influent water treating the secondary effluent of a conventional waste water treatment plant with RO membranes. The organic compounds were identified by the mass spectrum library, NIST08.LIB, considering only those compounds with match spectra higher o equal than 95%. Other compounds with match between 85-95% were also tentatively identified. Different families of compounds were found by the different fibres, being PA and PDMS/DVB/CAR complementary fibres which together could mainly characterize the organic compounds in the influent water. For instance, more polar compounds such as fatty acids, acids and amides (16%, 3% and 5% of the total organic compounds extracted) were found in the case of PA fibre than the other types of fibres, such as PDMS which only the 3% of the extracted compounds were fatty acids, because they are less polar fibres.

As a general terms, major constituents of the RO influent water can be classified into different families: aromatic hydrocarbons and linear hydrocarbons (identified by the library with match spectra higher o equal than 90%), ketones and alcohols (with match spectra higher than 85%), fatty acids, phenols and nitro-containing compounds (with match spectra higher than 90%), phthalates, fragrance allergens (d-limonene and tonalide), and hormones (diazoprogesterone) (with match spectra higher than 85%). In addition, there were several specific compounds, including butylated hydroxytoluene, 5,8-decadien-2-one, 5,9-dimethyl-, di-tert-butylphenol, benzonitrile 4-(4-butyl-1-cyclohexen-1-yl)-, dibutyl phthalate and tonalide, which were extracted by both fibres. Benzonitrile is characteristic nitrogen containing aromatic compound, such as nitrophtalic acid [1] and aromatic amino acid [2]. It could also be generated during the desorption of humic material [3]. Similarly, benzoic acid is a well known fragment of humic-like material, which might have more than one origin [4-5]. A probable pathway of benzoic acid formation from phthalates could be the release of the phtalic acid which is decarboxylated to benzoic acid.

On the other hand, phthalates are compounds present in numerous plastic materials, and also could produce the peak of benzoic acid [6]. A remarkable increase in abundance of benzonitrile and prominent signal of benzoic acid in the chromatogram of the influent water are signposts of the presence of either humic-like materials or phthalates, possible leached from plastics tubing and piping used in the plant.

In addition, there were some families of compounds extracted by using PDMS/DVB/CAR and not by PA fibre and vice versa. For instant, PDMS/DVB/CAR also extracted halogenated hydrocarbons (tetrachloroethylene), acetate derivates (isopulegol acetate), sulfur-containing compounds (1-propene-1-thiol), amines and sugars (all of them with match spectra higher than 85%), while in the case of PA fibre amides (propanamide, 2-methyl-) and acids (butanoic acid) were as well extracted (with match spectra higher than 89%).

Conventional LLE was performed in the water influent with a mixture of dichloromethane and isopropanol organic solvents, in order to compare it with the SPME extraction method. When comparing both chromatograms, it cound be observed that SPME fibres extracted higher number of compounds and higher response areas than the chromatograms obtained by the LLE extraction. The families of organic compounds found were hydrocarbons (being the 44% of the total organic compounds extracted), ketones, alcohols, fatty acids, phenols and amides. Therefore, as a general conclusion, the influent water was better characterized by the PDMS/DVB/CAR and PA SPME fibres than the LLE followed by GC-MS.

For the analysis of the organic fouling in the membrane surface, membrane fouling extraction was performed and SPME GC-MS was done. The fibres tested were mentioned before. The organic foulants found by the four fibres belong to different families of compounds. For the PDMS/DVB/CAR extraction, 6% of the organic compounds extracted were hydrocarbons (i.e. dodecane and tetramethyloctane), 6% ketones (i.e. 2-nonanone), 13% acids, 13% sulphur-containing compounds (i.e. dimethyl trisulfide), 6% alcohols (i.e. 1-hexanol, 2-ethyl), 6% fragrance allergens (i.e. tonalide), 13% aromatic hydrocarbons (i.e. benzene,1-methyl-2-(1-methylethyl)-), 6% amides (i.e. 4-ethylbenzamide), 19% fatty acids (i.e. ectadecanoic acid, ethenyl ester and benzoic acid, 5-acetyl-2-methoxy-, methyl ester) and 13% sugars (i.e. D-arabino-hex-1-enitol, 1,5-anhydro-2-deoxy-). There were some families of compounds not extracted by all the fibres, for instance, hydrocarbons (71%) and alcohols (29%) were extracted with the PDMS fibre, while the PA fibre extracted hydrocarbons (46%), alcohols (23%), fatty acids (15%) and halogenated hydrocarbons (15%). PDMS/DVB fibre extracted more families of compounds than PDMS and PA. However, the PDMS/DVB/CAR fibre extracted more families than PDMS/DVB, being the best fibre tested in terms of compound families extracted.

Water membrane extraction was also performed, cutting a section of 4 cm^2 over the length of the membrane element and placing it in a 40 mL sealed vial. The volume of water used was 20 mL. The sample included the influent spacer and the membrane leaf. HS-SPME GC-MS analysis was done into the sample for organic compounds identification and the families of compounds found were the same as those families found in the direct membrane fouling analysis. The results are shown on the Figure

12 and 13 below with the chromatograms and the families of compounds found in each extraction. The families of compounds found were hydrocarbons, ketones, acids, sulphur-containing compounds, esters, nitro-containing compounds, alcohols, fragrance allergens, aromatic hydrocarbons, amines, amides, fatty acids and sugars.

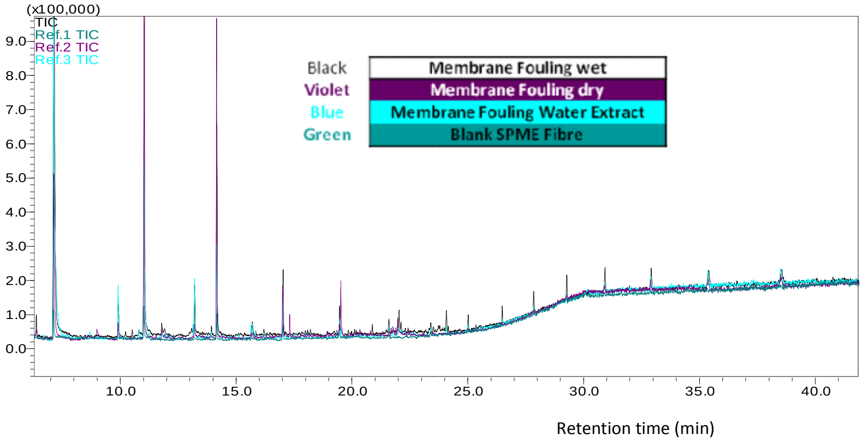


Figure 12. GC Chromatograms of the different extractions done with PDMS/DVB/CAR fibre.

Membrane organic solvent extraction was also done, testing different polarity solvents, including acetonitrile (ACN), isopropanol (IPA), hexane, methanol (MeOH) and dichloromethane (DCM). The most polar solvent was MeOH, followed by ACN, IPA and DCM, with intermediate polarity. Finally, hexane was the less polar organic solvent. The best solvent for the extraction was the hexane, due to it could extract the apolar compounds, such as some hydrocarbons (including eicosane, pentadecane and nonadecane), as well as the most volatile compounds which appeared at the beginning of the GC chromatogram, such as fatty acids (docosanoic acid, docosyl ester), alcohols (tetradecadien-1-ol) and ketones (benzophenone). In addition, it could also be observed that with hexane the extraction was more sensitive than with the other solvents obtaining high responses. Linear hydrocarbons (including eicosane, dodecane, 2-methyl-6-propyl-, nonadecane, tricosane, hexacosane, hepdatecane- tetramethyl- and octadecane, 2-methyl-) are the family of compounds most extracted all of them with match spectra higher than 95%. In the case of isopropanol, dichloromethane and hexane extractions, the hydrocarbons represented more than the 58% of organic compounds extracted. However, in the acetonitrile and methanol extractions more families of compounds were extracted such as aromatic hydrocarbons (benzene, 1,3-trichloro and indole, 3-methyl-), alcohols (9-decen-2-ol, hexadecen-1-ol, trans-9- and tridecan-1-ol), acids (phtalamic acid), nitro-containing compounds (benzonitrile, 4-(4-butyl-1-cyclohexen-1-yl)-) and sulphur-containing compounds, all of them being identified with match spectra higher than 90%.

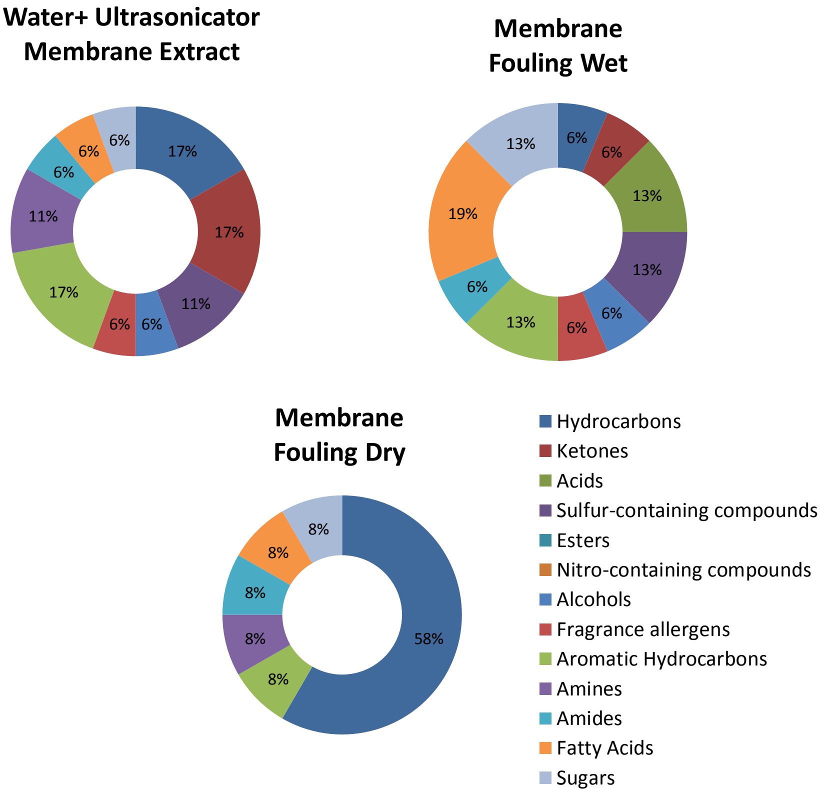


Figure 13. Families of compounds found in each extraction with PDMS/DVB/CAR fibre.

As mentioned before, the same families of organic compounds were extracted by the water membrane extraction as well as by the direct fouling extraction. However, for the study was selected the extraction of the fouling wet because the GC chromatogram showed high response areas of the majority of compounds detected.

When comparing extraction methodologies, SPME and organic solvent extraction, it has been demonstrated that similar families of compounds were found. Moreover, SPME requires a total of 30 minutes for the extraction and allows complete elimination of organic solvents in the pretreatment step decreasing the steps for sample preparation, while the organic solvent extraction needs more time and consumes more solvents. In addition, higher number of families has been found in the fouling with the new tested SPME method than the organic solvent extraction of the membrane, providing valuable information for organic fouling.

Currently, SPME technique has been used for the determination of the organic compounds from the RO influent water [7-8]. Therefore, common compounds have been found in the influent water and membrane surface fouling. All of them were identified by the mass spectrum library with a match higher than 95%. The results indicated that there were several common families of compounds found in the influent water and in the membrane surface fouling being: fatty acids (i.e. benzoic acid, 5-acetyl-2-methoxy-, methyl ester), amines (i.e. 3,6-Bis(N-dimethylamino-9-ethylcarbazole), alcohols (i.e. 1-hexanol, 2-ethyl), aromatic hydrocarbons and fragrance allergens. Those families of organic compounds found are characteristic carboxylic acids, amino acids, proteins and carbohydrates, and they could promote bacterial growth in the aquatic environment and biofilm growth causing operational problems in the RO system such as clogging of the influent channel at very low concentrations [9] due to the biofouling layer formation [10].

The adsorbed organic foulants might change the membrane surface characteristics which resulted in severe flux decline and affected the rejection pattern. Therefore, fouling led to increase adsorption of micropollutants, produced narrower membrane pores and decreased mass transport by the imposed hindrances of the fouling partitions causing higher diffusion of solutes across the membrane [11].

References

[1] J.M. Patterson, C.Y. Shiue, W.T. Smith, J. Org. Chem. 38 (1973) 2447.

[2] E.L. Bandurski, B. Nagy, Acta 40 (1976) 1397.

[3] H.R. Schulten, M. Schnitzer, Biol. Fertil. Soils 26 (1997) 1.

[4] A.H. Gillam, M.A. Wilson, Org. Geochem. 8 (1985) 15.

[5] M.A. Wilson, R.P. Philp, A.H. Gillam, T.D. Gilbert, K.R. Tate, Acta 47 (1983) 497.

[6] P. Kusch, 2012. Pyrolysis-gas chromatography/mass spectrometry of polymeric materials. In: Mohd, M.A. (Ed.), Advanced Gas Chromatography e Progress in Agricultural, Biomedical and Industrial Applications. InTech, Rijeka, Croatia, pp. 333-362. Available from: http://cdn.intechopen.com/pdfs/32828/InTech-Pyrolysis_gas_chromatography_mass_spectrometry_of_polymeric_materials.pdf.

[7] J.B. Quintana, I. Rodríguez, Anal Bioanal Chem 384 (2006) 1447.

[8] C. Martínez, N. Ramírez, V. Gómez, E. Pocurull, F. Borrull, Talanta 116 (2013) 937.

[9] T. Nguyen, F.A. Roddick, L. Fan, Membranes 2 (2012) 804.

[10] A.H. Gillam, M.A. Wilson, Org. Geochem. 8 (1985) 15.

[11] K.O. Agenson, T. Urase, Sep. Purif. Technol 55 (2) (2007) 147.

CHAPTER 4

CONCLUSIONS

The main conclusions drawn from the studies presented in this Doctoral Thesis can be summarised as follows:

1. HS-SPME coupled to GC-MS has been successfully applied to determine VOCs, EDCs, fragrance allergens, odours, pesticides and DBPs in natural waters such as brackish water, sea water and waste water.

2. Different SPME polarity fibres have been tested due to the different compound polarities. The best results were obtained by using intermediate polarity fibres such as PDMS/DVB and PDMS/DVB/CAR for volatile micropollutants and DBPs, respectively.

3. The methods developed allowed us to detect the studied contaminants at ng·L^{-1} levels in all samples analyzed.

4. Dow FILMTEC^{TM} reverse osmosis membranes applied as advanced urban waste water tertiary treatments, enhanced rejection efficiency of most of the trace organic contaminants studied.

5. Fragrance allergens and EDCs were the families of the micropollutants with high rejections, being higher than 83% due to their low polarity as well as their high molecular weight.

6. SPME technique has been tested for the first time, to provide valuable information regarding the organic fouling in membrane deposits as well as water organic foulants.

7. PA and PDMS/DVB/CAR fibres gave complementary information to characterize the potential organic foulants present in the influent water and the organic membrane fouling.

8. SPME demonstrated to be more powerful technique than LLE for the characterization of organic fouling and foulants, because it allowed detecting a higher number of compounds without organic solvent consumption.

9. The organic foulants identified with a match factor higher than 95% in the RO influent water belonged to different families, including aromatic hydrocarbons, phenols, fatty acids and amides.

10. Some compounds have been identified in both studied matrices, which belong to different families such as fatty acids, amines, alcohols, aromatic hydrocarbons and fragrance allergens.

APPENDIX

Appendix I. Abbreviations used in this Doctoral Thesis.

ACN	Acetonitrile
BOD_5	Biological oxygen demand
CIP	Cleaning in place
COD	Chemical Oxygen demand
CTQ	Chemistry Technology Centre
D/DBP	Disinfectants/disinfection by-products
DBP	Disinfection by-product
DCM	Dichloromethane
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
DW&PS	Dow water and process solutions
EDC	Endocrine disrupting compound
EDSP	Endocrine disruptor screening program
EDX	Energy dispersive X-ray
EEM	Excitation emission matrix fluorescence spectroscopy
EI	Electron impact
EPA	Environmental protection agency
EPS	Extracellular polymers
EQS	Environmental quality standards
ESCA	Electron spectroscopy for chemical analysis
EU	European Union
FOG	Fats, oils and greases
FTIR	Fourier transform infra-red spectroscopy
GAC	Granular activated carbon
GC-EDC	Gas chromatography electron capture detection
GC-FID	Chromatography flame ionization detection
GC-MS	Gas chromatography-mass spectrometry
GFD	Gallons per square foot per day
H_2SO_4	Sulphuric acid
HAN	Halogenated acetonitrile
HK	Halogenated ketone
HNM	Halogenated nitromethane
HS-SDME	Headspace single drop microextraction

HS-SPME	Headspace solid phase microextraction
HX	Hexane
ICP	Inductively coupled plasma emission spectroscopy
IFRA	International fragrance association
IPA	Isopropanol
ISO	International organization for standardization
I-THM	Iodinated-trihalomethane
LC-OCD	Liquid chromatography with organic carbon detection
LC	Liquid chromatography
LLE	Liquid liquid extraction
LOD	Limit of detection
LOI	Loss on ignition
LOQ	Limit of quantification
LPME	Liquid-phase microextraction
MBR	Membrane bioreactor
MCL	Maximum contaminant level
MeOH	Methanol
MF	Microfiltration
MS/MS	Tandem mass spectrometry
NaCl	Sodium chloride
NF	Nanofiltration
OM	Organic matter
PA	Polyacrylate
PAC	Powdered activated carbon
PCP	Personal care products
PDMS	Polydimethylsiloxane
PDMS/DVB	Polydimethylsiloxane/divinylbenzene
PDMS/DVB/CAR	Polydimethylsiloxane/divinylbenzene/carboxen
PEG	Polyethylenglicol
PFBHA	Pentafluoro-benzylhydroxylamine
PPCP	Pharmaceutical and personal care products
PTHF	Polytetrahydrofuran
PVA	Poly(vinylacohol)
REACH	Registration evaluation and authorization of chemicals
RO	Reverse osmosis

SBSE	Stir-bar sorptive extraction
SEM	Scanning electron microscopy
SPE	Solid phase extraction
SUVA	Specific ultraviolet absorption
TDS	Total dissolved solids
THM	Trihalomethane
TMP	Transmembrane pressure
TN	Total nitrogen
TOC	Total organic carbon
TSS	Total suspended solids
UF	Ultrafiltratiom
UV	Ultraviolete
VOC	Volatile organic compound
WHO	World health organization
WWTP	Waste water treatment plant

Appendix II. List of publications.

C. Martínez, N. Ramírez, V. Gómez, E. Pocurull, F. Borrull, *Simultaneous determination of 76 micropollutants in water samples by headspace solid phase microextraction and gas chromatography-mass spectrometry,* Talanta 116 (2013) 937–945.

C. Martínez, V. Gómez, F. Borrull, E. Pocurull, *Simultaneous determination of 20 disinfection by-products in water samples from advanced membrane treatments by headspace solid phase microextraction and gas chromatography-mass spectrometry,* Analytical and Bioanalytical Chemistry Research 1 (2014) 38-49.

C. Martínez, V. Gómez, D. Dubert, K. Majamaa, E. Pocurull, F. Borrull, *Study of reverse osmosis treatment for micropollutants rejection in water reuse applications,* Desalination and Water Treatment, Published online (2014) 1-10. DOI: 10.1080/19443994.2014.940208

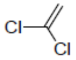
C. Martínez, V. Gómez, E. Pocurull, F. Borrull, *Characterization of organic fouling in reverse osmosis membranes by headspace-solid phase microextraction and gas chromatography-mass spectrometry,* Water Science & Technology (Accepted).

C. Martínez, V. Gómez, F. Borrull, E. Pocurull, *Headspace-Solid Phase Microextraction: useful technique to characterize organic foulants in water reuse applications,* Desalination and Water Treatment (Submitted).

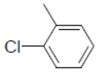
Appendix III. Compound Structures.

Volatile organic compounds (VOCs). The VOCs regulated by the Directive 2008/105/CE are marked in bold.

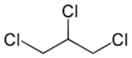
1,1-dichloroethene



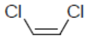
1-chloro-2-methylbenzene



1,2,3-trichloropropane



(Z)-1,2-dichloroethene



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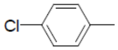
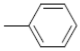
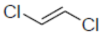


toluene



(E)- 1,2-dichloroethene



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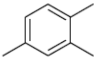

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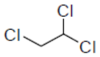

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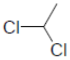

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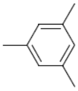
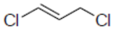


1,3-dichloropropane

(E)-1,3-dichloro-1-propene



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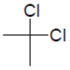
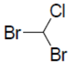


dibromochloromethane



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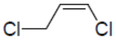
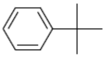


tert-butylbenzene



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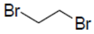
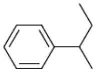
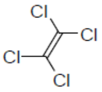


bromochloromethane

sec-butylbenzene



tetrachloroethene



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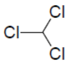

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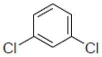

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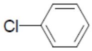

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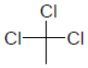
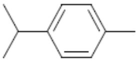
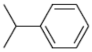


p-isopropilbenzene

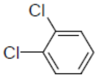


isopropilbenzene

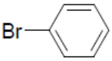


1,2-dichloroethane

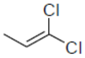
1,2-dichlorobenzene



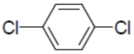
bromobenzene



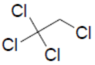
1,1-dichloro-1-propene



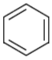
1,4-dichlorobenzene



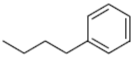
1,1,1,2-tetrachloroethane



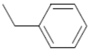
benzene



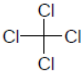
butylbenzene



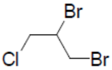
ethylbenzene



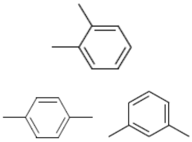
carbon tetrachloride



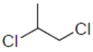
1,2-dibromo-3-chloropropane



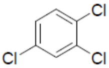
o/p/m-xylene



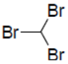
1,2-dichloropropane



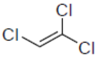
1,2,4-trichlorobenzene



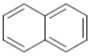
tribromomethane



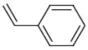
trichloroethene



naphthalene

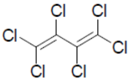


styrene

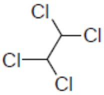


dibromomethane

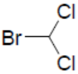
hexachlorobutadiene



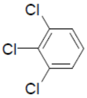
1,1,2,2-tetrachloroethane



bromodichloromethane



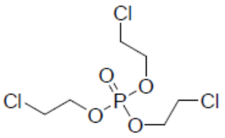
1,2,3-trichlorobenzene



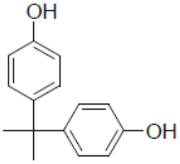
Endocrine disrupting compounds (EDCs)

Tris(2-chloroethyl) phosphate

(TCEP)

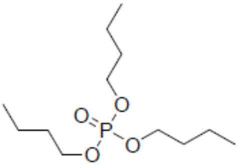


Bisphenol-A



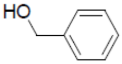
Tributhyl phosphate

(TBPA)

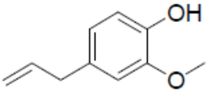


Fragrance allergens

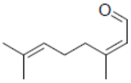
Benzyl alcohol



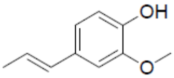
Eugenol



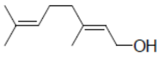
Citral



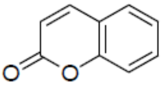
Isoeugenol



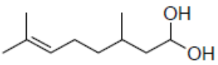
Geraniol



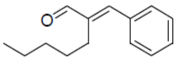
Coumarin



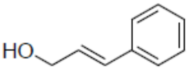
Hidroxicitronellal



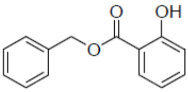
Amyl cinnamaldehyd



Cinnamyl alcohol

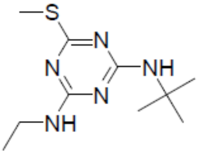


Benzyl salicylate

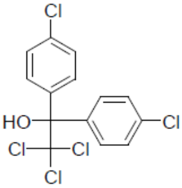


Pesticides. They have been proposed for regulation by the European Commission, on the 31th of June of 2012.

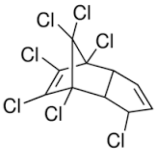
Terbutryn



Dicofol

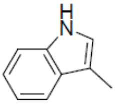


Heptachlor

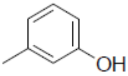


Odours

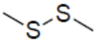
Skatole



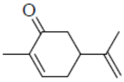
m-Cresol



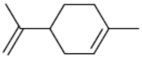
Dimethyl disulfide (DMDS)



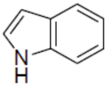
Carvone



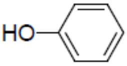
Limonene



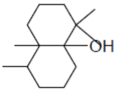
Indole



Phenol

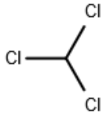


Geosmin

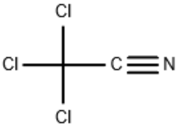


Disinfection by-products (DBPs)

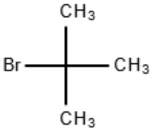
Chloroform



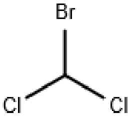
Trichloroacetonitrile



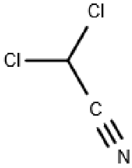
2-Bromo-2-methylpropane



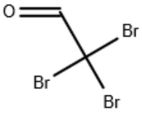
Bromodichloromethane



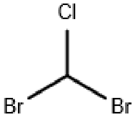
Dichloroacetonitrile



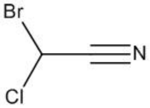
Tribromoacetaldehyde



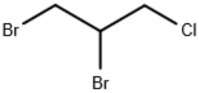
Dibromochloromethane



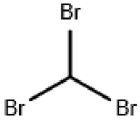
Bromochloroacetonitrile



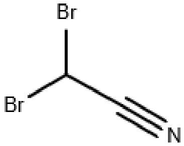
1,2-Dibromo-3-chloropropane



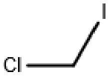
Bromoform



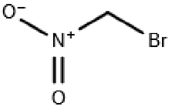
Dibromoacetonitrile



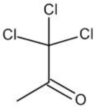
Chloroiodomethane



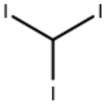
Bromonitromethane



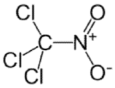
1,1,1- Trichloro-2-propanone



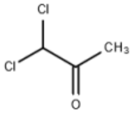
Triiodomethane



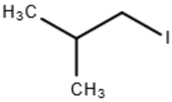
Trichloronitromethane



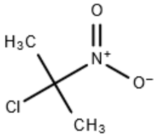
1,1- Dichloro-2-propanone



1-Iodo-2-methylpropane



2-chloro-2-nitropropane



2-Chloro-2-methylpropane