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Ph.D. Program: Chemical Processes Engineering

**NUTRIENT RECOVERY FROM WASTE WATER TREATMENT
PLANT BY SORPTION PROCESSES: TECHNICAL AND
ECONOMIC ANALYSIS**



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Abstract

In the last years has been performed a huge number of research related to nutrients (mainly N and P) recovery from waste water in order to promote their reuse and also to avoid eutrophication. Recovering nutrient from waste water can promote the circular economy, minimize the environmental footprint of waste water treatment and reduce anthropogenic alteration of nitrogen and phosphorus natural cycle.

Among the different techniques studied, sorption is nowadays one of the most interesting alternatives as requires less energy than electrochemical or membrane technologies and sorbents can be regenerated for being reused. Thus, the overall sorption performance of different ion exchangers was characterized for nutrient recovery from waste water treatment plant effluents.

Two commercial polymeric ion exchangers doped with Hydrated Ferrous Oxide (HFO) (Lewatit FO36 and Fiban-As) were assessed for phosphate uptake from waste water streams. Equilibrium and kinetics studies have been performed through batch experiments and the dynamic studies were carried out by fixed-bed column. The experimental study covered from the simplest monocomponent synthetic water (phosphate solutions) to the most complex real water from waste water treatment plant (WWTP) which contains ions, TSS and organic matter.

Sorption experiments reported for both sorbents high selectivity towards phosphate ions as sorption capacity did not significantly decrease in presence of competing ions. Loaded sorbents were regenerated through alkaline and acid desorption in order to reuse resin and obtain a high concentrated phosphate solution, which could be used for high quality fertilizer production. Results in dynamic flow experiments reported up to 80% of loaded phosphate extraction, although during desorption process was observed sorption capacity decrease up to 30% after three sorption-desorption working cycles.

Besides, salt modified synthetic zeolites were assessed for being used both as one charge (divalent forms) and reusable (mono-valent forms) sorbent. Raw zeolites provided in sodium form as well as its modification in potassium form showed high sorption capacity for ammonium uptake but poor performance for phosphate recovery from waste water streams as the sorption mechanism is mainly ion exchange. Regeneration experiments showed that both Ze-Na and Ze-K can be reused several sorption-desorption working cycles without significant sorption capacity decrease (< 5%).

Nevertheless, after salt modification to calcium and magnesium forms, the precipitation of phosphate salts was favoured obtaining hydroxyapatite and struvite in loaded Ze-Ca and Ze-Mg, respectively. As hydroxyapatite's solubility and phosphorus availability is similar to commercial fertilizers, loaded Ze-Ca could be potentially recycled for agricultural uses.

Finally, an economic assessment simulation was performed by applying Ze-Ca in the Baix Llobregat Waste Water Treatment Plant, located in the Metropolitan Area of Barcelona. The study reported that the implantation Ze-Ca filtration for nutrient recovery would be economically feasible, despite that more research is required in order to fit technical issues as the loaded sorbent disposal or the capability of loaded zeolites to be used as fertilizer.

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Glossary

BV: Bed Volume

CAPEX: Capital expenditure

ED: Electrodialysis

FO: Forward Osmosis

HAP: Hydroxyapatite

HFO: Hydrated ferrous oxide

IRR: Internal rate of return

MAP: Monoammonium Phosphate

MD: Membrane Distillation

NPV: Net present value

OPEX: Operating expenditure

PAO: Phosphate Accumulating Organism

ROI: Return of Investment

RPI: Retail Price Index

SWW: Synthetic waste water

TP: Total Phosphorus

TRL: technology readiness Level

TSP: Triple SuperPhosphate

TSS: Total Suspended Solids

UF: Ultrafiltration

WWE: Waste water effluent

WWTP: Waste water treatment plant

Introduction

1. Introduction

1.1. Environmental Impact of Nitrogen and Phosphorus Cycles alteration

Human alteration of ecosystem by transforming native soils to cultivated fields and pasture for supplying the growing world food demand with more than 7 billion people altered intensively nitrogen and phosphorus cycles as large amounts of reactive nitrogen (N) and phosphorus (P) are needed for crop production (Groffman and Rosi-Marshall, 2013).

The largest source of N on Earth is the atmospheric $N_2(g)$, which is not a component of the common rocks on Earth's crust. Thus, the use of N by primary producers depends on the fixation of $N_2(g)$ into soluble forms. The increase in fossil fuel combustion as well as major technological advance for $N_2(g)$ fixation by Haber-Bosch process drove to doubling global N fixation since 1950 (Galloway et al., 2003; Galloway and Cowling, 2002). The human alteration of nitrogen natural cycle interacts with atmosphere, terrestrial and aquatic ecosystems causing a series of air and water quality problems is illustrated in the Figure 1.1.

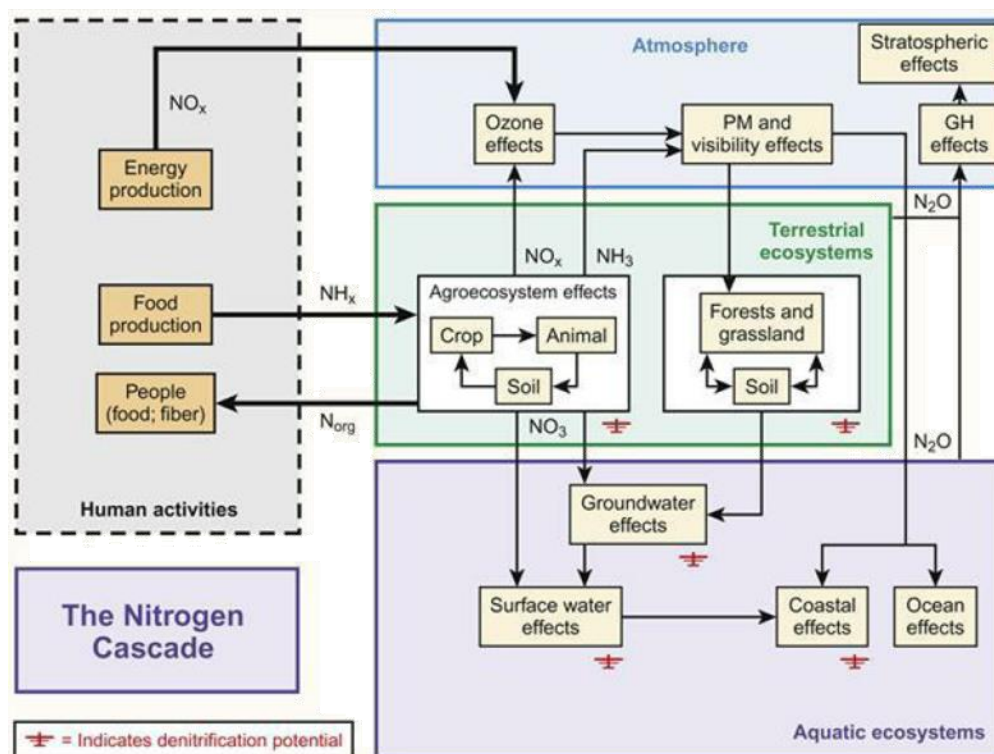


Figure 1.1: The human alteration of Nitrogen cycle (Galloway and Cowling, 2002)

Phosphorus is an essential element for life and plays a crucial role in limiting primary production in agricultural ecosystems as 20 million metric tons of P are mined per year for fertilizer production (Cordell et al., 2011; Mayer et al., 2016; Reijnders, 2014; Schipanski and Bennett, 2012). As can be observed in the Figure 1.2, human activity has heavily unbalanced the phosphorus global cycle

by using in days or years what in the nature least millions of years to create (Bennett and Schipanski, 2013).

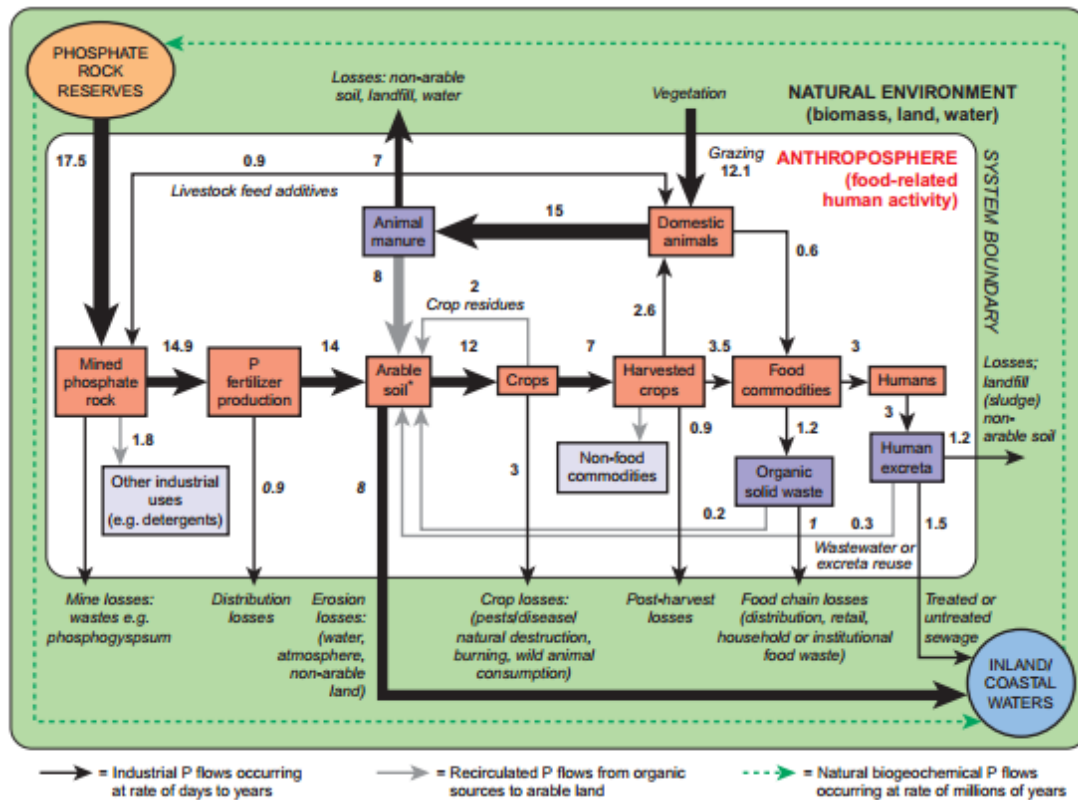


Figure 1.2: Anthropogenic Global Phosphorus Cycle (Cordell et al., 2009)

Moreover, phosphatic rock is present in small quantities on Earth (Filippelli, 2008) and it is located in just few countries or regions that have P-rich deposits, namely United States, China, Morocco and the Western Sahara (Jasinski, 2015; Mayer et al., 2016). In addition, evaluation of the supply chain reveals that almost 80% of mined phosphorus is lost during the extraction process (Schröder et al., 2010).

Aquatic ecosystem is one of the most affected by nitrogen and phosphorus massive use as fertilizer due to both soil erosion and mining process losses, which result in an excess of nutrients in surface water leading to eutrophication (Manuel, 2014). Excessive nutrient loading on receiving waterways has been identified worldwide as the main contributor to the degradation of water quality as well as significant reduction in aquatic life diversity (Aloe et al., 2014). P is limited in estuarine and freshwater systems whereas N tend to be limited in marine systems (Water Environment Federation, 2010).

1.2. Resource Management

The linear value chains that begin with the extraction of a natural resource and end with its safety disposal turns to the current schema of circular economy where materials can be recycled and returned into the economy as secondary raw materials, increasing the security of supply (Caspersen and Garrot, 2018; Scholz, 2017).

Recycling mineral nutrients and energy from household wastewater is a key step more in the development of a circular economy based society and became a key priority in EU's action plan for the Circular Economy (European Commission, 2015). Due to the world's continuing growing population as well as energy crisis, WWTPs are not any more considered as pollution removal facilities (van der Hoek et al., 2016; Vaneckhaute et al., 2018) and efforts are focused on the materials and energy recovery and promotes the search for technologies aimed to source separation and revalorization (Kabbe et al., 2017; Ribanova et al., 2017; Scholz, 2017; Wang et al., 2017) by integrating low-energy consumption processes in wastewater treatment layouts (Chen et al., 2015).

As the N and P consumed in food exceeds the nutritional requirements, it results in small assimilation (Jonsson et al., 2004; Liu et al., 2008) and the remainder goes to WWTPs. In addition, nutrient containing streams can be also used for metal, minerals and energy recovery (Drexler et al., 2014; Peccia and Westerhoff, 2015).

1.2.1. Phosphorus

As can be observed in Figure 1.3, the continuous growth in population causes the increasing use of fertilizers, resulted in an increasing demand of phosphoric rocks as agricultural food production accounts for approximately 90% of mined phosphate rock (Cordell et al., 2009; Smil, 2002).

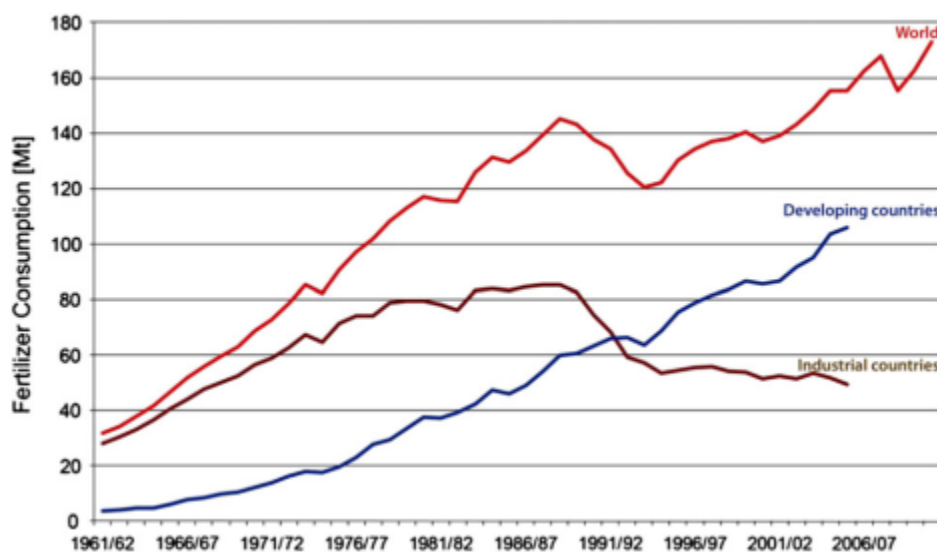


Figure 1.3: Trends of fertilizer consumption in the world (Röhling, 2010)

Currently, reuse of wastewater-derived P is mostly performed through effluent reuse and land application of sewage sludge (Mihelcic et al., 2011). Conventional chemical precipitation of phosphates by using iron and aluminum salts can efficiently incorporate P into solids, although obtained P containing minerals reports very low solubility, which means not being bioavailable for crop growth. (Mihelcic et al., 2011; Muster et al., 2013).

Thus, the most P-recovery process relies on precipitation/crystallization of struvite or hydroxyapatite (HAP) for recovering secondary phosphate minerals that can be used by the fertilizer industry. In fact, due to its solubility and bioavailability, HAP is a substitute that can be directly compared to rock phosphate (Cornel and Schaum, 2009).

1.2.2. Nitrogen

Recovery of N is often considered a lower priority than energy or P recovery as the atmosphere supplies an almost unlimited amount of N that can be recovered using the Haber-Bosch process (Burn, 2014). However, it is important to notice that Haber-Bosch process used for fertilizer production is a high energy consuming endothermic reaction, which accounts approximately 1% of global energy consumption and contributes to substantial Greenhouse Gas emissions (Dinar and Mendelsohn, 2011; Puchongkawarin et al., 2014).

Therefore, the recovery of N from WWTPs is one of the challenges to achieve the sustainability of these facilities. One of the most widely studied approach for recovering N from domestic wastewater is ammonia stripping from anaerobic digestion supernatants followed by a sorption step, in combination with biogas production and struvite precipitation (Boehler et al., 2015).

Other approaches are being studied, which are not focused on fertilizer industry but for direct use as food and feed by recovering N as microbial protein (Matassa et al., 2015). Nevertheless, it requires a full re-engineering of WWTPs.

1.2.3. Metals

A survey of metals in U.S. municipal sludge found levels between 1 – 30 g/ kg dry solid of Na, Ca, P, K, Mg, Fe, Al and Ti. However, despite they are in smaller concentration in waste water effluents, according to their enrichment in municipal wastewater compared to soil and their market price, the most promising metals to recover includes Au, Ag or Ti (Peccia and Westerhoff, 2015; Westerhoff et al., 2015).

As P and N, K is also an essential macronutrient for plant growth, therefore K recovery from wastewater effluents could help to satisfy global demand replacing its mineral form (Batstone et al., 2014; Carey et al., 2016). The recovery path includes the precipitation of potassium struvite, achieving simultaneous recovery of P and K (O'Neal and Boyer, 2015).

Currently it is estimated that 360 tons of Au is accumulated annually in wastewater sludge and, in the future, metal concentration in municipal sludge may increase mainly due to the manufacture and use of nanomaterials. In fact, nowadays, more than 60% of produced nano-Ti and nano-Ag

each year are found in municipal WWTPs (Gottschalk et al., 2009; Mueller and Nowack, 2008; Wiesner et al., 2006).

1.2.4. Energy

A significant quantity of waste biomass is generated as a result of current enhanced biological treatment of nutrient containing waste streams (Energy Information Administration, 2006), which can be digested for renewable energy recovery by producing bio-methane or hydrogen.

Studies revealed that only about 25 – 30% of available energy and nutrient is recovered from waste biomass and, between 30 – 80% of N and 15 – 18% of P are lost prior any form of recovery (Milbrandt, 2005).

Therefore, it is a great opportunity for enhancing the generation of renewable energy from nutrient containing wastewater streams. In addition, simultaneous recovery of energy and nutrients from wastewater also can alleviate major environmental problems related to nutrient pollution in ground and surface water sources (Carey et al., 2016).

1.3. Regulation

A review of legal framework regarding P discharge limits reported that Africa and Latin American are the regions with more permissive regulations as in most countries there are no P discharge limit and, for example, in Chile, the Total Phosphorus (TP) limit in discharged water is set in the range 2 mg/L– 15 mg/L depending on the discharged media (lakes or rivers, respectively) (República de Chile, 2001).

Nowadays, most European WWTPs have a TP limit in the range 1mg/L – 2 mg/L as France or Spain. However, some countries such as the United Kingdom reported more restrictive regulation as maximum permitted TP is set on 0.3 mg/L (Comisión Europea, 2017).

In the United States, most of WWTPs have a TP limit in the range of 0.5 mg/L – 1.5 mg/L although some states such as Massachusetts (0.1 mg/L), New Hampshire (0.2 mg/L) or Michigan and Maryland (0.3 mg/L) have lower permit limits (USEPA, 2017).

Thus, N and P discharge limits will become increasingly stringent as is reported a growing concern of the worldwide Governments for improving surface water quality and for protecting aquatic environment towards eutrophication through the control of specially P inputs from WWTPs (Bashar et al., 2018).

1.4. Available technologies for nutrient removal and recovery from WWTP

Most of waste water treatment plants are composed by the water line where the wastewater is treated and by the sludge line where the sludge is separated from the water and purged or recycled (Fung and Wibowo, 2013).

Currently, in most WWTP worldwide, N and P are removed from wastewater streams by enhanced biological nutrient removal, which is not capable to reach required low levels of P. Thus, the remaining P content is precipitated with iron or aluminum salts resulting in biologically non-profitable phosphorus based minerals due to its low solubility.

Moreover, huge amount of sludge is produced, which reported difficulties in its management as well as low reusability. Thus, in the last years, several studies have been focused on integrating nutrient recovery processes in WWTPs working schema.

Barat et al. (2009) evaluated the ammonium and phosphate content as well as flow rate and pH value of ten sampling points in a WWTP from Murcia, Spain. WWTP working schema is shown in Figure 1.4 and streams characterization results are reported in Table 1.1.

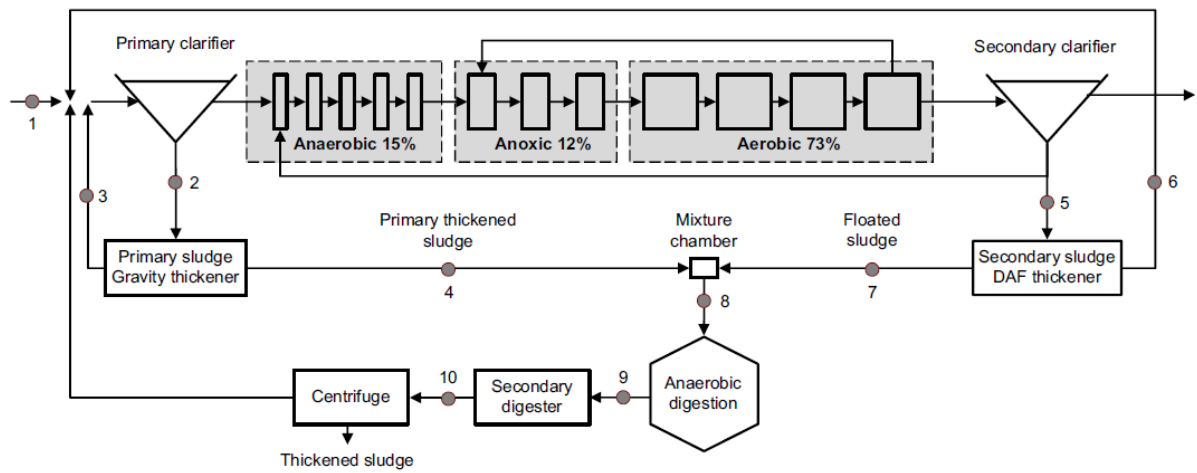


Figure 1.4: Urban waste water treatment plant flow chart (Murcia WWTP) (Barat et al., 2009)

Table 1.1: Average analytical measurements in sampling points of Murcia WWTP (Barat et al., 2009)

Sampling point	Flow rate [m ³ ·d ⁻¹]	Ammonium [mg NH ₄ ·dm ³]	Phosphate [mg PO ₄ ·dm ⁻³]	TSS [mg·dm ⁻³]	pH
1	89500	49.9	7.3	343	7.5
2	6110	51.5	9.6	5165	7.7
3	5751	57.8	13.4	224	7.6
4	359	195.8	176.4	59500	6.9
5	2204	3.1	120.3	9875	7.2
6	1695	1.0	7.2	44	7.4
7	448	93.8	1291.4	45500	6.7
8	807	139.2	755.2	51727	6.8
9	807	922	598.3	36333	7.5
10	807	928.5	491.3	33750	7.4

Based on data shown in the Table 1.1, where all sample points can be potentially used for nutrients recovery, depending on the technology used. However, in all cases, it is important to install a filter system in order to reduce the amount of total suspended solids (TSS), which is a critical parameter with a negative influence in nutrient recovery performance.

Several studies have been carried out with the aim to remove and recover nutrients from aqueous solutions. Some of them use biological reactors; other use electrochemical technologies such as electrocoagulation. Also, in some studies, it was attempted to precipitate phosphate salts, but the most studied method in the last years has been sorption or filtration by integrating membrane technologies.

1.4.1. Electrochemical

In electrochemical processes, the direct current field is the driving force where cations and anions migrate towards the cathode and anodes, respectively (Xie et al., 2016). Traditionally, electrochemical processes reported lack of selectivity towards ions as well as high-energy consumption.

Selectivity towards phosphate and ammonium ions was improved by the integration of ion selective monopolar membranes leading to electrodialysis (ED) (Xie et al., 2016; Yan et al., 2018). Moreover, energy consumption was reduced by integrating electrochemical to the biological process in order to profit the bioelectricity generated from oxidation of organic compounds (Chen et al., 2017; Kelly and He, 2014; Zhang et al., 2014).

In the ED process, nutrients can be selectively separated from the feed solution obtaining phosphate-rich and ammonium-rich solutions in anode and cathode chamber, respectively as is shown in Figure 1.5. Concentration factor up to 7 is achieved, and phosphate selectivity could be improved by increasing current density or feed solution pH (Tran et al., 2015, 2014).

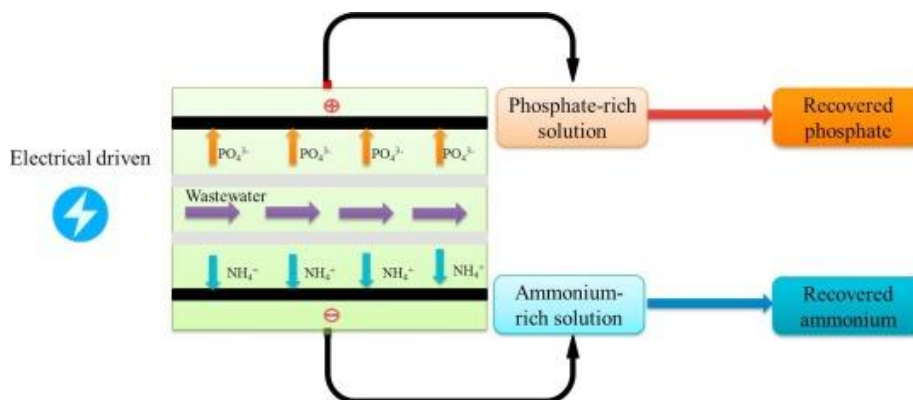


Figure 1.5: Schematic representation of ED-based system for nutrient recovery (Yan et al., 2018)

An increase in the voltage would promote bipolar membrane fouling, mainly in the forms of calcium phosphate salt precipitation, which reduces its lifetime (Wang et al., 2011). Experimental results at

pilot scale showed that the application of a struvite pre-treatment would reduce significantly precipitation formation (Ward et al., 2018). Furthermore, higher pH also improves phosphate enrichment; it may lead conversion of ammonium ions into volatile ammonia, which decreases the ammonium accumulation.

1.4.2. Biological

On traditional Enhanced Biological Reactors, phosphate content in wastewater is accumulate as polyphosphate in aerobic/anoxic environments by phosphate accumulating organisms (PAOs), resulting in a P-rich sludge (Zhao et al., 2015). However, the recovered product cannot be used directly in agriculture as it contains heavy metals, toxic organic micropollutants and pathogens (Schoumans et al., 2015). In the case of N, it is recovered as ammonia and stripped via air/N₂, which is adsorbed to form ammonium salts such as ammonium sulphate or ammonium carbonate (Iskander et al., 2016; Kelly and He, 2014; Wu and Modin, 2013).

Nutrient containing secondary effluent can be also used for microalgae growth, which reports dual benefit as it achieves almost a complete removal of N and P and the cultivated biomass can be used for biogas and bio-fertilizer production promoting circular economy (Arashiro et al., 2018; Arias et al., 2018) and sustainable plant harvesting strategies (Luo et al., 2018).

Furthermore, microalgae cultures can be converted into bio-char for soil remediation as well as for improving agricultural profitability (Arif et al., 2017; Arun et al., 2018; Santos and Pires, 2018; Uzoma et al., 2011). It improves soil residual nitrogen and carbon and electrical conductivity (Rizwan et al., 2018); as well as crop quality due to microalgae contained vitamins, carotenoids and amino acids (Coppens et al., 2016). In addition, bio-char can be also used to mitigate pollution and manage the risk of eutrophication, since it shows a good sorption capacities for organic and inorganic micro-pollutants (Cao and Harris, 2010; Mohan et al., 2014), retains the N and P (Mukherjee et al., 2011) and have the potential to sequester CO₂ from atmosphere (Lehmann et al., 2006).

1.4.3. Membranes Technology

Studies on phosphorus recovery are mainly focused on concentrated streams although diluted effluents, such as treated wastewater, often contains a significant portion of phosphorus mass and lower levels of TSS, which may result in less operational issues. Thus, membrane technology is useful for concentrate phosphorus in the retentate stream in order to favor the subsequent recovery (Nir et al., 2018). Forward osmosis (FO), and membrane distillation (MD) are the main membrane technologies for nutrient concentration in wastewater (Xie et al., 2016, 2014).

FO process is based on a semipermeable membrane which uses the osmotic pressure gradient between the feed and the permeate solution as driving force (Yan et al., 2018). It is capable to concentrate more than tenfold concentrations of nutrient in the feed solution (Vanotti et al., 2017; Xue et al., 2015).

The pH of the feed solution may influence the nutrient retention in the feed side since the surface of the membrane is negatively charged at alkaline pH, which favors the migration of ammonium ions to the permeate side and increases the retention of phosphate ions (Cartinella et al., 2006; Xue et al., 2015; Yan et al., 2018).

The MD process is a thermally driven membrane technology, where the feed solution is heated to create the vapor pressure gradient. Normally, phosphate ions are concentrated in the feed solution due to the non-volatility while ammonium ions are accumulated in the permeate side by reacting with the receiving solution (e.g. HCl or H₂SO₄) in the form of ammonium salts (Thygesen et al., 2014; Zarebska et al., 2014; Zhao et al., 2013).

By using membrane technologies, phosphate ions are concentrated in the feed solution which also contains Ca²⁺, Na⁺ or Mg²⁺ ions. Therefore, rejected stream can be used for crystallization of Ca-P and Mg-P minerals, which can be both used as raw material for phosphate acid production or directly disposed as local fertilizer (Nir et al., 2018).

1.4.4. Precipitation

Chemical precipitation and crystallization are generally of high efficiency in the treatment high concentrated wastewater effluents of nutrient (Abarca et al., 2017; Ronteltap et al., 2010). As result, can be obtained a high purity Hydroxyapatite (HAP) or struvite (MAP), which can be used as slow-release fertilizer with low heavy metal content compared to phosphate rock (Dai et al., 2017, 2016; Tarayre et al., 2016).

The main operational parameters which affect the formation of P precipitates are pH and molar ratio of participating ions (Peng et al., 2018; Ye et al., 2017). The pH value influences on the phosphate concentration, which impacts on crystals average size as well as size diversity. (Le Corre et al., 2007; Matynia et al., 2006; Rahman et al., 2014). To improve the effectiveness of precipitation, the optimum Ca:P and Mg:NH₄:PO₄ ratio for HAP and MAP production was set on 1.67:1 and 1.15:1:1, respectively (Huang et al., 2017a; Shih et al., 2017; Wang and Nancollas, 2008).

Mg and Ca materials are usually employed as the precipitators for the formation of MAP and HAP, respectively (Yan et al., 2018). However, the product purity is highly dependent of metal sources (Huang et al., 2017a; Liu et al., 2016).

Specific surface area, pore structure, particle size as well as environmental compatibility are key parameters to consider for crystallization seeds chose (Duan et al., 2010; Rahaman et al., 2008). Many natural seeds as quartz sand (Battistoni et al., 2000), struvite (Yu et al., 2013), calcite (Liu et al., 2012; Song et al., 2006), dolomite (Karaca et al., 2006; Yin and Kong, 2014), xonotlite (Chen et al., 2009), gastropod shells (Oladoja et al., 2013, 2012) or cow bone (Gu et al., 2015) have been assessed due to their abundance in nature, chemical stability, lack of toxicity and good biodegradability.

In addition, some synthetic materials which are byproducts of industrial production such as tobermorite rich waste compounds from construction industry (Berg et al., 2006), plant ash (Huang

et al., 2017b), converter slag (Kim et al., 2006) or synthetic calcium silicate hydrate (CSH) (Guan et al., 2014; H. Li et al., 2017; Okano et al., 2016) were also studied in the new circular economy schema reporting high efficiency inducing HAP precipitation.

1.4.5. Sorption

Nutrient recovery by sorption shows advantages such as simple operation and design as well as low cost. After sorption, nutrient-loaded sorbent can be desorbed for obtaining phosphate rich solution or, in the case of calcium and magnesium based adsorbents, can be used for direct land applications (Ye et al., 2017; You et al., 2017). Nutrient sorption mechanisms are mainly based on ion exchange, surface complexation and surface precipitation (Ye et al., 2017).

Natural sorbents, mainly clays (Rahmani et al., 2013), biochar (Takaya et al., 2016) or calcium containing shells (Abeynaike et al., 2011) have been assessed for nutrient recovery. As many of them reported low selectivity and low sorption capacity, salt modification and pH-based sites activation processes were carried out for improving overall adsorption performance.

Layered Double Hydroxides (LDHs), also named hydrotalcite-like compounds or anionic clays, have been widely assessed as adsorbent for phosphate recovery due to its high anion exchange capacity and outstanding thermal stability (Chitrakar et al., 2010). However, it reported poor selectivity towards phosphate species, which have been improved by altering the interlayer anion with organic compounds as pyromellitic acid, benzoic acid, terephthalic acid or trimesic acid (Yu et al., 2015); and with metals such as iron (Seida and Nakano, 2002), aluminum (Novillo et al., 2014), zirconium or magnesium (Drenkova-Tuhtan et al., 2016).

Zeolites are hydrated aluminosilicate minerals with porous structure which allows water retention and high cation exchange-capacity (Ramesh et al., 2011; Sherry, 2003). Application of zeolites as low-cost adsorbent for water and wastewater treatment have been widely studied since the last years (Tashauoei et al., 2010) due to their significant worldwide occurrence, the possibility to be synthesized from fly ash and the well performance reported as slow release fertilizer carrier (Ramesh et al., 2010). In addition, zeolites reported availability for improving soil physicochemical and microbial capacity (Abdi et al., 2006) as well as for enhancing nitrogen and phosphorus use efficiency (Gruener et al., 2003; Hua et al., 2006; McGilloway et al., 2003).

There is a wide variety of natural zeolites with ammonium adsorption capacity in the range of 2.7 – 30.6 mg/g, concluding that zeolites in sodium form are those which reports better adsorption performance (Wang and Peng, 2010). Zeolites can be treated with salts (Mitrogiannis et al., 2018), acids and alkalis in order to improve the adsorption performance though the modification of functional cation as well as inner porous structure.

Loaded zeolites can be desorbed and regenerated by using alkaline solutions and regeneration processes reported improvement on NH_4^+ removal as it increases zeolite's structure microporosity (Zhang et al., 2017). Moreover, loaded di-valent and tri-valent functionalized zeolites, which contains P-based salts precipitates could be directly disposed for agricultural uses or soil remediation purposes (Mitrogiannis et al., 2018; You et al., 2017).

Synthetic sorbents, mainly based on functionalized polymeric matrix (O'Neal and Boyer, 2013) and metal oxides such (e.g., iron oxide nanotubes (Kim et al., 2016), or layered rare earth hydroxides (Jeon et al., 2018), among others) were also widely assessed for nutrient removal and recovery.

A comparison of nutrient loading capacities for different adsorbents reported in the literature is collected in Table 1.2. It can be observed that most synthetic adsorbents resulted in higher capacity. Loaded natural sorbents were more suitable to be used directly for soil remediation while synthetic sorbents are designed for being capable to be reused for several sorption – desorption working cycles and obtaining nutrient rich streams during regeneration.

Table 1.2. Comparison of nutrient adsorption capacity data reported in literature for different adsorbent materials

	Support	Active Phase	Model	¹ Q _{max} (mg P/g) ² Q _{max} (mg N/g)	Reference
Ca-Z	Zeolite	Ca ²⁺	FU	11.1 ¹	(Mitrogiannis et al., 2018)
KAIC		Al ³⁺	WWE	6.3 ¹	(Guaya et al., 2016)
KFeC		Fe ³⁺	WWE	5.6 ¹	
KMnC		Mn ²⁺	WWE	9.6 ¹	
Z-Mn		Mn ²⁺	SWW	1.8 ¹ 17.9 ²	(Guaya et al., 2017)
CMZFA		-NH ₂	SWW	1.3 ¹	(Xie et al., 2013)
Ch-zeolite		Na ⁺ , K ⁺	SWW	8.2 ²	(Englett and Rubio, 2005)
ActZ (NaCl)		Na ⁺	SWW	4.6 ²	(Alshameri et al., 2014)
ActZ (NaOH)		Na ⁺	SWW	3.6 ²	
Chende-Ze		Na ⁺	SWW	7.3 ²	(Huang et al., 2010)
LC-Z		Ca ²⁺	SWW	22.3 ²	(Zhang et al., 2011)
HC-Z		Ca ²⁺	SWW	4.7 ²	
Na-Y		Na ⁺	SWW	17.6 ²	(Wang et al., 2007)
13X		K ⁺	SWW	6.7 ²	(Zheng et al., 2008)
MgO-biochar	Biochar	MgO	SWW	130.1 ¹	(R. Li et al., 2017)
HAIX	Quaternary ammonium	HFO	FU	10.1 ¹	(O'Neal and Boyer, 2013)
			HU	6.9 ¹	
			GW	5.53 ¹	
DETA-PES-Cu(II)	Polyethersulfone membrane	Cu ²⁺	SWW	26.7 ¹	(Song et al., 2016)

Table 1.2. Comparison of nutrient adsorption capacity data reported in literature for different adsorbent materials (cont.)

	Support	Active Phase	Model	¹ q _{max} (mg P/g) ² q _{max} (mg N/g)	Reference
I-Re(OH) ₃	Layered Double Hydroxides	Sm	SWW (pH=5)	45.5 ¹	(Jeon et al., 2018)
			SWW (pH=7)	37.7 ¹	
			SWW (pH=9)	23.9 ¹	
		Gd	SWW (pH=5)	52.5 ¹	
			SWW (pH=7)	43.6 ¹	
			SWW (pH=9)	25.7 ¹	
		Er	SWW (pH=5)	34.1 ¹	
			SWW (pH=7)	28.1 ¹	
			SWW (pH=9)	20.2 ¹	
		Y	SWW (pH=5)	29.6 ¹	
SWW (pH=7)	24.8 ¹				
SWW (pH=9)	16.2 ¹				
Zn, Fe, Zr	Fe ₃ O ₄ /SiO ₂	WWE (T ^a = 15°C)	24.7 ¹	(Drenkova-Tuhtan et al., 2017)	
		WWE (T ^a = 24°C)	30.5 ¹		
		WWE (T ^a = 35°C)	62.7 ¹		
		WWE (T ^a = 50°C)	1087.7 ¹		
AAO		Al ₂ O ₃	SWW	20.9 ¹	(Xie et al., 2015)
LO		La-OH	SWW	46.9 ¹	
Iron oxide nanotubes		FO	SW	2.235 ¹	(Kim et al., 2016)

SWW = Synthetic Wastewater; WWE = Wastewater Effluent; FU = Fresh Urine; HU = Hydrolyzed Urine

1.4.6. Integrated systems

In order to improve the efficiency of WWTPs and their self-sustainability, most of the research has focused on integrating nutrient recovery systems into existing facilities instead of finalist technologies. Therefore, the aim of many studies and also this PhD. thesis is valorizing nutrients contained in WWTPs effluents while minimizing energy consumption and sludge production.

Enhanced biological nutrient recovery technology can be improved by integrating membranes to the bioreactor (Yan et al., 2018) as the membrane can highly reject nutrient and mineral salts which favors HAP and MAP precipitation (Zou and Wang, 2016). Furthermore, as nutrients are rejected by the membrane, P-rich sludge production is reduced (Qiu et al., 2015; Qiu and Ting, 2014).

Moreover, precipitation and crystallization processes are combined with biogas production (Tervahauta et al., 2014) in order to improve WWTPs energy sustainability.

Finally, it is worth to note that nutrient removal impacts significantly in WWTPs operational costs as the most important factors which determines economics in a WWTP management are the chemicals and energy consumption in precipitation and aerobic processes, respectively (Revollar et al., 2017; Santín et al., 2017).

Within this context, integrating nutrients recovery technologies in WWTPs seems to be a feasible alternative to conventional nutrients removal schema as it may lead to a reduction of energy and chemical consumption, sludge production, valorization of recovered nutrients and promotion of circular economy.

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Objectives

2. Objectives

2.1. Aim and main objective

The main objective of the current PhD. thesis is to evaluate different technologies to recover inorganic form of phosphorus and nitrogen from wastewater treatment effluents. As nitrogen will be present mainly as ammonium and phosphorus as phosphate the processes to be used should take into account their different ionic nature

As it is shown in Figure 1, sorption processes based on ion exchange and precipitation have been used as main technology for the recovery of N and P from wastewater treatment plants. Loaded adsorbents can re-used after proper regeneration or they could be managed for fertilizer production in order to promote circular economy as well as sustainability of WWTPs.

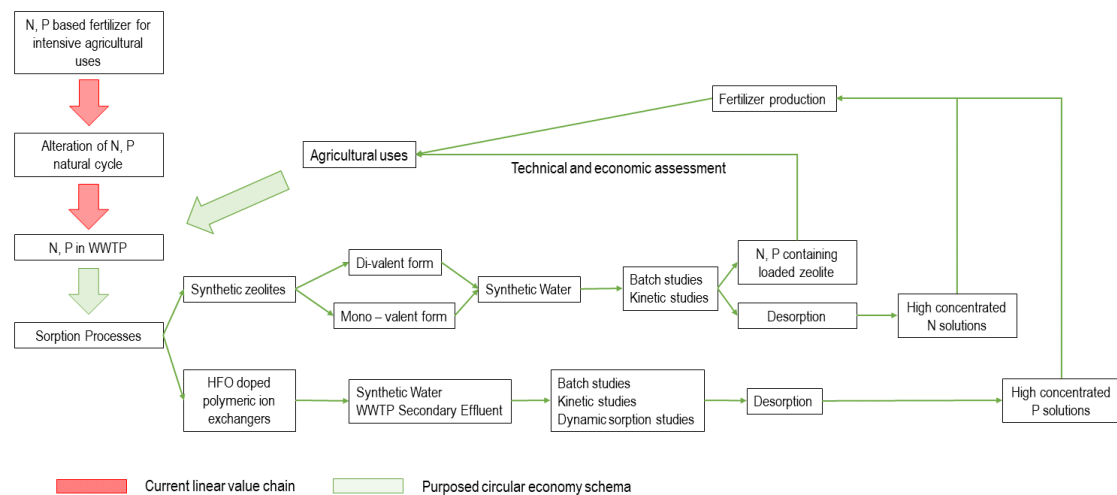


Figure 2.1. Schema of the thesis dissertation: sorption processes for N, P recovery

2.2. Specific objectives

This thesis aims to identify the best available technologies as well as optimal operation conditions of the valorization process of N and P from WWTPs. Therefore, the specific objectives of this PhD. thesis are listed below:

- Evaluate HFO doped polymeric ion exchangers and synthetic zeolites for N and P recovery
- Determine the sorption capacity, regeneration efficiency and reusability of different sorbents
- Perform a technical and economic analysis of the integration of both nutrients recovery in a WWTP

Table 2.1. summarizes the specific objectives depending on the assessed sorbent

Table 2.1. PhD. specific objectives depending on the sorbent

Polymeric Ion Exchanger	To recover phosphate from WWTP Secondary Effluents
	To efficiently desorb loaded sorbents
	To obtain high concentrated P solutions
	To evaluate sorption performance after several sorption - desorption working cycles
Inorganic sorbent: Zeolite in mono-valent form	To recover ammonium from Synthetic Wastewater
	To efficiently desorb loaded zeolites
	To obtain high concentrated N solutions
	To optimize loaded zeolites regeneration step for reusing in several sorption - desorption working cycles
Inorganic sorbent: Zeolites in di-valent form	To simultaneously recover ammonium and phosphate from Synthetic Wastewater
	To promote surface precipitation of phosphate minerals onto sorbents
	To assess the technical and economic feasibility of integrating alternative nutrients recovery in WWTP

It is outside the scope of the PhD, when regeneration of sorbents is carried out the treatment processes to recover both nutrients in appropriate form.

2.3. Thesis overview

In this work, sorption technologies using ion exchange materials, namely polymeric ion exchangers and zeolites, have been assessed for nutrient (N, P) recovery from WWTP. Main contributions of this PhD. thesis is summarized in Table 2.2.

Polymeric ion exchangers doped with HFO were studied for selective removal of phosphate from WWTP treated secondary effluents (Publication 1 and Publication 2). In addition, adsorbed P was recovered through alkaline desorption by obtaining high concentrated P solutions as well as regenerated adsorbent which suitability for being reused was tested (Publication 3).

Synthetic zeolites provided in sodium form were modified through K, Ca and Mg salts treatment in order to study the effect of counter ion in adsorption performance. Ze-Na and Ze-K were tested for ammonium removal and an optimization of regeneration step was carried out in order to recover ammonium through desorption and to obtain a regenerated sorbent which can be reused for several sorption – desorption working cycles (Publication 4).

Di-valent zeolites (Ze-Ca, Ze-Mg1 and Ze-Mg2) have been used for achieve the simultaneous recovery of both nutrients by precipitation of N and P containing salts, such as HAP and MAP, onto adsorbents surface (Publication 5). Loaded zeolites could be used directly for agricultural purposes although the nutrient bioavailability for crop disposal was not assessed.

Finally, an economic assessment of implementing alternative nutrient recovery technologies, filtration by gravity with Ze-Ca and ultrafiltration, was performed using El Prat WWTP as case study (Chapter 9).

Publication 1

Xialei You, Diana Guaya, Adriana Farran, César Valderrama, José Luis Cortina. *Phosphate removal from aqueous solution using a hybrid impregnated polymeric sorbent containing hydrated ferric oxide (HFO)*. Journal of Chemical Technology and Biotechnology 91, (2016), 693 – 704.

Publication 2

Xialei You, Adriana Farran, Diana Guaya, César Valderrama, Vladimir Soldatov, José Luis Cortina. *Phosphate removal from aqueous solutions using a hybrid fibrous exchanger containing hydrated ferric oxide nanoparticles*. Journal of Environmental Chemical Engineering 4, (2016), 388 – 397.

Publication 3

Xialei You, César Valderrama, Vladimir Soldatov, José Luis Cortina. *Phosphate recovery from treated municipal wastewater using hybrid anion exchangers containing hydrated ferric oxide nanoparticles*. Journal of Chemical Technology and Biotechnology 93, (2018), 358 – 364.

Publication 4

Xialei You, César Valderrama, Xavier Querol, José Luis Cortina. *Recovery of Ammonium by Powder Synthetic Zeolites from Wastewater Effluents: Optimization of the Regeneration Step*. Water Air Soil Pollution, (2017), 228 – 396.

Publication 5

Xialei You, César Valderrama, José Luis Cortina. *Simultaneous recovery of ammonium and phosphate from simulated treated wastewater effluents by activated calcium and magnesium zeolites*. Journal of Chemical Technology and Biotechnology 92, (2017), 2400 – 2409.

Chapter 9

Xialei You, César Valderrama, José Luis Cortina. *Nutrients recovery from Treated Secondary Mainstream in an Urban Waste Water Treatment Plant: An economic assessment case study* (Sent to Resources, Conservation and Recycling).

Table 2.2. Main contributions of the thesis

	Best Available Technologies					
	<i>Polymeric Ion Exchangers</i>		<i>Zeolites</i>			
			Mono - valent		Di - valent	
	Fiban - As	Lewatit FO36	Ze-Na	Ze-K	Ze-Ca	Ze-Mg1 Ze-Mg2
Remove phosphate from WWTP Secondary Effluents	Publication 2	Publication 1				
Obtain high concentration of eluted nutrients						
Optimize the loaded adsorbents regeneration step for reusing in several adsorption – desorption working cycles		Publication 3		Publication 4		
Recovery of ammonium from WWTP Secondary Effluents						
Simultaneous recovery of phosphate and ammonium						Publication 5
Precipitate phosphate minerals onto adsorbents						
Assess the economic feasibility of implementing alternative nutrient recovery technologies in WWTP						Chapter 9

Materials and Methods

3. Materials and Methods

A series of research activities were carried out in order to find the optimal operation conditions of the nutrients recovery and valorization process from WWTPs:

- i. Test HFO doped polymeric ion exchangers and salt modified synthetic zeolites on equilibrium sorption conditions in order to obtain the maximum sorption capacity.
- ii. Design of a fractional factorial experiment for studying the effect of competing ions in phosphate sorption performance onto polymeric ion exchangers
- iii. Determine the sorption rate of ammonium and phosphate ions onto synthetic zeolites through kinetic studies
- iv. Regenerate Ze-Na and Ze-K for obtaining high concentrated N solutions and reusing zeolites in several sorption – desorption working cycles
- v. Evaluate phosphate sorption onto polymeric sorbents under flow dynamic conditions through modelling by Thomas, Yoon-Nelson and Bed Depth Service Time Model for obtaining the breakthrough sorption capacity.
- vi. Desorption and regeneration of polymeric sorbents under flow dynamic conditions for assessing P concentration factor and sorbents reusability
- vii. Technical and economic analysis of integrating nutrient recovery in WWTPs

3.1. Sorbents

3.1.1. Polymeric ion exchangers

Two different types of polymeric ion exchangers have been used, Lewatit FO36 resin was provided by the Lanxess Company (Germany) and fibrous ion exchanger Fiban-As was synthesized at the Institute of Physical Organic Chemistry, National Academy of Sciences (Belarus).

The typical characteristics of Lewatit FO36 and Fiban-As are summarized in Table 3.1 (Lanxess, 2011; Vatutsina et al., 2007). Both ion exchangers were used on the sorption experiments in the form delivered.

Table 3.1. Physicochemical properties of FO36 and Fiban-As (Lanxess, 2011; Vatutsina et al., 2007).

	Lewatit FO36	Fiban-As
Matrix	PS-DVB	Acrylic
Structure	Macroporous	Fibre
Functional groups	Tertiary amine groups P-CH ₂ -N-(CH ₂ -CH ₃) ₂	Secondary amine groups -N- (CH ₃) ₂
Iron content	18 – 23%	1.07 mmol/g
Physical form	Brown, round beds	Brown fibre
pH range	4.5 – 8.5	4.5-8.5

3.1.2. Synthetic Zeolites

Raw zeolite provided in sodium form (Ze-Na) was synthesized from Narcea coal fly ash by an optimized conventional zeolite synthesis method using a 3M NaOH solution at 125°C and 8h of reaction (Moreno et al., 2001; Querol et al., 1996).

This material was modified to Calcium (Ze-Ca), Magnesium (Ze-Mg) and Potassium (Ze-K) forms in order to simultaneously adsorb ammonium and phosphate in order to improve the sorption performance of zeolites in sodium form that reported low phosphate sorption rate. The Ze-Na modification procedure was adapted from the method reported by Wu et al. (Wu et al., 2006).

Preparation of salt modified zeolites

In the case of calcium and magnesium salts modification, for the pre-treatment, 30 g of Ze-Na was placed in a flask and was mixed with 250 mL of 1 mol/L NaCl solution and the slurry was boiled with reflux for 4 h with continuous stirring. As zeolites with Silica Aluminium Ratio (SAR) between 1.5 and 1.8 (1.7±0.1 in the case of Ze-Na) show more affinity for potassium than sodium ions (Pauling, 1960; Sherry, 2003), the salt modification was performed without heating. Thus, pre-treatment for Ze-K was performed by continuous stirring with a 1 mol/L NaOH solution at room temperature for 24 h.

The solid phase was separated by filtration and was mixed with 250 mL of 1 mol/L CaCl₂, MgCl₂ or KCl solution and the slurry was boiled twice for 4 h with continuous stirring in the case of Ze-Ca and Ze-Mg and without heating in the case of Ze-K.

The solid phase was separated by filtration and washed with deionized water for several times in order to washing out residual salts. Finally, the salt modified zeolites were dried in an oven at 50°C for 72 h and stored in airtight containers for subsequent experiments.

Furthermore, in order to reduce energy consumption, a study about the effect of temperature on zeolite modification was performed by repeating the salt modification to magnesium by continuous stirring at room temperature instead of boiling process, obtaining Ze-Mg-b, which after being dried in an oven was also stored in airtight containers.

3.2. Batch experiments

Equilibrium sorption, and a factorial experiment were performed in order to assess the influence of competing ions in phosphate sorption onto polymeric ion exchangers.

In the case of zeolites, equilibrium sorption and desorption as well as kinetic studies were carried out for the characterization of the sorption process.

3.2.1. Equilibrium sorption studies

A series of test solutions were prepared in a wide range of concentrations and mixed with a certain amount of sorbent. The samples were mixed with a mechanical shaker at room temperature during at least 24 hours at constant agitation to achieve the equilibrium nutrient uptake. After phase separation, total ammonium and phosphate concentration was determined by ionic chromatography (Dionex ICS1000 CS-16 (Vertex, Molins de Rei, Spain)).

The experimental data were fitted using the isotherm equations of Langmuir, Freundlich and Langmuir-Freundlich. The Langmuir isotherm (Foo and Hameed, 2010) assumes that sorption takes place in one molecule in thickness (monolayer sorption), only occurs at a finite number of definite localized sites and all sites possess equal affinity for the sorbate (Eq. 3.1). The Freundlich isotherm (Foo and Hameed, 2010) describes a heterogeneous and reversible sorption not restricted to the formation of a monolayer in which the energy in the Langmuir equation varies as a function of surface coverage due to variation of the sorption (Eq. 3.2). Langmuir-Freundlich isotherm, also known as Sip's equation, is an improved expression that can simulate both Langmuir and Freundlich behaviours (Eq. 3.3).

$$q = \frac{K_L q_m C_e}{1 + K_L C_e} \quad \text{Eq. 3.1}$$

$$q = K C_e^{\frac{1}{n}} \quad \text{Eq. 3.2}$$

$$q = \frac{q_m (K_{LF} C_e)^n}{(K_{LF} C_e)^n + 1} \quad \text{Eq. 3.3}$$

where, q_m is the maximum loading of the sorbent (mg/g), K_L is the Langmuir sorption constant (L/mg sorbent), K is the sorption Freundlich constant (mg/g)(mg/L)^{-1/n}, K_{LF} is the Sip's affinity constant for sorption (L/mg) and, n is the Freundlich exponent, values of $n > 1$ represent favourable sorption.

3.2.2. Fractional factorial experiment

The influence of anions present in solution (HCO_3^- , Cl^- , SO_4^{2-} and NO_3^-) on the removal of phosphate by FO36 and Fiban-As was studied in batch configuration using a two-level factorial experimental design (Jafari Nejad et al., 2011; Mee, 2009). Competing anions solutions were prepared by dissolving the appropriate amount of NaCl, NaHCO_3 , Na_2SO_4 or NaNO_3 salts in deionized water. The experiments were carried out at fixed pH ranged between 6.5 and 7.5.

The fractional factorial experiment was build using the program Minitab from a full factorial experiment by choosing an alias structure (Trabelsi et al., 2011). The levels studied were defined by the common values found in WWTP secondary effluent for competing anions, thus the average concentration of each anion at low and high levels assigned by (-) and (+), respectively are collected in Table 3.2. Data treatment was performed using Minitab software.

Table 3.2. Factors and levels used in the 2^{5-1} factorial design study

Factors	Units	Low level (-)	High level (+)
A: PO_4^{3-}	mg P- $\text{PO}_4^{3-}/\text{dm}^3$	10	50
B: HCO_3^-	mg C- $\text{HCO}_3^-/\text{dm}^3$	200	300
C: Cl^-	mg Cl^-/dm^3	150	300
D: SO_4^{2-}	mg S- $\text{SO}_4^{2-}/\text{dm}^3$	150	250
E: NO_3^-	mg N- $\text{NO}_3^-/\text{dm}^3$	20	50

3.2.3. Kinetic studies of zeolite sorption performance

1 g of zeolite was added into a precipitate glass flask containing 250 mL of ammonium solution with concentration of 10 mg L^{-1} . The system was agitated with magnetic stirrers in order to maintain the sorbent suspended in the solution. The simultaneous sorption experiments were carried out using a solution containing 5 mg L^{-1} of ammonium and 15 mg L^{-1} of phosphate.

Samples of 6 mL were taken every minute for the first 10 minutes, every 5 minutes until half an hour, every 30 minutes until reaching 3 hours and finally one more sample at 24 hours. The distribution of sampling times was established based on previous studies that reported fast kinetics for ammonium and phosphate removal, where up to 75% of sorption performance occurred at the first 30 minutes

The kinetic models selected to describe kinetic data were three approaches widely used for fitting ion exchange data (Guaya et al., 2015), the Homogeneous Particle Diffusion Model (Eq. 3.4 - 3.7), the Shell Progressive Model (Eq. 3.6 – 3.8) and the Intraparticle Diffusion Model (Eq. 3.9). (Ferrier et al., 2016; Valderrama et al., 2010b).

$$\text{Particle diffusion} \quad -\ln(1 - X^2(t)) = \frac{2\pi^2 D_e}{r^2} t \quad \text{Eq. 3.4}$$

$$\text{Liquid film diffusion} \quad -\ln(1 - X(t)) = \frac{3DC}{rC_r} t \quad \text{Eq. 3.5}$$

$$\text{Liquid film diffusion} \quad X = \frac{3C_{A0}K_F}{a_s r C_{S0}} t \quad \text{Eq. 3.6}$$

$$\text{Particle diffusion} \quad 3 - 3(1 - X)^{2/3} - 2X = \frac{6D_e C_{A0}}{a_s r^2 C_{S0}} t \quad \text{Eq. 3.7}$$

$$\text{Chemical reaction} \quad 1 - (1 - X)^{1/3} = \frac{k_s C_{A0}}{r} t \quad \text{Eq. 3.8}$$

$$q_t = k_{dt} \sqrt{t} + A \quad \text{Eq. 3.9}$$

3.2.4. Alkaline regeneration of loaded zeolites

The regeneration of sorbents only was performed for Za-Na and Ze-K. Thus, 10 mL of NaOH or KOH 1 mol/L were putted in contact with Ze-Na and Ze-K, respectively in polyethylene tube containing loaded zeolites. The samples were mixed with a mechanical shaker (Heidolph Reax 2) at room temperature during 4 hours at constant agitation. After the zeolite was deposited in the bottom of the polyethylene tube by gravity, the supernatant solutions were extracted with a Pasteur pipette stored in plastic bottles to squirrel away in the refrigerator.

In order to clean up the samples, ultrapure water was put in each tube and mechanical shaker was used to mix the sample for clean better the zeolite during 4 hours at constant agitation and at room temperature. Finally, the regenerated zeolites were dried in an oven at 50°C for 72 h before being reused.

3.3. Flow Dynamic Experiments

3.3.1. Dynamic phosphate sorption experiments onto polymeric sorbents

All column experiments were conducted in duplicate in glass columns of 100 mm length and 15 mm internal diameter (Omnifit), uniformly packed with 3.4–3.5 g of sorbent. During the column sorption operation, a phosphate aqueous solution (10 mg PO₄³⁻/L) was pumped upwards through the column at a constant flow rate 2 mL/min. A synthetic solution containing 300 mg/L of chloride and hydrogen carbonate, 150 mg/L of sulphate and 50 mg/L of nitrate was used for experiments with multicomponent composition. These concentrations were selected accordingly to the average background composition of WWTP secondary effluent. Moreover, a WWTP secondary effluent was also used (characteristics are summarized in Table 3.3) in dynamic experiments.

Samples at the exit of the column were collected by a fraction collector (Gilson FC204) at given time intervals. Initially, the columns were conditioned with deionized water for half an hour. The wet bed volume was used as reference to convert the supplied solution volume into bed volumes (BV).

Table 3.3. Main chemical parameters of an urban wastewater treatment plant secondary effluent of a WWTP of the Barcelona Metropolitan Area

pH	8.34	Chloride (mg Cl ⁻ /L)	395.8
Conductivity (μS/cm)	218	Nitrate (mg NO ₃ ⁻ /L)	0.13
TOC (mg C/L)	14	Sulphate (mg SO ₄ ²⁻ /L)	233.52
Phosphate (mg PO ₄ ³⁻ /L)	10.36		

3.3.2. Desorption and regeneration

Sorbents were considered saturated when column effluent concentration reached the 95% of inlet concentration. Saturated columns (loaded sorbents) were washed in close loop with deionized water for 30 minutes and then were regenerated using NaOH solution (20 g/L) at the same flow rate than sorption experiments (2 mL/min).

Later on, 0.1 M HCl (500 mL) was pumped into the column in order to regenerate the functional groups of the sorbent bed and finally it was conditioned with deionized water (1 L) before reusing. Regeneration capacity was evaluated through five sorption-desorption cycles.

Breakthrough sorption capacity

The breakthrough point is chosen arbitrarily at some low value, C_b (mg/L); and the sorbent is considered to be essentially exhausted when the effluent concentration, C_x (mg/L), reaches the 90% of C_0 (initial concentration of PO₄³⁻, mg/L). The capacity at exhaustion q_{column} (mg/g) is determined by calculating the total area below the breakthrough curve. This area represents the amount of solute sorbed by mass of sorbent in the sorption zone from the breakpoint to exhaustion (Florida et al., 2010; Gupta et al., 2000).

$$q_{column} = \frac{\int_{V_b}^{V_x} (C_0 - C) dV}{m_s} \quad \text{Eq. 3.10}$$

Where C is the outlet PO₄³⁻ concentration (mg/L) and m_s is the mass of the sorbent (g).

Three models were used to describe the phosphate sorption under flow dynamic conditions. It is important to point out that these three models are mathematically equivalent despite they provide different information about the sorption performance.

The Thomas Model assumes Langmuir sorption isotherm, no axial dispersion and that the driving force obeys second-order reversible reaction kinetics (Yılmaz İpek et al., 2013). The linear form of Thomas model is expressed as equation 3.11.

$$\ln\left(\frac{C_0}{C} - 1\right) = \frac{k_{Th}q_e m}{Q} - K_T C_0 t \quad \text{Eq. 3.11}$$

where K_T is the Thomas rate of constant (mL/min·mg), q_0 the PO_4^{3-} sorption capacity (mg/g), Q the flow rate (mL/min) and m the mass of sorbent (g).

The Yoon-Nelson model based on the theory of sorption and breakthrough of PO_4^{3-} probability (Lim and Aris, 2014):

$$\ln \frac{C}{C_0 - C} = K_{YN}t - \tau K_{YN} \quad \text{Eq. 3.12}$$

where t is the time (min), K_{YN} the rate of constant (1/min) and τ the time required for 50% of PO_4^{3-} breakthrough (min).

The Bed Depth Service Time (BDST) model is frequently selected for the delineation of fixed-bed column breakthrough for the initial state of the operation (Lim and Aris, 2014; Valderrama et al., 2010a):

$$C_0 t = \frac{N_0 h}{u} - \frac{1}{K} \ln \left(\frac{C_0}{C} - 1 \right) \quad \text{Eq. 3.13}$$

where N_0 is the PO_4^{3-} sorption capacity of the bed (mg/dm³), h the column bed depth (cm), u the linear flow velocity (cm/h) and K the sorption rate constant (L/mg·h).

3.4. Analytical methods

Characterization of sorbents

Polymeric sorbents were sliced using a thin cutter after being frozen with liquid nitrogen for carrying out the mapping analysis of the samples along the particle diameter was completed. Virgin and loaded samples of zeolites were washed with ultrapure water and then dried in the oven at 60 °C during 24h for physicochemical characterization.

Samples morphology as well as their chemical composition were analysed by using a JEOL 3400 Field Emission Scanning Electron Microscope coupled to an Energy Dispersive Spectroscopy system (FSEM-EDS). Reported samples composition is the average of three analyses in different points of the sample.

The mineralogical composition was also analysed by using a Bruker D8 A25 Advance X-Ray Diffractometer. The specific surface of samples was determined by the nitrogen gas sorption method with an automatic sorption analyser (Micrometrics). Infrared absorption spectra in the range of 4000-550 cm⁻¹ were obtained by using a Fourier Transform FTIR 4100 Jasco spectrometer.

Aqueous liquid samples analysis

Samples obtained from both batch and flow dynamic experiments were filtered with 0.20 µm filters and total ammonium and phosphate content as well as competing ions concentration were determined by ionic chromatography (Dionex ICS1000 CS-16 (Vertex, Molins de Rei, Spain)).

3.5. Technical and economic analysis

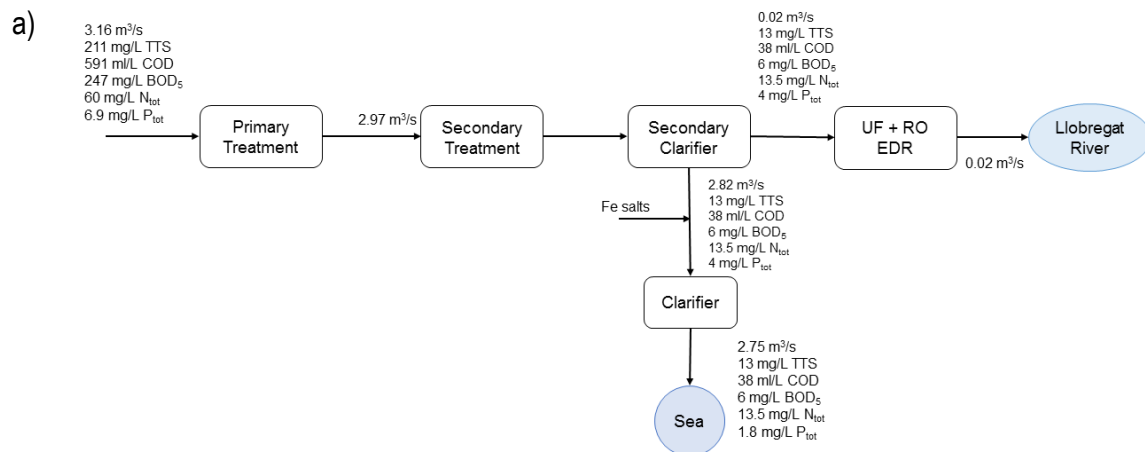
After assessing the sorption performance of polymeric ion exchangers and salt activated synthetic zeolites at the lab scale, the synthetic zeolite Ze-Ca was selected for the technical and economic analysis as it reported the best performance for simultaneous recovery of N and P from wastewater treated effluent in terms of sorption capacity for both nutrients and the faster sorption rate, which can lead to a short HRT.

Description of WWTP case study

For the case study was considered the Baix Llobregat WWTP (BLI-WWTP), which includes a water regeneration station based on filtration and reverse osmosis. This facility could be used for the filtration and separation of loaded zeolite from treated secondary effluent (Hermassi et al., 2016).

The BLI-WWTP is composed by 12 identical working lines consisting on a primary settlement, and a conventional secondary biological step. The main part of the treated effluent is discharged into the Mediterranean Sea through an emissary 3.2 km long (Köck-Schulmeyer et al., 2011).

The working schema of the BLI-WWTP and the main treatment stages is depicted in Figure 3.1a). As can be seen in Figure 3.1b), the zeolite filtration system is proposed to be installed after the secondary clarifier to use the existing ultrafiltration (UF) unit from the regeneration station for separating the loaded zeolite from the treated water as has been proved successfully elsewhere (Hermassi et al., 2016). Flow distribution showed in Figure 3.1b) is defined in order to obtain a final P concentration below 2 mgP/L as it is established by the EU regulation (Mas-Pla et al., 2006)



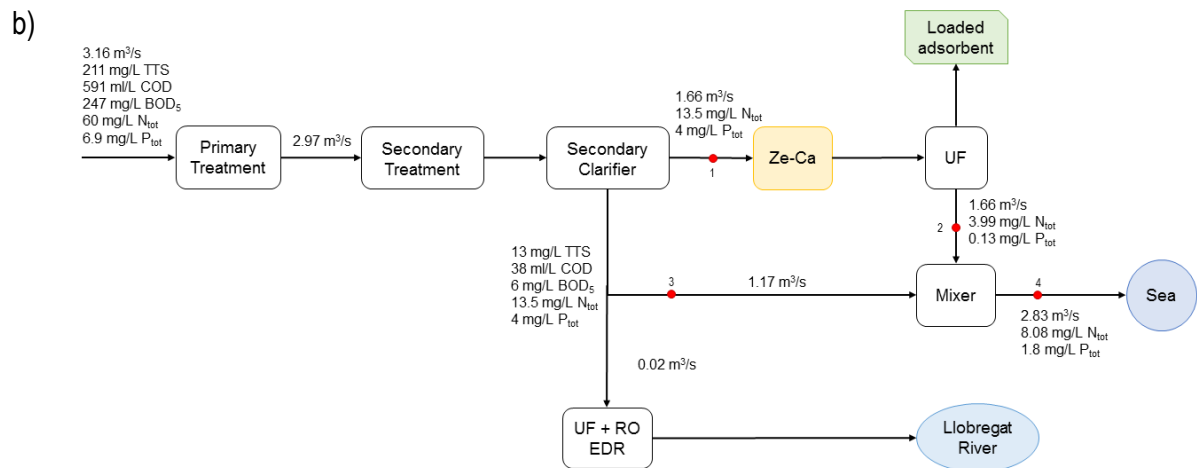


Figure 3.1. Summary of a) current and b) purposed working scheme and sampling data for recovery of nutrients at the BLI-WWTP. Flow-rates and composition of the main parameters have been provided by AMB (Àrea Metropolitana de Barcelona, 2017a)

The capital expenses (CAPEX) are required for the installation of zeolite filtration tanks as well as influent and effluent pumping systems and plant pipelines modification. No further investment is needed as the zeolite filtration will be performed by gravity (Alkas et al., 2013; Foreman, 1985; Hansen, 1997) and the separation system will use the existing ultrafiltration modules from the regeneration station.

It was considered a 5% increase of the current BLI-WWTP Operational Expenses (OPEX) (8.4 M €/year) due to the significant increase of operational demand of ultrafiltration modules in terms of energy and maintenance.

Finally, as the loaded zeolite contains calcium phosphate it can be sold as Triple SuperPhosphate (TSP) fertilizer with approximately a 15% of phosphorus nutrient content. In addition, the implantation of zeolite filtration system would lead to chemicals cost saving related to iron salt dosing for phosphate removal. According to a non-published study performed by SUEZ Spain, the average cost of the phosphorus chemical removal is estimated on 0.7 €/kg P_{in}.

A summary of variables considered for the economic analysis is listed in the Table 3.4.

Table 3.4. Summary of considered variables for economic assessment

BLI-WWTP lifetime	20 years	Discount rate	4%
P _{tot} after zeolite filtration	0.01 mgP/L	Raw zeolite price	115 €/ton
P _{tot} final	1.8 mgP/L	Loaded zeolite (15% of PO ₄ ³⁻ content)	220 €/ton
HRT	120 minutes	Chemical cost saving	0.7 €/kg P _{in}
Variation of BLI-WWTP treated flow	+ 1% per year	CAPEX	4090 k€
OPEX	420 k€/year		

Financial ratios used for economic analysis

The net present value (NPV), internal rate of return (IRR), return of investment (ROI) and payback period (PP) were estimated for assessing the feasibility of implementing Ze-Ca filtration facility in the BLI-WWTP.

Net Present Value (NPV) (Eq. 3.14) is expressed as the difference between the current value of cash of inflows and outflows over a period and it is used to analyze the profitability of any investment.

$$NPV = \sum_{t=1}^T \frac{B_t - C_t}{(1 + r)^t} \quad \text{Eq. 3.14}$$

where B_t and C_t are the inflows and outflows at the period t , and r is the discount rate.

Internal Rate of Return (IRR) is calculated by solving the Eq. 3.15 and it specifies whether the project breaks even with an NPV of zero; if the obtained result is greater than the discount rate, the project is feasible.

$$0 = investment + \sum_{t=1}^T \frac{B_t - C_t}{(1 + IRR)^t} \quad \text{Eq. 3.15}$$

Return of Investment (ROI) (Eq. 3.16) is a measure to evaluate the efficiency of an investment, since it measures the amount of return of an investment in relation to the cost of investment.

$$ROI = \frac{\text{Gain from investment} - \text{Cost of investment}}{\text{Cost of investment}} \times 100 \quad \text{Eq. 3.16}$$

The Payback Period (PP) (Eq. 3.17) is the time required to recover the cost of the investment. For ROI calculation, will be considered a lifetime of 20 years for the WWTP (Machado et al., 2007).

$$PP = \frac{\text{Cost of investment}}{\text{Annual Gain from investment}} \quad \text{Eq. 3.17}$$

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4. Publication 1: Phosphate removal from aqueous solution using a hybrid impregnated polymeric sorbent containing hydrated ferric oxide (HFO)

ATTENTION ;

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8. Publication 5: Simultaneous recovery of ammonium and phosphate from simulated treated wastewater effluents by activated calcium and magnesium zeolites

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9. Nutrients recovery from Treated Secondary Mainstream in an Urban Waste Water Treatment Plant: An economic assessment case study

Nutrients recovery from Treated Secondary Mainstream in an Urban Waste Water Treatment Plant: An economic assessment case study

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Abstract

This study presents the economic assessment for implementing an ammonium and phosphate simultaneous recovery process based on the use of calcium activated synthetic zeolites in a large urban Waste Water Treatment Plant (WWTP) located in the Metropolitan Area of Barcelona.

A calcium activated synthetic zeolites was selected, after a benchmarking analysis, as it reported capability for simultaneously recover ammonium and phosphate by a combined mechanism of ion exchange for ammonium and formation of insoluble mineral phase for phosphate. The loaded sorbent rich in ammonium and phosphate shows suitable properties as slow-release fertilizer.

Financial indexes such as Present Net Value, Internal Return Rate, Return of Investment and Payback Period were calculated concluding that the integration of a zeolite-based sorption treatment stage in the main stream is economically feasible, with a reasonable payback period. The need, to achieve low-levels of P and N on the discharged waters and the need to develop more sustainable WWTP facilities, promoting nutrients recovery will be and additional support to promote the deployment of nutrients recovery solutions. The sensibility analysis performed to define critical parameters for the economic performance of the technology concluding that the main variable in the feasibility of the nutrients recovery unit is related to the selective sorbent of nutrients, both the cost of purchase and the market for the sorbent loaded with nutrients.

Keywords: ammonium; phosphate; wastewater; nutrient recovery; zeolite; economic feasibility

9.1. Introduction

Nitrogen and phosphorus are essential elements for life and large amounts of these elements, mainly in the form of ammonium and phosphate, are needed for fertilizer production in order to supply growing population food demand (Roberts and Johnston, 2015; Röhling, 2010). It is estimated that about 22×10^6 ton/y of phosphorus from mined fossil phosphate resources are added to the world economy (Reijnders, 2014), which leads to a significant alteration of the natural cycle of these elements resulting in problems with air and water quality as well as overall ecosystem balance (Bennett and Schipanski, 2013; Driscoll et al., 2003; Galloway and Cowling, 2002; Groffman and Rosi-Marshall, 2013).

Furthermore, nitrogen and phosphorus discharge limits become increasingly stringent. European Urban Waste Water Treatment Directive set the maximum annual mean total nitrogen concentration between 1.5 and 10 mgN/L depending on the size of the urban area (Oenema et al., 2011) and phosphorus discharge regulation set its concentration on 2 mgP/L in Spain, 1 mgP/L in France, 0.1 mgP/L in UK or 0.01 mgP/L in different states of USA, for example.

In the case of phosphorus, conventional treatments such as chemical precipitation or biological removal are not able to reach concentrations below 0.1 mgP/L and it is necessary to identify technical and economically feasible technologies able to reach ultra-low levels.

Furthermore, urban WWTPs are not any more considered as pollution removal systems but as resources (nutrients and energy) recovery plants (van der Hoek et al., 2016). In this new proposed schema systems are mainly focused on the resource recovery and water reuse to promote the circular approaches where the pollution load becomes secondary sources of raw materials that can be recovered giving an added value to these sources (Kabbe et al., 2017; Ribanova et al., 2017; Scholz, 2017).

The use of secondary raw materials with sorption properties (e.g., natural sorbents or industrial wastes) is an area of increasing interest. Low cost sorbents with high affinity for ammonium and phosphate provide an attractive solution that offers the potential to recover nutrients of high quality that can be directly applied as a fertilizer as most of them will contain (N, P and K) (Egle et al., 2015; Scholz et al., 2013), which contribute to plant growth.

Furthermore, natural sorbent materials are often locally abundant, easy to dispose and include environmental friendly by-products such as shellfish shells (Abeynaike et al., 2011; Xiong et al., 2011), fly ash (He et al., 2012) or slag (Barca et al., 2012; Haddad et al., 2015; Jaouadi et al., 2014).

A summary of currently available phosphate and ammonium single recovery technologies from treated secondary effluent are listed in Table 9.1, most of them are already implemented in large WWTPs while in other cases has been applied to small scale wastewater treatment scale (e.g., household in isolated communities).

Table 9.1. Summary of available commercial phosphate and ammonium recovery technologies applied to Treated Secondary effluents including the removal mechanism of the technology, the technology provider, and the technology readiness level (TRL) level.

	Company	Mechanism	TRL	Reference
Phosphate Recovery Technologies				
PAdeCS	Nippon Concrete Industries	AD	3	(Iizuka et al., 2017, 2012; Ohtake and Okano, 2015)
Rintoru®	Taiheiyo Cement Con and Onoda Chemical Industry	AD	9 (1)	(Ohtake and Okano, 2015; Okano et al., 2016; Taiheiyo Cement Corporation, 2017)
Polonite®	Ecofiltration Nordic AB (EN)	AD	9 (6000)	(Ecofiltration Nordic AB, 2017a, 2017b)
PhosphoRedu c™	Water & Soils Solutions International –(WSSI)	AD	9 (15)	(Water and Soil Solutions International, 2017, n.d.)
Ammonium Recovery Technologies				
Air Extraction	-	ST	9	(Roch, 2009; Sengupta et al., 2015)
Bentonite	-	IX	4	(Buragohain et al., 2013; Kazemi et al., 2017)
Zeolite	-	IX	7	(Gupta et al., 2015; Roch, 2009)
Simultaneous Recovery of Phosphate and Ammonium				
Zeolite	UPC – Barcelona tech	IX/SF	4	(Guaya et al., 2015)
Ze-Ca	UPC – Barcelona tech	IX/SF	4	(You et al., 2017a)
Ze-Mg	UPC – Barcelona tech	IX/SF	4	(Hermassi et al., 2018; You et al., 2017a)

¹TRL: Technology Readiness Level (1-9): 1 (basic principles observed), 2 (technology concept formulated), experimental proof of concept; 4 (technology validated in lab), 5 (technology validated in relevant environment), 6 (technology demonstrated in relevant environment), 7 (system prototype demonstration in operational environment), 8 (system complete and qualified), 9 (actual system proven in operational environment). Values in brackets for TRL9, indicates the number of commercial full scale cases.

² Removal mechanism: IX (Ion exchange), SF (solid formation/precipitation), ST (stripping), AD (adsorption)

Four technologies were identified, among all options listed in Table 1, with a TRL greater than 8 (the system was completed and qualified through test and demonstration (United States Department of Defense, 2011)), which can produce effluents with ultra-low phosphorus concentration: Polonite, PhosphoReduc, CoMag and BluePro.

Polonite™ is an adsorption technology developed by Ecofiltration Company, which is based on a processed natural calcium silicate mineral (44,4% SiO₂, 47,1%CaO wt.) with a high surface area (14m²/g) due to its porosity (45%) and a density of 730 g/L (Nilsson et al., 2013). Polonite reports an adsorption capacity of 40 kg P/ton after one hour of Hydraulic Retention Time (HRT) and the loaded adsorbent can be used as slow release fertilizer after a brief drying process. The pH of the treated effluent was ranged between 12 and 14, which allows reducing bacterial presence and odors, but requiring the use of Personal Protective Equipment for effluent manipulation. Polonite can reduce phosphorus and total suspended solids (TSS) up to 90% and 13%, respectively, and

reported 48 months of high effective lifetime for a conventional filter containing 500 kg of adsorbent. Loaded sorbent can be used as slow release fertilizer after dewatering process. This technology is widely used in Sweden and Denmark, as evidenced by the more than 6000 references found.

PhosphoReduc is an adsorption technology based on a CaO and FeO rich industrial by-products that are capable to reduce phosphorus content more than 95% achieving concentration below 0.05 mg/L. In addition, it is also able to reduce the amount of TSS, bacteria load, dissolved metal ions, organic matter and nitrogen from treated effluents. Depending on the adsorbent, adsorption capacity ranged between 3.5 and 5.5 g PO₄/kg after 18 – 24 hours of HRT. Adsorbent showed lifetime between 5 and 7 years with a removal efficiency over 90% and loaded filtration media could be potentially used as a soil amendment or fertilizer, if it is allowed by the local legislation. It has been implanted in small and medium size WWTP in the USA, Brazil or Taiwan (Drizo, 2016, 2012).

CoMag is an improved flocculation, coagulation and clarification process by infusion of magnetite in the reaction tank to selectively precipitate phosphorus. Chemical flocks in the CoMag system reported a settle speed 30 times faster than conventional clarification. The system can handle a wide range of flows and loads, removes oil and grease and can achieve total phosphorus concentration below 0.05 mgP/L with low Capital Expense (CAPEX) and Operational Expense (OPEX). Currently, this process is used in 20 WWTPs in the USA and it is being studied under pilot plant conditions in UK (Bratby, 2016; Dery et al., 2015; Tozer, 2007).

BluePro is a reactive filtration process by using Fe functionalized sand surface as adsorbent. It is a modular process, which can be easily adapted for WWTP expansion and reported a payback period below 3 years. Potential applications of this technology include metals removal and denitrification, in addition of phosphorus reduction below 0.05 mgP/L of total phosphorus content (Evergreen Water Solutions, 2013).

For the case of ammonium not full commercial references for recovering ammonium from the treated effluents on WWTP incorporating conventional activated sludge and efforts still with lower TRL have been reported mainly in side-streams generated on the anaerobic sewage sludge treatment. It is worth to mention that most of proposed technologies have been developed for the single recovery of phosphate and ammonium in separate pathways whereas simultaneous phosphate and ammonium recovery by using calcium (Ca-Ze) and magnesium (Mg-Ze) activated zeolites have been recently evaluated and postulated at Barcelona Tech-UPC (Table 1). The use of zeolitic materials properly activated with Ca and Mg ions assures the simultaneous recovery of both nutrients. Additionally, their physical and morphological properties are suitable to be used as nutrient carriers for operating as slow-release fertilizers and they improve soils properties (e.g., texture, water content, etc...) were tested for the simultaneous recovery of these nutrients by obtaining a phosphorus and nitrogen rich fertilizer. Published studies demonstrated that, ammonium is immobilized on such sorbents by sorption, ion-exchange processes or retained as low solubility minerals forms (NH₄MgPO₄), while phosphate is mainly present as low solubility mineral phases (MgNH₄PO₄, CaHPO₄,) (Hermassi et al., 2018)

After the critical review of the state of the art, it can be concluded that there are several technologies available for the recovery of phosphorus from the WWTPs, but there is a lack of solutions focused on the recovery of nitrogen, since it is not a resource that presents scarcity, as if it exists for

phosphorus. Different initiatives are widely developed worldwide to recover P for fertilization application from wastes generated on WWTPs. All of them are centered in two main directions: a) recovery of P as struvite from the sludge anaerobic digestion side-streams and b) recovery of P as phosphoric acid from the mono-incineration ashes generated from thermal treatments of sewage sludge in most of the northern countries of Europe and Japan (Amann et al., 2018). However, any initiative to recover ammonium at full scale could be found and the need to promote the deployment of solutions is a real challenge for the next decade.

In view of that, the aim of this study is to assess the economic feasibility of implementing alternative technologies for simultaneous phosphorus and nitrogen recovery from WWTP treated secondary effluent considering the CAPEX and OPEX of the required facilities, and potential revenues from cost savings and the sale of loaded adsorbent. The economic feasibility assessment will be performed for a scenario in which the following boundary conditions has been selected: i) the use of a sorbent with dual capacity to sorb N and P simultaneously; ii) the implementation to a large WWTP (treatment capacity > 3m³/s) that incorporates a tertiary treatment; and iii) the saturated sorbent enriched on N, P will be commercialized as fertilizer.

9.2. Methodology for the economic feasibility study.

9.2.1. Ammonia and phosphate adsorbents selection.

In previous studies the sorption evaluation of polymeric adsorbents as well as different salt activated synthetic zeolites at the lab scale have been assessed. A summary of adsorption performances of these adsorbents is summarized in table 9.2 where $t_{90\%}$ is the time required for reaching the 90% of maximum adsorption capacity.

Table 9.2. Equilibrium and kinetic sorption properties of assessed adsorbents at lab scale

	q_N [mg N/g] ¹	q_P [mg P/g] ²	$t_{90\%}$ [min] ³	Reference
FO36	-	29.1	65	(You et al., 2016b)
Fiban-As	-	52.9	50	(You et al., 2016a)
Ze-Na	13.2	-	10	(You et al., 2017b)
Ze-K	22.6	-	2	
Ze-Ca	95.7	38.8	30	(You et al., 2017a)
Ze-Mg1	42.9	10.5	20	
Ze-Mg2	47.1	7.8	-	

¹ q_N [mg N/g] is the total sorption capacity for ammonium, ² q_P [mg P/g] is the total sorption capacity for ammonium, and ³ $t_{90\%}$ is the time required for reaching the 90% of maximum adsorption capacity.

The synthetic zeolite Ze-Ca was selected for the present economic feasibility study as it reported the best performance for simultaneous recovery of nitrogen and phosphorus from wastewater treated effluent in terms of sorption capacity for both nutrients and due to the kinetic parameters that showed a faster sorption rate, which can lead to a short HRT. In addition, tertiary reactive

media filtration proved to be one of the most cost effectiveness alternatives for phosphorus removal in municipal wastewater treatment (Bashar et al., 2018).

Furthermore, it is considered the Baix Llobregat WWTP as it is the largest and newest WWTP in the Metropolitan Area of Barcelona, which includes a water regeneration station, built in 2007 and which is based on filtration and reverse osmosis. This facility could be used for the filtration and separation of loaded zeolite from treated secondary effluent (Hermassi et al., 2016).

9.2.2. The Baix Llobregat WWTP (BLI-WWTP) as nutrients recovery site study.

The BLI-WWTP began to work at 2002 and several improvements have been introduced since then, such as the biologic treatment of wastewater, anaerobic digestion of sewage sludge or the implementation of a water regeneration station.

Nowadays, this plant treats the 36% of the wastewater generated in the Metropolitan Area of Barcelona and it provides service to approximately 2 million of population equivalent (PE) by treating 273330 m³/d of wastewater, which represents 65% of its design flow (4.86 m³/s) (Àrea Metropolitana de Barcelona, 2017a). According to the average composition of the wastewaters treated with influent values of 60 gN/m³ and 6.8 gP/m³ the amount of N and P reaching the WWTP approaches to 9200 ton/y and 1100 ton/y, respectively.

12 identical working lines consisting on a primary settlement, and a conventional secondary biological treatment compose the BLI-WWTP. The main part of the treated effluent is discharged into the Mediterranean Sea through an emissary 3.2 km long (Köck-Schulmeyer et al., 2011).

In addition, a regeneration station was installed in 2007, capable to provide tertiary treatment to WWTP effluent for reuse in agricultural irrigation, wetland conservation, groundwater hydraulic barriers against marine saline intrusion, and groundwater recharge of Llobregat river aquifer. The tertiary treatment consists on ultrafiltration (UF), reverse osmosis (RO), reverse electrodialysis (EDR) and disinfection (Köck-Schulmeyer et al., 2011). Analysis of the average composition of the treated water along 2012 indicates that approximately 1200 tonN/y and 390 tonP/y were discharged to the Mediterranean Sea.

The scheme of the BLI-WWTP and the main stages of treatment are shown in Figure 9.1. The zeolite filtration system is proposed to be installed after the secondary clarifier to use the existing ultrafiltration (UF) unit from the regeneration station for separating the loaded zeolite from the treated water as has been proved successfully elsewhere (Hermassi et al., 2016).

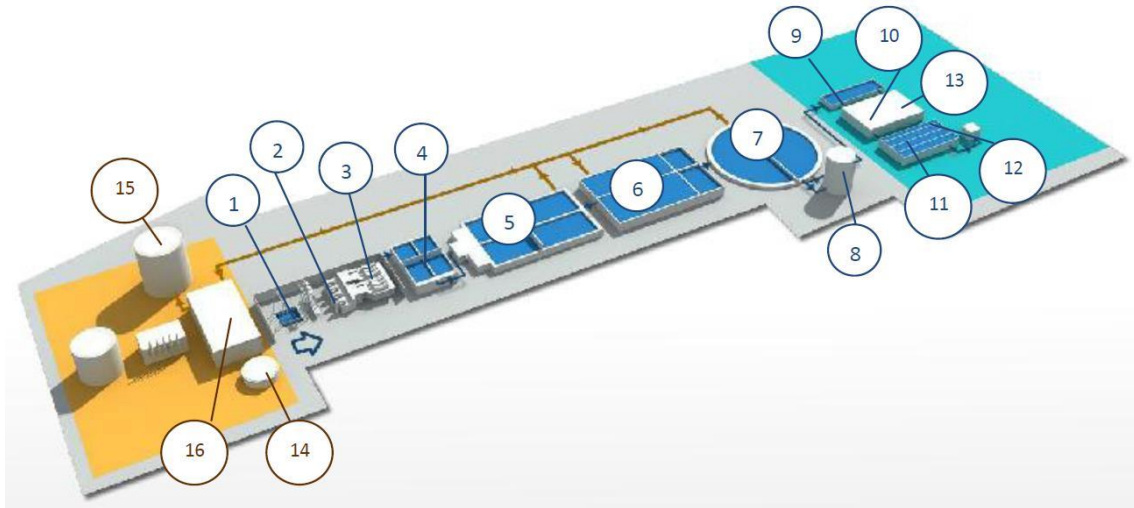
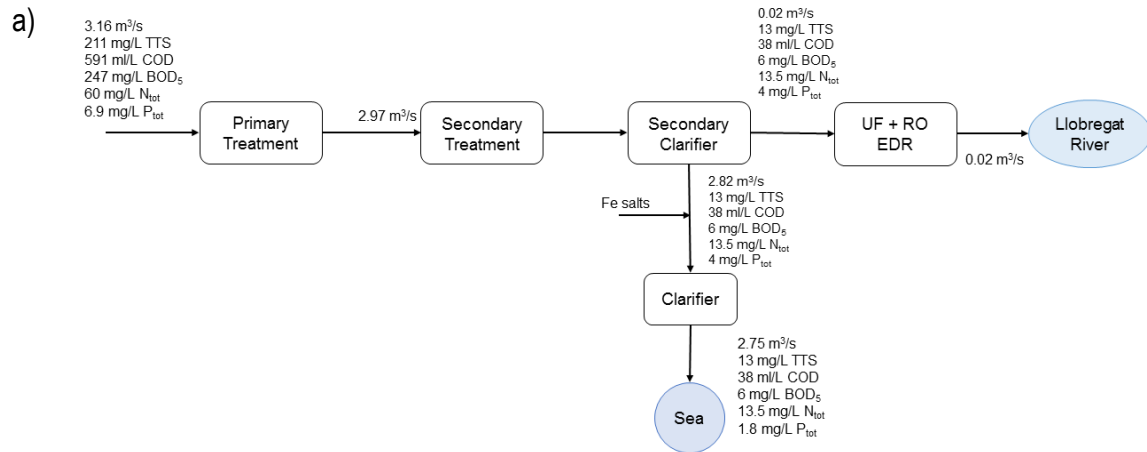


Figure 9.1. Scheme of the BLI-WWTP configuration (Àrea Metropolitana de Barcelona, 2017b)

¹ Sedimentation tank, ² Pumps, ³ Bar screen, ⁴ Grit chamber, ⁵ Primary clarifier, ⁶ Biologic reactor, ⁷ Secondary clarifier, ⁸ Treated water discharge, ⁹ Flocculation tank, ¹⁰ Lamella clarifier, ¹¹ Screening, ¹² Disinfection, ¹³ UF and RO, ¹⁴ Sludge thickener, ¹⁵ Sludge Digester, ¹⁶ Sludge thermic dewatering

Finally, the current phosphorus removal working scheme in BLI-WWTP (Figure 9.2a) and the proposed scheme for nutrients recovery (Figure 9.2b) are depicted in Figure 9.2. Flow distribution shown in Figure 9.2b is defined in order to obtain a final P concentration below 2 mgP/L as it is established by the EU regulation (Mas-Pla et al., 2006)



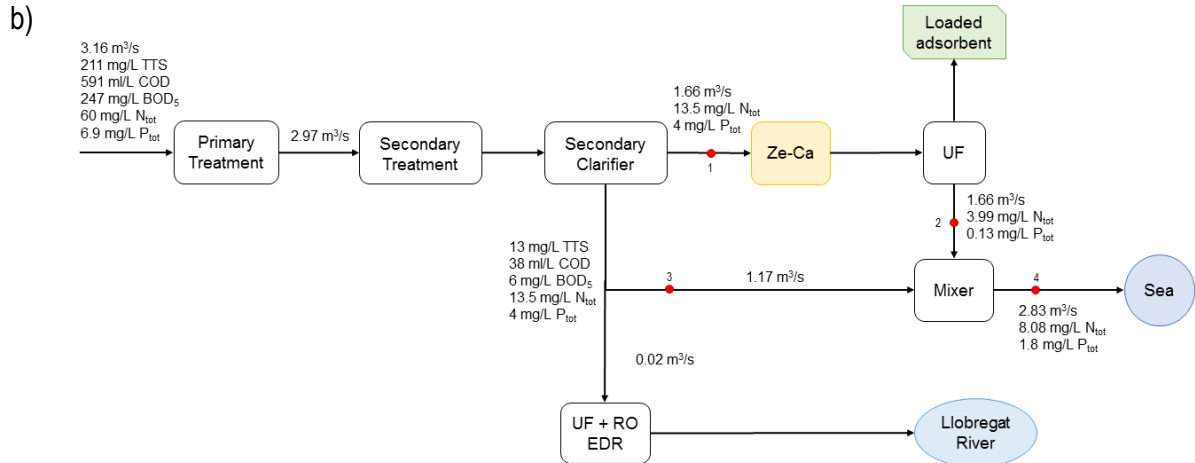


Figure 9.2. Summary of a) current and b) purposed working scheme and sampling data for recovery of nutrients at the BLI-WWTP. Flow-rates and composition of the main parameters have been provided by AMB (Àrea Metropolitana de Barcelona, 2017a)

It is worth to mention that average wastewater sampling data shown in Figure 9.2 are from 2010, but because the BLI-WWTP has not introduced any significant technical modifications since then, composition of initial and treated wastewater would present no relevant changes and can be used for this analysis. However, BLI-WWTP total treated flow is updated to the last available records (2015).

9.2.3. Economic Assessment

Financial ratios were used in this work for assessing the feasibility of implementing Ze-Ca facility in the BLI-WWTP. The net present value (NPV), internal rate of return (IRR), return of investment (ROI) and payback period (PP) were estimated for this purpose.

Net Present Value (NPV) (Eq. 9.1) is expressed as the difference between the current value of cash of inflows and outflows over a period and it is used to analyze the profitability of any investment.

$$NPV = \sum_{t=1}^T \frac{B_t - C_t}{(1 + r)^t} \quad \text{Eq. 9.1}$$

where B_t and C_t are the inflows and outflows at the period t , and r is the discount rate.

Internal Rate of Return (IRR) is calculated by solving the Eq. 9.2 and it specifies whether the project breaks even with an NPV of zero; if the obtained result is greater than the discount rate, the project is feasible.

$$0 = investment + \sum_{t=1}^T \frac{B_t - C_t}{(1 + IRR)^t} \quad \text{Eq. 9.2}$$

Return of Investment (ROI) (Eq. 9.3) is a measure to evaluate the efficiency of an investment, since it measures the amount of return of an investment in relation to the cost of investment.

$$\text{ROI} = \frac{\text{Gain from investment} - \text{Cost of investment}}{\text{Cost of investment}} \times 100 \quad \text{Eq. 9.3}$$

The Payback Period (PP) (Eq. 9.4) is the time required to recover the cost of the investment. For ROI calculation, will be considered a lifetime of 20 years for the WWTP (Machado et al., 2007).

$$\text{PP} = \frac{\text{Cost of investment}}{\text{Annual Gain from investment}} \quad \text{Eq. 9.4}$$

The investment is required for the installation of zeolite filtration tanks as well as influent and effluent pumping systems and plant pipelines modification. No further investment is needed as the zeolite filtration will be performed by gravity (Alkas et al., 2013; Foreman, 1985; Hansen, 1997) and the separation system will use the existing ultrafiltration modules from the regeneration station.

For zeolite filtration tank dimensioning it was considered the BLI-WWTP maximum treatment flow, the volume of zeolite for targeting a phosphorus concentration of 0.01 mg/L and the volume of wastewater for 120 minutes of HRT by using a scaling factor of 4 to the kinetic parameter obtained at the laboratory scale (Table 9.2). Taking into account these criteria it was determined that the volume needed for the filtration tanks was 1320 m³.

The OPEX were calculated considering the cost of adsorbent as well as a 5% increase of the current BLI-WWTP OPEX (8.4 M €/year) due to the significant increase of operational demand of ultrafiltration modules in terms of energy and maintenance.

Finally, as the loaded zeolite contains calcium phosphate (You et al., 2017a) it can be sell as Triple SuperPhosphate (TSP) fertilizer with approximately a 15% of phosphorus nutrient content. According to Maaß (2014) the commodity price for fertilizer which contains 20% of phosphorus nutrient is set on 220 €/ton. In addition, the implantation of zeolite filtration system would lead to chemicals cost saving related to iron salt use in order to fitregulation phosphorus levels in discharged water. According to a non-published study performed by SUEZ Spain, the average cost of the phosphorus chemical removal is estimated on 0.7 €/kg P_{in}.

9.3. Results and Discussion

9.3.1. Economic Assessment

For CAPEX estimation it was taken as a reference the cost calculation performed by Blasco Saiz (2010) for a 1000 m³ tank resulting in 250.6 k€ at 2010. Thus, considering a linear increase of the cost with the tank volume and a Retail Price Index (RPI) increase of 11.6 % (Instituto Nacional de Estadística, 2017) from 2010 to December 2017, the investment for each sedimentation tank can be estimated on 370 k€. For achieving 1.8 mgP/L of total phosphorus concentration at the discharged wastewater stream, the installation of zeolite filtration tank in 7 operating lines is needed, leading to a cost of 2590 k€.

Furthermore, according to the project for reusing BLI-WWT treated water quotation for the BLI-WWTP regeneration station, pumping facilities and pipelines installation would cost around 1500 k€ (Depuradora Baix Llobregat S.A., 2007), leading to a total initial investment of 4090 k€.

Wastewater production in Barcelona Metropolitan Area have been quite constant with a fluctuation of $\pm 1\%$ in the last 3 years, thus, for the economic assessment during BLI-WWTP lifetime, it was considered an annual increase of treated flow of 1%. In addition, it was considered a discount rate of 4% and adsorbent cost of 115 €/ton. A summary of variables considered for the economic analysis is listed in the Table 9.3.

Table 9.3. Summary of considered variables for economic assessment

BLI-WWTP lifetime	20 years	Discount rate	4%
P_{tot} after zeolite filtration	0.01 mgP/L	Raw zeolite price	115 €/ton
P_{tot} final	1.8 mgP/L	Loaded zeolite (15% of PO_4^{3-} content)	220 €/ton
HRT	120 minutes	Chemical cost saving	0.7 €/kg P_{in}
Variation of BLI-WWTP treated flow	+ 1% per year		

The expected cash flow of the zeolite filtration facility for the BLI-WWTP lifetime is summarized in Table 9.4 and the evolution of NPV (according to Eq. 9.1 – 9.4) is exhibited in Figure 9.3.

Table 9.4. Expected cash flow and working parameters for the BLI-WWTP

	Flow (hm^3/y)	Ze-Ca (ton/y)	OPEX (k€/y)	Income (k€/y)	Chemical Saving (k€/y)	Profit (k€/y)
2018						-4090.0
2019	99.7	5051	825.9	1569.2	249.6	535.0
2020	100.7	5102	831.7	1582.9	252.2	542.9
2021	101.7	5153	837.7	1596.7	254.7	550.8
2022	102.7	5205	843.6	1610.7	257.2	558.8
2023	103.8	5258	849.7	1624.8	259.9	566.9
2024	104.8	5311	855.7	1639.1	262.5	575.1
2025	105.9	5364	861.9	1653.5	265.1	583.4
2026	106.9	5418	868.1	1668.0	267.8	591.7
2027	108.0	5473	874.4	1682.7	270.5	600.1
2028	109.1	5528	880.7	1697.6	273.2	608.6
2029	110.2	5583	887.1	1712.6	275.9	617.2
2030	111.3	5640	893.6	1727.7	278.7	625.9
2031	112.4	5696	900.1	1743.0	281.5	634.7
2032	113.5	5754	906.7	1758.4	284.4	643.5

Table 9.4. Expected cash flow and working parameters for the BLI-WWTP (cont.)

	Flow (hm ³ /y)	Ze-Ca (ton/y)	OPEX (k€/y)	Income (k€/y)	Chemical Saving (k€/y)	Profit (k€/y)
2033	114.6	5812	913.3	1774.0	287.2	652.4
2034	115.8	5870	920.1	1789.8	290.1	661.5
2035	116.9	5929	926.9	1805.7	293.0	670.6
2036	118.1	5989	933.7	1821.8	296.0	679.8
2037	119.3	6049	940.6	1838.0	299.0	689.1
2038	120.5	6110	947.6	1854.3	302.0	698.5

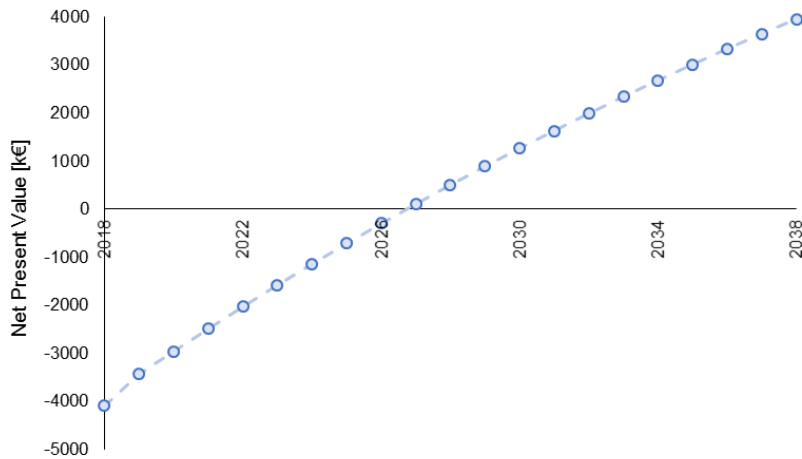


Figure 9.3. Evolution of Net Present Value during WWTP lifetime

The NPV values are plotted as a function to time (years) (Figure 9.3), indicating that positive values are achieved after eight years of the operation of the nutrients recovery process.

Few data are available in the literature in terms of payback periods (PP) for the implementation of nutrients recovery option on waste water treatment plants. The most successfully technology in terms of wide deployment, could be the P recovery units from side streams of sludge anaerobic digestion. Published reports from technology providers or WWTP facilities shown that similar PP have been reported from 10 up to 20 years, as it is mainly dependent on the price allocated for recovered struvite fluctuating from negative values up to positive values (300 €/ton struvite) (Cornel and Schaum, 2009; Dockhorn, 2009; Peng et al., 2018)

According to data showed in the Table 9.4, the financial ratios were calculated in order to assess the feasibility of implementing zeolite filtration for nutrients recovery from the BLI-WWTP and are summarized in Table 9.5.

Table 9.5 Financial ratios estimated according for the nutrients recovery in the BLI-WWTP

Net Present Value [k€]	3950.4
Internal Rate of Return [%]	13
Return of Investment [%]	300
Payback Period [years]	7.6

As shown in results (Table 9.5), the investment in zeolite nutrients recovery unit is economically feasible with a relatively short payback period and the obtained IRR is greater than the considered discount rate. It is worth mentioning that this positive result is due to the existence of the ultrafiltration unit as part of the regeneration station. Otherwise, the cost of the ultrafiltration equipment and the installation of its control systems is estimated at 9.1M € (Depuradora Baix Llobregat S.A., 2007) and the results of the financial ratios would be less favorable as summarized in Table 9.6.

Table 9.6. Financial ratios estimated according for the nutrients recovery in the BLI-WWTP including UF unit

Net Present Value [k€]	-4799.6
Internal Rate of Return	-0.6
Return of Investment [%]	93
Payback Period [years]	24.6

Thus, the implementation of this technology for phosphorus and nitrogen recovery from wastewater secondary treated effluent is not feasible for smaller WWTPs that do not have tertiary treatment facilities based on membrane technologies (e.g., ultrafiltration).

9.3.2. Sensitivity analysis

As a WWTP lifetime has been set on 20 years for this analysis, some operations parameters are expected to be not constant. Then, a sensitivity analysis was performed considering four scenarios as follows: i) increasing the cost of zeolite; ii) reduction of the market price of zeolite loaded with nutrients; iii) reducing phosphorus discharge limit; and iv) increasing treated flow-rate.

The sensitivity analysis was carried out by considering the following variations in the key parameter:

- i. The price of raw and loaded zeolites is studied with variations of 5% taking into account possible market fluctuations as well as Retail Price Index increase along the WWTP lifetime.
- ii. The variation of phosphorus discharge limit is set on 0.2 mg/L at concentrations higher than 0.4 mgP/L and variations of 0.05 mgP/L for concentrations lower than 0.4mgP/L. These two variation limits are set according to technical possibilities for reducing phosphorus content in waste water effluents.
- iii. The WWTP treated flow is studied in increase intervals of 0.1 m³/s according to population increase in Barcelona Metropolitan Area and the trend in water consumption showed by the last five years.

Resulting financial ratios are showed on Figure 9.4.

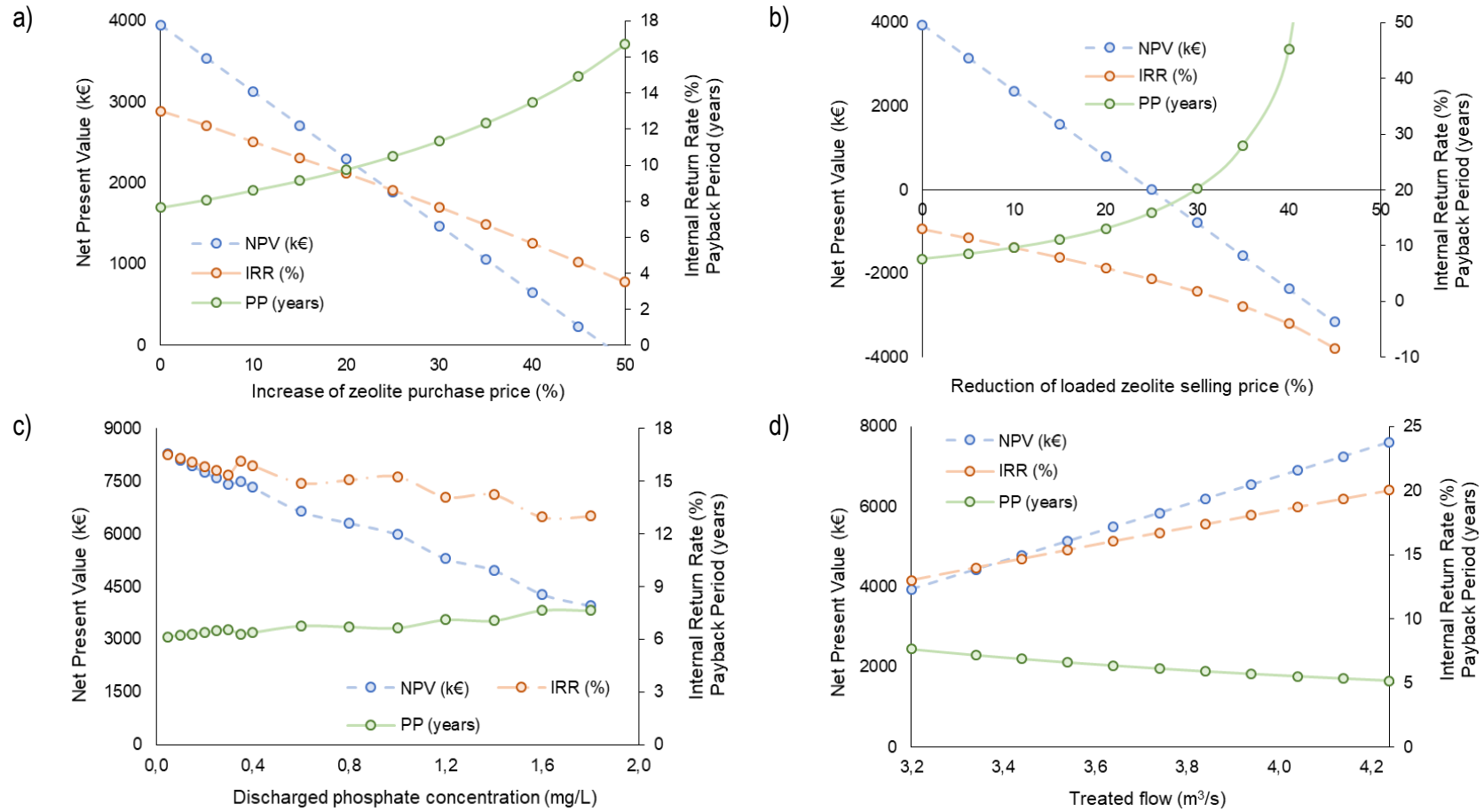


Figure 9.4. Evolution of financial ratios by varying a) zeolite purchase price; b) loaded zeolite selling price; c) phosphorus discharge limit; and d) treated flow

Increasing the cost of zeolite. As is shown in Figure 9.4a), with an increase in the purchase price of zeolite higher 45%, an Internal Return Rate of 3.5 is obtained, lower than the considered discount rate (4%); as well as a negative Net Present Value. These values indicate that the implementation of zeolite filtration system for nutrient recovery is not economically feasible.

As the Ze-Ca is obtained by hydrothermal synthesis from fly ash (Querol et al., 1996), is important to improve the efficiency of the process in order to avoid a significant increase of adsorbent's cost as well as reduce environmental impact of chemical and energy consumption in the synthesis stage. Analysis of the synthetic route of the zeolite production with zeolites producers as Industrias Químicas del Ebro (IQE) in Spain, the main reduction of the zeolite cost will be associated to the removal of final stage of drying. As the sorption process could be carried out using zeolites in a slurry mode the cost of the zeolite could be reduced by a factor of two.

Reduction of the market price of zeolite loaded with nutrients. Sensibility analysis reported that if zeolite selling price decreases over 25 %, Internal Return Rate would be smaller than the considered discount rate of 4% and the reported Net Present Value would be -2.4 k€, which means that the investment related to the construction of Ze-Ca filtration tanks and pumping system would not be recovered along the BLI-WWTP lifetime.

Since there is a great interest in the recovery of nutrients from WWTP, it is feasible to expect a reduction in the price of phosphorus-based fertilizer. Thus, is important to research more efficient sorption processes in order a sorbent loaded with more N and P content and thus increase its market value.

In the case of Europe, the inclusion of phosphorous and the phosphatic rock, as one of the elements inside the Critical Raw Materials List (European Commission, 2017), the recovery of P from secondary resources will be mandatory. It has been estimated that up-to 30-40% of the total P needs at EU level could be recovered from the urban waste water cycle, and this has been traduced that in countries like Switzerland recovery of nutrients from WWTP is an obligation from 2016 (United Nations World Water Assessment Programme, 2017). The main initiatives have been centered on the recovery of P from sewage sludge sidestreams as struvite or as phosphoric from monoincineration ashes of sewage sludge. In both cases the economic feasibility of the technologies developed is not clear, however political and regulatory support is being developed to support both recovery options.

It is important to develop new initiatives which allows not only to recover nutrients (N , P and K) from WWTP, but also renewable energy, metals and minerals in order to increase the economic profitability (Mayer et al., 2016).

Reducing phosphorus discharge limit. As the proposed WWTP configuration implies the installation of Ze-Ca filtration tanks in only 7 working lines in order to minimize the project capital expenses, the reduction of discharge limits implies the deviation of treated secondary effluent to zeolite filtering system for being mixed with unfiltered secondary effluent. This fact leads to the need of more filtration tanks. Thus, more investment is needed for the installation of additional filtration tanks and related pumping facilities, resulting in financial ratios fluctuation showed in Figure 9.4c.

However, more restrictive regulation in phosphate discharge limits would not affect negatively the economic feasibility of the implantation of the Ze-Ca filtration facility. On the contrary, as is shown in Figure 9.4c, more stringent regulations would lead to NPV and IRR increase as well as a reduction of Payback Period.

Increasing treated flow. Increasing treated flow leads to an improvement of all financial ratios. This fact makes much more attractive the installation of zeolite filtration system for nutrients recovery since the density of population in the Metropolitan Area of Barcelona increases continuously, improving economic benefits from the implementation of zeolite filtration system. However, it is important to note that as higher is the treated flow, the lifetime of the UF membrane will be shorter and the impact of this parameter needs to be evaluated in a more detailed economic evaluation.

After performing the economic assessment of the implantation of Ze-Ca filtration for nutrient recovery, resulted in an average operational cost (OPEX/treated flow) of 0.089 €/m³, significantly lower than 0.15 €/m³ for PhosphoReduc or 0.114 €/m³ for Necovery, reported for phosphorus and nitrogen recovery, respectively.

Currently, the operational cost of BLI-WWTP is estimated on 0.084 €/m³, slightly lower than 0.089 €/m³ after substituting phosphorus chemical precipitation by zeolite filtration system. However, if an analysis is made of total value of the recovery of nutrients taking into account the savings in chemical, the production of fertilizers, the improvement of the operation and the performance in the BLI-WWTP, the net balance is an economical benefit of 0.005 €/m³.

Furthermore, it is important to point out other non-economic benefits as protection and improvement of Water Quality or food Security improvement and social equity (Mayer et al., 2016). Thus, the implementation of Ze-Ca for nutrient recovery from WWTP secondary effluents leads to multiple benefits as:

- i. Promotes circular economy by valorizing the fly ash, a byproduct of coal power plant, as a sorbent for nutrients recovery
- ii. Reduces the environmental issues due to the metal lixiviation of fly ash disposal
- iii. Simultaneous recovery of ammonium and phosphate from WWTP in order to obtain a nutrient rich fertilizer
- iv. Capacity to scale and adapt to new regulation by increasing HRT in the filtration tank and the sorbent dosage
- v. Economic benefit when selling the sorbent loaded as slow release fertilizer

9.4. Conclusions

In this study, the feasibility of implementing a simultaneous ammonium and phosphate recovery system in the BLI-WWTP based on the sorption by a calcium-activated synthetic zeolite was assessed.

Results shown that the implementation of this alternative technology in BLI-WWTP is economically profitable, since it reported a payback period of less than 8 years and a IRR of 13%, much higher than considered discount rate. It is important to point out that these values are obtained due to the existence of an Ultrafiltration unit in the regeneration station of the studied WWTP. Otherwise, the required capital expense would be quite larger, and the economic assessment may not result feasible.

Sensitivity analysis showed that the critical parameters in economic feasibility are those related to the sorbent, both the cost of the sorbent (an increase of 45%) and the sale price (a decrease of 25%) could make the implementation economically unfeasible.

More research is needed in synthesis and activation of zeolites to reduce the effects of price fluctuation of the sorbent. In addition, more studies at the scale of the pilot plant of the performance of the uptake of nutrients as well as the potential uses of loaded zeolites are needed, which will allow to evaluate the economic feasibility of its implementation and would lead to a significant improvement both in the treatment of wastewater and to the management of fly-ash.

Finally, before the implementation of this system in a WWTP it is necessary to consider some problems such as the impact on the UF membranes, the needs of treated water flow to the zeolites filtration system and the logistics necessary to evacuate 5000 tons/y of zeolites loaded.

Acknowledgment

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Conclusions

10. Conclusions

Nowadays, due to the world's continuing growing population as well as current global energy crisis, WWTPs are no longer considered only as facilities for pollution reduction, but also as a source for the recovery of nutrients and energy. In addition, excessive nutrient loading on surface and ground water has been identified as the main contributor to the degradation of water quality and the reduction of aquatic life diversity.

In this thesis, several sorbents that include polymeric ion exchangers (Lewatit FO36 and Fiban-As); mono-valent (Ze-Na and Ze-K) and di-valent (Ze-Ca, Ze-Mg1 and Ze-Mg2) salt activated synthetic zeolites were assessed for nutrient recovery from urban WWTP secondary effluent in order to close the anthropogenic cycles of N and P, as well as promote the circular economy through the valorization of N and P recovered from WWTP as fertilizer. In addition, technical and economic analysis of integrating nutrients recovery in WWTPs was performed by choosing El Baix Llobregat WWTP (Barcelona, Spain) as case study.

Polymeric ion exchangers reported higher phosphate maximum sorption capacity than synthetic zeolites as well as a simpler operation through a fixed bed column configuration, while synthetic zeolites require ultrafiltration modules to separate the loaded sorbent from the treated water.

However, polymeric sorbents are not capable to remove both ammonium and phosphate since they only selectively uptake phosphate anionic species from aqueous solution. Moreover, desorption and regeneration studies revealed that although FO36 and Fiban-As can achieve a phosphate concentration factor up to 360, they cannot be reused.

Mono-valent zeolites resulted to be a feasible alternative sorbent for ammonium recovery from WWTP secondary effluent since not only can they be regenerated and reused, but they can increase the sorption capacity after each regeneration step. However, mono-valent zeolites were not capable to simultaneously recover ammonium and phosphate from wastewater treated stream.,

Di-valent zeolites were able to uptake both nutrients from waste water and reported the presence of P-containing minerals on loaded sorbents surface. Therefore, loaded di-valent zeolites could potentially be disposed directly for agricultural used.

The most relevant conclusions of each sorbent as well as technical and economic assessment are discussed below. Finally, as still a large effort on further research is required, prospects for future work are also detailed.

10.1. Key findings on polymeric ion exchangers

Both polymeric ion exchangers reported high selectivity for phosphate ions in the presence of common competing anions in urban WWTP such as chloride, nitrate, sulfate or bicarbonate. Moreover, FO36 and Fiban-As exhibited excellent phosphate removal capacity without any pH adjustment. The sorption mechanism of anionic phosphate species onto FO36 and Fiban-As could be explained by the formation of surface complexes and inner sphere bidentate complexes, respectively.

In presence of competing ions, FO36 and Fiban-As reported phosphate maximum sorption capacity of 89 ± 3 and 21 ± 2 mg $\text{PO}_4^{3-}/\text{g}$ FO36 and, 156 ± 9 and 13 ± 2 mg $\text{PO}_4^{3-}/\text{g}$ Fiban-As in equilibrium sorption and dynamic experiments, respectively.

Regeneration studies showed that the sorbent can be eluted efficiently with NaOH solutions (95 \pm 3% of elution) achieving pre-concentration factors in the range of 360 allowing the valorisation of these rich PO_4^{3-} solutions as Ca and Mg mineral phosphates. However, sorbents revealed not being suitable for reuse as during desorption process it showed iron content release as well as noticeable sorption capacity reduction.

10.2. Key findings on mono – valent zeolites

Modification of Ze-Na to potassium form (Ze-K) improved sorbent capability to be desorbed and reused despite the initial decrease of ammonium sorption capacity. In the first working cycle, Ze-Na and Ze-K reported sorption capacity of 109 ± 11 and 21 ± 3 mg NH_4/g , respectively, while in the third working cycle, the sorption capacity of both zeolites was around 45 ± 6 mg NH_4/g .

Neither Ze-Na nor Ze-K reported significant phosphate loading capacity, which would require the mixture of Ze-Na/Ze-K with zeolites capable to uptake phosphate from aqueous solution such as zeolites in di-valent (e.g., Ca, Mg...) and tri-valent (e.g., Fe, Al...) forms.

During the modification, sodium ions were fully exchanged by potassium ions at room temperature as the high Silicate Aluminum Ratio (SAR) zeolites such as Ze-Na, are more selective as bigger is the ionic radius. This selectivity explains the increasing affinity towards to potassium ions as well as the reduction of ammonium sorption capacity after the modification of Ze-Na to Ze-K.

Ammonium sorption mechanism onto both Ze-Na and Ze-K is mainly due to the ion exchange between ammonium ions present in aqueous solution and sodium and potassium ions present on the surface of zeolite as counter ion.

Moreover, Ze-K increased its sorption capacity after each regeneration step due to alkaline activation of its pores. Therefore, Ze-K is suitable for being reused in several sorption – desorption working cycles and good alternative for the recovery of concentrated ammonium streams from loaded sorbents desorption.

10.3. Key findings on di – valent zeolites forms

Salt activation of Ze-Na to calcium and magnesium forms (Ze-Ca, Ze-Mg1 and Ze-Mg2) improved the zeolite phosphate sorption capacity. In the case of Ze-Ca, higher ammonium sorption capacity compared to Ze –Na was reported, since an increase in temperature during activation represented an increase in zeolite porosity, therefore in its specific surface.

In ammonium – phosphate binary solutions, Ze-Ca, Ze-Mg1 and Ze-Mg2 reported maximum phosphate sorption capacity of 120 ± 7 , 60 ± 14 and 24 ± 4 mg PO_4/g , respectively. The phosphate sorption mechanism onto Ze-Ca and Ze-Mg is mainly due to the formation of phosphate minerals

such as calcium phosphate hydrated, magnesium phosphate hydrated, HAP or MAP on zeolite surface and into aqueous solution.

In binary solutions, maximum ammonium sorption capacities of 123 ± 9 , 55 ± 2 and 32 ± 2 mgNH₄/g were reported for Ze-Ca, Ze-Mg1 and Ze-Mg2, respectively. Ammonium sorption mechanism onto zeolites is mainly due to ion exchange with calcium or magnesium ions.

The process of modifying zeolites depends on temperature since high SAR zeolites reported more affinity towards the monovalent ions than the divalent ones. Therefore, the heating provides the energy required to exchange calcium and magnesium ions for sodium ions. This behavior was observed in the modification of zeolites to the magnesium form, where the modification of zeolite at high temperature (Ze-Mg1) reported more than twice the magnesium content than the process at room temperature (Ze-Mg2).

It should be noted, the high affinity of the Ca / Mg zeolites for ammonium and phosphate ions, the potential slow release of nutrients since their extraction is carried out through the formation of Ca-P and Mg-NP minerals and the capacity of soil improvement, all the aforementioned allows to postulate the loaded zeolites charged as potential slow-release inorganic fertilizer.

10.4. Key findings on economic assessment

As described in Chapter 9, the implementation of alternative N and P simultaneous recovery technology based on a hybrid system (Ze-Ca bed filtration and UF) in a WWTP is economically profitable, although the result depends to a large extent on the existing facilities of the WWTP, since UF equipment is required to separate the loaded zeolites from water stream. The case study showed that the capital expenditure required for the installation of filtration modules can lead to an unfeasible economic evaluation.

The sensitivity analysis showed that the critical parameters in economic feasibility are those related to the zeolite market, the sorbent purchase price and the sale price of the loaded zeolite. An increase of the first and a decrease of the second could make the implementation of nutrient recovery in the WWTP economically unfeasible. In addition, the effect of the economy of scale was observed in terms of the treated flow. Thus, the implementation of the filtration system based on Ze-Ca may not be economically viable for a WWTP smaller than BLI-WWTP.

However, is important to point out that total value of nutrient recovery includes other non-economic benefits as follows:

- i. Closes the anthropogenic cycle of phosphorus and reduces the demand of mined phosphatic rocks
- ii. Closes the anthropogenic cycle of nitrogen and reduces the energy consumption for N₂ fixation through Haber-Bosch process
- iii. Promotes the circular economy by re-valORIZING nutrients contained in wastewater streams
- iv. Improves the water quality, food security and social equity

10.5. Prospects for future work

The United Nations established long term sustainability, water sanitation and responsible production as main topics among the 17 Sustainable Development Goals for the year 2021. In this framework, N and P recovery from urban WWTP through sorption and their revalorization as fertilizer may result in a feasible alternative to phosphatic rock mining for supplying world food demand.

However, additional research is required as sorption processes assessed in this thesis were only studied at laboratory scale and proper scaling factors needed to be proven at pilot plant scale for finally be integrated in urban WWTP facilities.

In addition, solubility of P-containing minerals precipitated onto zeolites surface as well as P release rate must be studied to establish the bioavailability of loaded nutrients, that is, its capability to be used as fertilizer.

Finally, it may be necessary to consider technical and logistical issues. In the case of implementing Ze-Ca filtration, the lifetime reduction in WWTPs UF equipment due to the requirement of a separate treated water stream from loaded zeolites and the management of evacuation of more than 1000 tons of loaded zeolites per year for agricultural purposes should be assessed.