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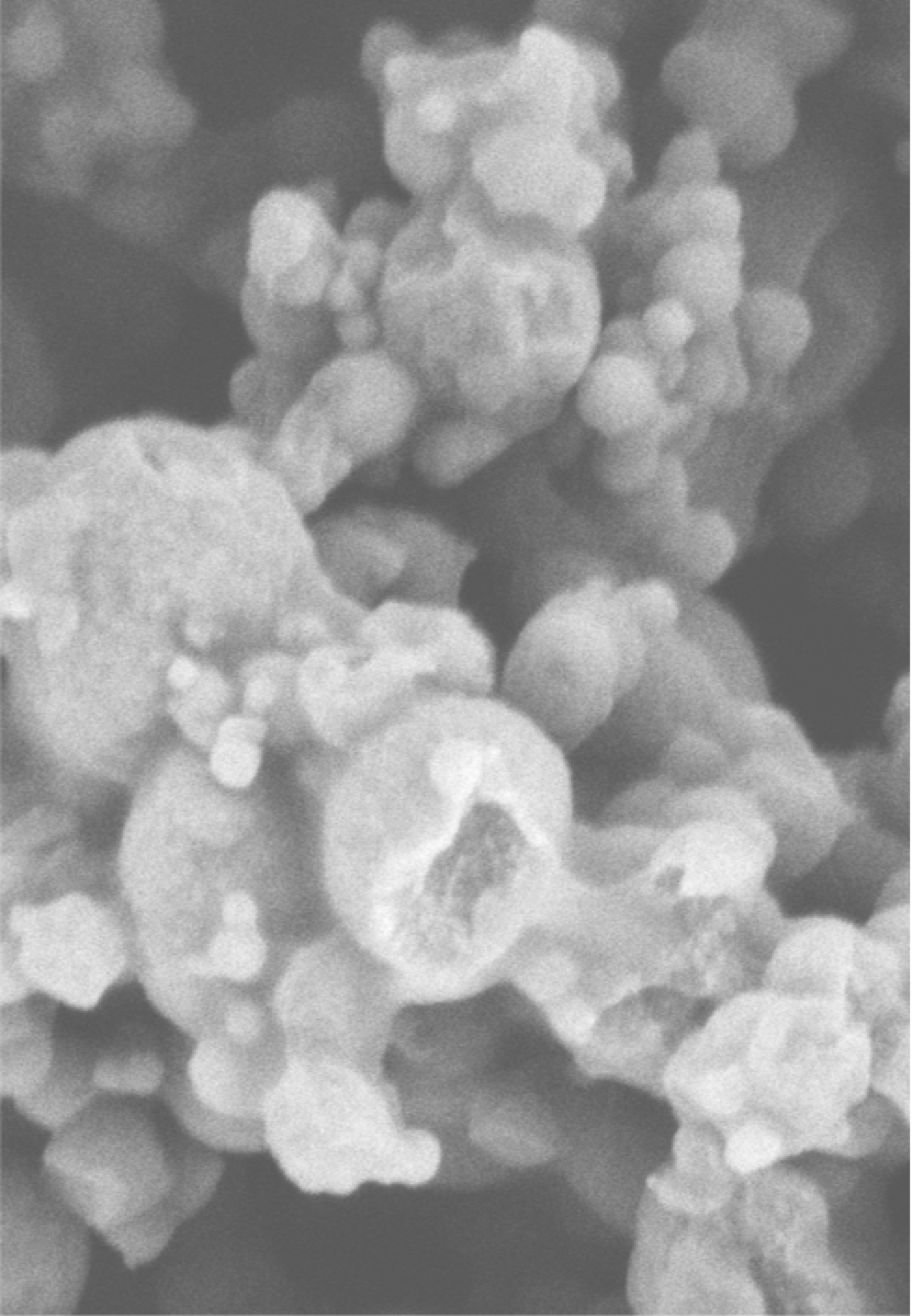

Tesi Doctoral

Miquel A. Riera Torres

2010

Institut d'Investigació Tèxtil
i Cooperació Industrial
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UPC

Departament d'Enginyeria
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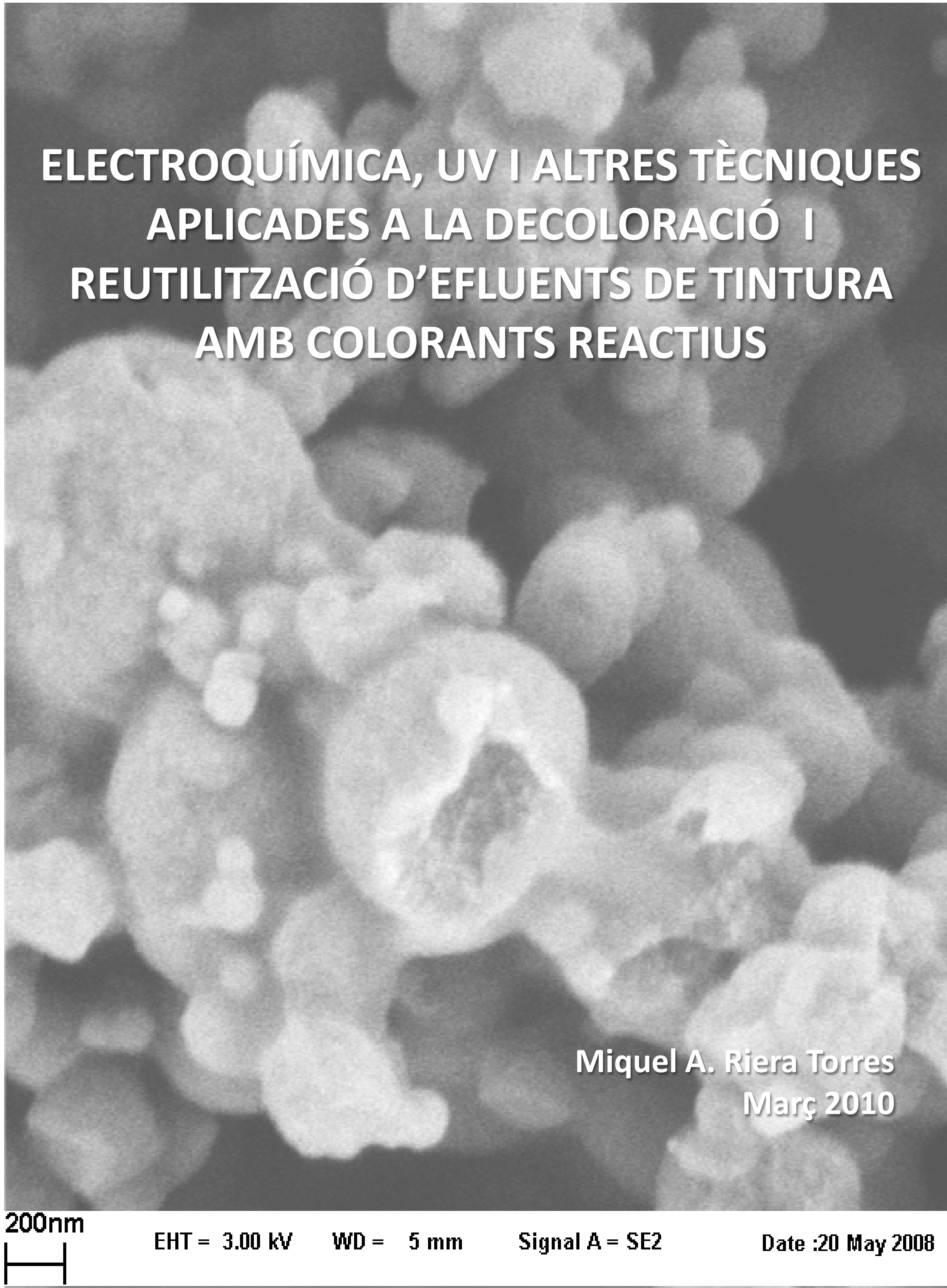
UNIVERSITAT POLITÈCNICA DE CATALUNYA

ELECTROQUÍMICA, UV I ALTRES TÈCNIQUES APLICADES A LA DECOLORACIÓ I REUTILITZACIÓ D'EFLUENTS DE TINTURA AMB COLORANTS REACTIUS

Miquel A. Riera Torres
Març 2010



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Memòria presentada per en

Miquel A. Riera Torres

per optar al grau de Doctor

per la Universitat Politècnica de Catalunya

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Terrassa, 9 febrer 2010

Aquesta tesi doctoral forma part dels estudis realitzats amb el suport econòmic dels projectes:

- “Aplicación de métodos electroquímicos a la degradación de colorantes reactivos y reutilización de las aguas residuales de tintura”, referència CTM2004-05774-CO2-01/TECNO finançat pel Ministerio de Educación y Ciencia.

- “Procesos electroquímicos aplicados a la degradación de colorantes reactivos y a la reutilización de las aguas residuales de tintura”, referencia CTM2007-66570-C02-01/TECNO, finançat pel Ministerio de Ciencia e Innovación.

Una paret pot ser un límit o un repte, depèn de tu

Agraïments

Els agraïments és un dels apartats que des d'un principi vaig tenir més clars a l'hora de començar a redactar la tesi i un dels que més il·lusió em feia escriure. Avui, a falta de pocs dies per acabar la tesi, m'agradaria creure que aquestes primeres pàgines transmetran a tots aquells que hi apareixen el sentiment que amaguen i que potser no he estat capaç de transmetre durant aquests anys.

En primer lloc, voldria agrair a la directora de la tesi, Dra Gutiérrez-Bouzán, la seva ajuda incondicional durant tots aquests anys. En segon lloc, expressar el meu agraïment al Dr Crespi i al Laboratori de Control de la Contaminació Ambiental d'INTEXTER així com al mateix centre i les persones que el formen, per tots els esforços dedicats. Igualment, al Departament d'Enginyeria Tèxtil i Paperera i a la Universitat Politècnica de Catalunya. Außerdem möchte ich Dr. Tauer und dem Max Planck Institut danken. També vull agrair la col·laboració, especialment en la part experimental de la tesi de les següents persones (citades per ordre cronològic): Tiina Ahokas, Lahti University (Finland); Laura Ruíz, UPC (Catalunya); Pedro Cardoso, Germano Torres i Mª Helena Pinto, Universidade Católica Portuguesa (Portugal); Marta Ruíz i Ariadna Saez, UPC (Catalunya) i Catarina Pereira, Universidade Católica Portuguesa (Portugal).

Finalment, no puc oblidar a altres persones que d'una manera o altre també han contribuït en aquesta tesi: Víctor, ara Dr López-Grimau, per haver establert el punt de partida d'aquest treball; Hugo, ahora Dr Hernández, por tu apoyo durante mi estancia en el Max Planck Institute y por tu amistad; Nicola Ritter, por ayudarme a personalizar estos agradecimientos; J. A. Navarro, per la seva ajuda en les tintures i Mireia Sala, aviat Dra Sala, a qui espero aquest treball resulti útil.

A més dels agraïments anteriors, formals i alguns en part protocol·laris, no vull deixar de fer-ho a les persones que m'han acompanyat durant aquesta tesi. En primer lloc, i indubtablement, a les noies del laboratori: Carmen, Mercè i Montse i al Crespi. A la Carmen… la veritat és que caldria escriure una altre tesi per agrair-li tot el que li agrairia. Senzillament ho faré per haver confiat en un noi que als matins no sempre arribava amb els ulls gaire oberts (espero no haver-te decebut massa), per tot el seu temps i molt especialment per la seva relació personal. A la meva "tieta" Mercè (espero que no t'importi la llibertat que m'acabo de prendre ;)) en gran part pel que per mi significa poder fer aquesta broma i perquè per a mi ha estat una sort haver compartit moments amb tu dels que guardo i guardaré molt bons records. A la Montse, per ser com és, per haver-me alegrat tants dies, per haver fet la millor portada de tesi que mai s'ha vist i per haver contestat sempre amb un somriure d'orella a orella totes les vegades que al laboratori vaig dir: "Ummm.... Montse.... ?" sabent que aquella frase solia significar .... "tinc un problema...." i al Crespi, per la seva ajuda i per haver estat un model a seguir.

Klaus hat mich durch seine Passion für die Wissenschaft daran erinnert warum ich Chemie studiert habe. Während des Aufenthaltes in Deiner Gruppe hast Du mir das Gefühl gegeben, Wissenschaftler zu sein und das war großartig.

I com no, a tota la meva família. Especialment als meus pares, el Miquel i la Maria, per haver cregut que ho podia fer, per haver-me donat suport tantes vegades que fa temps vaig perdre el compte, per fer-ho tot més fàcil i per tantes altres coses que hauria d'escriure una tercera tesi per agrair-los-ho tot. També a les meves germanes, Leonor i Caty , per fer-me sentir que esteu orgulloses del vostre germà. El meu cunyat Toni també es mereix una important menció en aquest apartat, i no només per la seva forma de ser sinó per haver contestat innumerables trucades de telèfon que començaven amb un: "Toni, com es diu aquesta paraula en anglès?" sense importar-li mai ni el dia ni l'hora; així que: "thank you brother in law!!!!". Als meus nebodets, de moment els que hi ha fins ara, als qui espero algun dia poder explicar-los que aquest treball és en gran part la resposta a la pregunta: "*tiu* Miquel, perquè no dorms a Sa Carroca?". No m'oblido de cap dels altres membres de la meva família, tots ells d'una manera o altre han intervingut en aquesta tesi.

Pel que fa als meus amics i altres persones que en un moment o altre s'han interessat per la tesi o fins i tot n'han patit les seves conseqüències, els vull agrair a tots ells i elles haver estat al meu costat o haver-me preguntat: "com portes la tesi?" en alguns moments aquesta senzilla pregunta s'agraeix molt. Vaig intentar fer una llista de tots ells però sempre sentia que em deixava algú o que prioritzava uns o altres, i no ho vull fer, per aquest motiu i com ja he comentat amb alguns d'ells, no escriuré noms propis.

Vull recordar també a moltes persones a les quals malauradament i per diferents motius cadascuna, no trucaré per dir-los que ja he acabat la tesi. Especialment a una, a qui temps enrere li vaig escriure que, si *Déu volia, algun dia seria doctor*....

I per no acabar els agraïments amb una nota trista, ho faré dient que aquest treball no seria el mateix sense la que una tarda una companya del laboratori va batejar com "la cançó del bon rotllet" (live is life d'Opus) ni sense una frase que fa uns anys va dir un dels meus cosins i que tantes vegades, al recordar-la, em motiva a seguir treballant: "jo no estudio per ser metge, jo estudio per ser un bon metge".

A la meva família

Resum

En aquesta tesi s'estudien diverses tècniques per a la decoloració d'efluents de tintura amb colorants reactius i per a la reutilització dels efluents decolorats en noves tintures.

Les tècniques utilitzades per eliminar el color són: electroquímica, irradiació UV, coagulació-floculació, nanofiltració i ozonització. A més d'aquestes tècniques, es proposa l'aplicació de material microencapsulat per a la mateixa finalitat, estudiant prèviament el seu mètode de preparació. S'avalua també la influència en el resultat de les tintures d'un tractament electroquímic previ a la reutilització dels banys de tintura.

De les tècniques aplicades per a la decoloració dels efluents tractats, la irradiació UV posterior a un tractament electroquímic va ser la principal. Es varen estudiar diferents formes d'aplicació de la llum UV, optimitzar la intensitat de corrent necessària i concentració de clorurs al medi i avaluar aquestes variables pel que fa la possible formació tant de compostos orgànics halogenats com d'amines aromàtiques durant el tractament electroquímic amb mètodes cromatogràfics posats a punt en aquesta tesi.

Els tractaments de coagulació-floculació i nanofiltració es varen aplicar tant per separat com combinats en el tractament de decoloració dels banys anteriors. De la mateixa manera que abans, es van estudiar i optimitzar els paràmetres més influents de cada tècnica per separat i proposar el seu tractament conjunt.

L'ozonització es va utilitzar com a mètode per comparar i intentar establir els mecanismes de degradació dels colorants reactius en el tractament combinat electroquímica i irradiació UV i l'ozonització, essent ambdues tècniques d'oxidació.

Finalment, es valora la viabilitat de l'ús d'hipoclorit sòdic encapsulat combinat amb irradiació UV com a alternativa per a la decoloració dels efluents estudiats. Previ a la seva aplicació, es va procedir a la seva microencapsulació per polimerització interficial.

Pel que fa a la reutilització dels efluents, es va estudiar la influència d'un tractament electroquímic dels efluents previ a la seva reutilització avaluant les diferències de color DE (CMC(2:1)) entre les fibres tenyides amb aigua reutilitzada respecte una referència tenyida amb aigua sense reutilitzar.

Abstract

In this thesis diverse techniques for the decolourization and reuse of reactive dye bath effluents are studied.

The techniques applied to remove colour are: electrochemical, UV irradiation, coagulation-flocculation, nanofiltration and ozonation. Besides these techniques, it is proposed the application of microencapsulated material for colour removal. The encapsulation method was previously studied. The influence of an electrochemical pre-treatment prior to dye bath reuse was also studied.

Among the techniques used for the decolourization of the effluents, the application of UV irradiation after an electrochemical treatment was the main. Different ways of application of the UV irradiation were evaluated. The influences of the current density applied in the electrochemical treatment and the chloride ion concentration present in the effluent were studied in the organic halogenated compounds and aromatic amines generation during the electrochemical treatments. The analyses of these compounds were performed by chromatographic methods established in this thesis.

The coagulation-flocculation and nanofiltration treatments were applied separately and combined for the decolourization of the previous effluents. Following the same methodology than before, the most influential parameters of each technique were studied and optimized.

Ozonation was used to compare and propose the degradation mechanisms of the reactive dyes in the combined UV irradiation and electrochemical treatment and ozonation. Both techniques are based on oxidation.

Finally, the viability of the application of encapsulated sodium hypochlorite in combination with UV irradiation was studied as a new alternative for the decolourization of the studied effluents. The microcapsules preparation method was previously studied.

The influence of the application of an electrochemical pre-treatment before dye bath reuse was studied and evaluated in terms of colour differences DE (CMC(2:1)) between fabrics dyed with reused water and reference fabrics.

Índex

Capítol 1

Introducció

Capítol 1. Introducció

1.1 L’ aigua, la seva importància

L’aigua cobreix el 70% de la superfície terrestre, essent el 97,5% de l’aigua salada i sols el 2,5% dolça. Els casquets de gel i els glacials contenen el 74% de l’aigua dolça del món mentre que els rius i llacs tan sols el 0,3%, la resta es troba a les profunditats de la terra o en forma d’humitat. Per a ús humà es pot accedir a menys de l’1% de l’aigua dolça superficial del planeta [1.1].

Malgrat la gran quantitat d’aigua en el nostre planeta i segons va afirmar l’Organització de les Nacions Unides al 2003, l’aigua promet ser al segle XXI el que va ser el petroli per al segle XX, el bé preuat que determina la riquesa de les nacions. En el mateix sentit i segons el *Programa de les Nacions Unides pel Medi Ambient* (PNUMA) del mateix any, dos-cents científics de cinquanta països van determinar que la falta d’aigua serà un dels dos problemes més importants del nou mil·lenni (l’altre és el canvi climàtic).

En qualsevol cas, i segons l’informe de les Nacions Unides sobre el desenvolupament dels recursos hídrics al Món (WWDR) també del 2003, més que un problema d’escassetat d’aigua, es tracta d’una crisi de gestió dels recursos hídrics, essencialment motivada per la utilització de mètodes inadequats.

L’abastiment d’aigua potable insuficient i inadequat implica riscos i representa un problema constant per a la salut de la població mundial. L’Organització Mundial de la Salut (OMS) estima que el 80% de les malalties en el Món en desenvolupament són degudes a la falta d’aigua neta i sanejada. Com a terme mig, l’ús domèstic diari d’aigua dolça d’una persona d’un país desenvolupat és deu vegades superior al d’una persona d’un país del tercer món.

L'aigua però, també pot ser una font d'energia pràcticament inesgotable. Serveix per exemple per moure les bobines d'una central elèctrica i en el futur s'espera que sigui possible fer servir l'enorme quantitat de deuteri que es troba als oceans per a les primeres etapes d'obtenció d'energia per fusió nuclear. A més, actua com a agent termoregulador de la temperatura, és un dissolvent molt potent i serveix de medi de reacció en molts processos biològics.

L'aigua del mar conté, encara que en diferent proporció, gairebé tots els elements químics naturals; és per tant una font de matèries primeres. Al 3,5% de salinitat, s'hi troben com a valors mitjans: 19.400 ppm de clorur, 10.800 ppm de sodi, 1.290 ppm de magnesi, 904 ppm d'ió sulfur, 411 ppm calci i 392 ppm de potassi. En quantitats compreses entre 0,001 i 0,1 ppm es troben: brom, àcid bòric, estronci, fluor, rubidi, alumini, silici, liti, bari, iode, magnesi, ferro, estany i vanadi. En quantitats menors, però amb possibilitats en alguns casos de benefici tècnic: zinc, coure, arsènic, urani, plom, seleni, wolframi, or, crom, cesi, cadmi, bismut, plata, molibdè, etc [1.2]. Per tot això, és necessari mantenir l'aigua de que disposem en bones condicions, fer-ne un ús controlat, no malbaratar-la i tant com sigui possible reutilitzar-la per a nous usos. En definitiva, cada gota d'aigua té un valor que no se l'ha reconegut.

1.2 L' aigua en la indústria tèxtil

1.2.1 Consum d'aigua

La indústria tèxtil utilitza grans quantitats d'aigua en els seus processos productius, es podria dir que l'aigua és una matèria primera més, com ho poden ser els colorants o el mateix teixit. Degut a l'elevat consum d'aigua, aquest sector és també conegut com el del Ram de l'Aigua.

Segons dades obtingudes a partir de l'Institut Català d'Energia (ICAEN) i dades aportades per l'Institut Tèxtil i Cooperació Industrial de Terrassa (INTEXTER), el consum d'aigua mitjà es situa al voltant dels 125 L/kg de producte acabat [1.3] Aquestes dades coincideixen amb altres fonts [1.4]. Cal afegir que, a part de l'aigua, tenyir un kilogram de cotó amb colorants reactius implica també un consum de 0,6 kg de NaCl i 40 grams de colorant [1.5].

A més dels consums directes d'aigua, la indústria tèxtil també té altres consums indirectes, el que es coneix com la "imprempta hídrica" [1.6]. A tall d'exemple, i segons dades del 2001 proporcionades pel Banc Mundial, per obtenir un kilogram de blat o d'arròs es requereixen 1.500 L i 4.500 L d'aigua respectivament mentre que el cotó en necessita 10.000 L.

1.2.2 Utilització de l'aigua

Segons indica la figura 1.1 un 73% de l'aigua emprada pel sector d'ennobliment del tèxtil s'utilitza en les operacions de procés: preparació, tintura i acabats, aquesta última operació en menor mesura.

En el procés de tintura, l'aigua és emprada en els banys de tintura i els rentats que s'apliquen als productes tèxtils, primer per incorporar-hi els productes i, posteriorment, per extreure'n els productes sobrants.

El 27% restant de l'aigua s'utilitza en operacions de refrigeració, condicionament, calderes, etc. distribuït com es detalla a continuació. L'aigua de refrigeració, el 8%, correspon a l'aigua consumida en les purgues de les torres de refrigeració i evaporació o bé pot ser aigua que es llenci directament a un circuit obert si no es disposa de torres de refrigeració. Els tractaments condicionadors, principalment la descalcificació de l'aigua i regeneració de resines, representen el 6% del total del consum d'aigua. L'aigua consumida en calderes, el 5%, prové de les purgues i els condensats de vapor no recuperats. Aproximadament un 4% del consum d'aigua correspon a altres processos, fuites i errors de mesura del cabal. Les neteges de motlles, maquinària i instal·lacions suposa un 3% del total. Finalment, l'aigua d'ús sanitari representa tan sols un 1% del total.

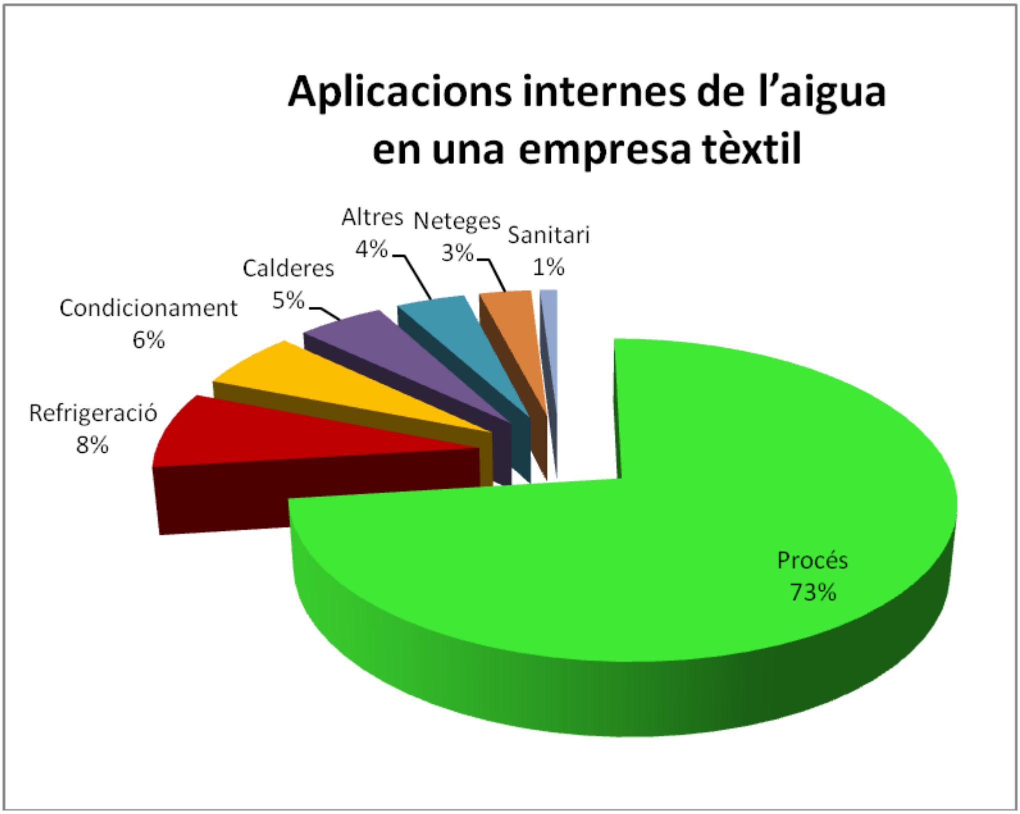

Figura 1.1 Aplicacions internes de l'aigua en una empresa tèxtil. (Font: ICAEN. Elaboració pròpia).

1.2.3 Comparació amb altres indústries quant a consum d'aigua

Segons les últimes dades trobades de l'any 2004, els consums d'aigua percentuals de la indústria espanyola no varen experimentar canvis significatius respecte els anys anteriors. A la figura 1.2 es representa la distribució percentual del consum d'aigua dels diferents sectors industrials en el nostre país. S'observa que el tèxtil era el tercer sector en consum d'aigua, només superat per la indústria química i la indústria paperera [1.7].

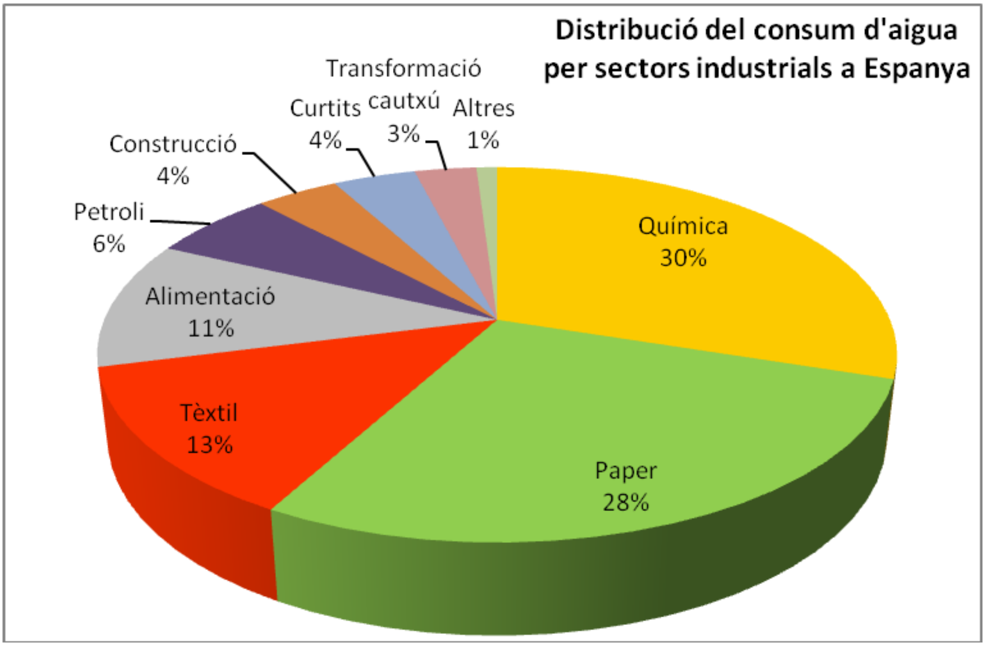

Figura 1.2 Distribució del consum d'aigua per sectors industrials a Espanya. (Font: ICAEN. Elaboració pròpia).

Actualment la situació presentada a la figura 1.2 es preveu diferent. La important deslocalització d'empreses tèxtils i la gran caiguda del sector de la construcció alteren aquesta distribució, modificant per tant els consums relatius de cada sector respecte el global.

1.3 EFLUENTS TÈXTILS, LA SEVA IMPLICACIÓ AMBIENTAL

1.3.1 Classificació i caracterització dels efluents tèxtils

Les característiques de les aigües residuals generades per una planta tèxtil depenen principalment de les operacions específiques que es realitzen, del tipus de fibra tractada i de la maquinària emprada. A la taula 1.1 s'indiquen les operacions realitzades en cada fase del procés d'ennobliment, segons el tipus de fibra [1.3].

Taula 1.1 Operacions aplicades segons el tipus de fibra en el procés d'ennobliment. (Font: ICAEN. Elaboració pròpia).

Fases	**Operacions**	**Tipus de fibra**		
		Cotó	**Llana**	**Polièster**
Preparació	Desencolatge	*		*
	Desengreixatge		*	
	Carbonització		*	
	Batanatge		*	
	Descruatge	*		*
	Merceritzatge	*		
	Blanqueig	*	*	
Tintura	Tintura/Estampat	*	*	*
Acabats	Acabats	*	*	*

A causa de la gran varietat de processos i de productes químics utilitzats, les aigües residuals produïdes a la indústria de fibres naturals, a excepció de les procedents del rentat de la llana, es caracteritzen per una gran variabilitat de cabal i càrrega contaminant, així com un baix contingut en matèries col·loïdals i en suspensió. Generalment són acolorides, la seva càrrega orgànica mitja és aproximadament el doble que la d'una aigua residual urbana i no acostumen a portar productes tòxics ni microoganismes patògens, a més, són deficitàries en nutrients, principalment nitrogen [1.8].

Les indústries dedicades a la tintura i acabat de fibres naturals generen una càrrega contaminant que depèn molt de si tinten fil, floca, teixit de cotó, teixit de llana, gènere de punt o estampació. A la taula 1.2 s'expressen les càrregues contaminants més probables per aquests efluents [1.8].

Taula 1.2 Càrregues contaminants mitjanes de diferents subsectors de l'ennobliment tèxtil. (Font: ICAEN. Elaboració pròpia).

PARÀMETRE	**FIL**	**FLOCA**	**TEIXIT COTÓ**	**TEIXIT LLANA**	**GÉNERE DE PUNT**	**ESTAMPACIÓ**
pH	5-12	6-10	8-12	6-8	6-11	7-10
DQO (mg/L)	500-900	4000-7000	1000-3000	300-1000	800-1300	2000-4000
DBO_5 (mg/L)	150-350	1200-2200	300-1000	100-400	200-450	500-1500
MES (mg/L)	50-150	50-150	50-300	100-150	50-150	200-600
Volum (L/kg)	10-80		100-300	100-300	80-120	
Color (Pt-Co)	300-1000	300-1000	300-3000	200-1500	100-1000	1000-6000
MI (Equitox/m^3)	3-10	3-10	4-15	5-25	4-10	

1.3.2 Implicacions mediambientals de la indústria tèxtil

La coloració de les aigües residuals, principalment quan contenen colorants reactius, presenta un seriós problema mediambiental a la indústria tèxtil.

A Espanya, la taula 3 del Reglament del Domini Públic Hidràulic del Reial Decret 849/1986 de l'onze d'abril de 1986 (la més restrictiva i la que s'aplica generalment a Catalunya) permet l'abocament d'efluents acolorits a la llera pública, sempre que en diluir-los vint vegades no s'apreciï visualment el color (B.O.E. Nº 103). En conques de rius amb baix cabal, com és el cas de la conca del Tordera, l'abocament és més restrictiu, arribant a demanar que el color no sigui apreciable en dilucions 1/10.

Quan l'abocament es fa a clavegueram, connectat a un estació depuradora d'aigües residuals (EDAR), aquest límit és menys restrictiu. A Catalunya el Reglament Guia de l'Ús i els Abocaments d'Aigües Residuals al Clavegueram exigeix que el color no sigui apreciable al fer dilucions 1/30.

Altres països fixen valors més precisos en la seva legislació. Així, al Regne Unit, la *Enviromental Agency* estableix uns límits per cada àrea geogràfica segons el cabal dels rius receptors. Aquests límits estan quantificats en valors d'absorbància presos cada 50 nm en cubetes de 1 cm. Els valors de color acceptats van de 0.013 unitats d'absorbància (a 700 nm) fins 0.115 unitats d'absorbància (a 400 nm) [1.9].

1.3.3 Normativa d'abocaments d'efluents tèxtils

Les normes i procediments que afecten als abocaments d'aigües residuals són diverses i canviants [1.10].

Les disposicions legislatives, relatives a la qualitat de les aigües, han de considerar els següents aspectes fonamentals [1.11]:

a) Conservació dels recursos
    - Aigües superficials
    - Aigües subterrànies
    - Cursos d'aigües navegables
    - Cursos d'aigües no navegables

b) Garantir la salut pública
  - Protecció sanitària de l’aigua i aliments
  - Protecció contra la contaminació

c) Garantir la vida de la fauna i la flora
  - Protecció de la qualitat de l’aigua
  - Protecció contra la contaminació

d) Ubicació adequada de les indústries i activitats incòmodes, insalubres i perilloses i d’aquelles la contaminació de les quals no és coneguda.

1.3.3.1 Legislació europea d’aigües residuals

Des de la fundació de la Unió Europea s’han desenvolupat cinc programes d’acció a favor del medi ambient, on s’estableix el marc per a les línies d’acció i el desenvolupament de la legislació mediambiental europea. L’últim programa (segons dades de l’any 1998) anomenat Vè Programa a favor del Medi Ambient *Cap a un desenvolupament sostenible* tenia vigència des del 1993 fins al 2000 en tots els països de la Unió Europea. Aquest programa tenia com un dels objectius principals la protecció del medi hídric, juntament amb la prevenció de la contaminació, la rehabilitació de les aigües continentals i l’equilibri de la demanda d’aigua mitjançant un ús i una gestió més racional dels recursos hídrics.

1.3.3.2 Legislació espanyola d’aigües residuals

La legislació sobre aigües residuals espanyola té el seu origen a principis del segle XX. Durant les dècades dels 60 i 70 es va anar complementant i al 1985 va fer un gran avanç amb l’aparició de la nova Llei d’aigües 29/1985 del 2 d’agost, que qualifica l’aigua com un recurs escàs i unitari a l’estat espanyol.

Sota aquesta perspectiva es declaren públiques totes les aigües (amb regulació específica per a les aigües minerals i termals) abraçant les aigües subterrànies i superficials. Es declara la necessitat de preservar la seva qualitat sobre la base, imprescindible, d'una planificació hidrològica i el reconeixement d'aquest recurs com a bé estatal.

1.3.3.3 Legislació catalana d'aigües residuals

La Generalitat de Catalunya va aprovar la Llei 5/1981 del 4 de juny sobre el desenvolupament legislatiu en matèria d'evacuació i tractament d'aigües residuals. S'estableixen en aquesta llei una sèrie de principis (equitat, solidaritat, millora progressiva i rendibilitat), l'organització administrativa (Junta de Sanejament i administracions actuants com la de l'estat o locals), el finançament de les actuacions (cànon de sanejament) i el Pla de Sanejament.

La Llei 5/1990 del 9 de març d'Infraestructures Hidràuliques de Catalunya estableix el Cànon d'Infraestructura Hidràulica per al finançament de les infraestructures hidràuliques. El decret 320/1990 de 21 de desembre, defineix les normes específiques del Canon de Sanejament, l'Increment de la Tarifa de Sanejament (ITS) i el Canon d'Infraestructures Hidràuliques.

Posteriorment, la Generalitat de Catalunya va crear per Llei 4/1991 de 22 de març el Departament de Medi Ambient i li assignà competències i funcions pel Decret 67/1991 de 8 d'abril. D'acord amb la legislació vigent, els abocaments d'aigües residuals requereixen l'autorització administrativa, la qual s'ha de sol·licitar a l'organisme competent en cada cas. En el cas de les conques de Catalunya correspon a l'Agència Catalana de l'Aigua, l'A.C.A.

Ateses les diverses exigències tècniques i administratives que cal aplicar, la normativa diferencia entre abocaments al clavegueram, abocaments a la llera pública i abocaments al mar:

- Abocaments al clavegueram: Per utilitzar un clavegueram cal l'autorització del seu titular (ajuntament, mancomunitat o consorci de municipis, etc.). El titular esdevé l'organisme regulador dels abocaments al clavegueram dins el seu territori quant a limitacions, utilització de la xarxa, instal·lacions de tractament, mesures, inspeccions i sancions. Els límits de contaminació dels abocaments al clavegueram són molt més tolerants que els corresponents als de la llera pública, perquè aquests experimenten una depuració final conjunta.

- Abocaments a la llera pública: Es consideren abocaments a la llera pública els abocaments que es realitzen directament o indirectament a les lleres i els abocaments al subsòl o sobre el terreny, les basses o excavacions mitjançant evacuació, injecció o dipòsit. Els límits de contaminació de les aigües que s'aboquen a la llera pública els marca la taula III de l'annex de Títol IV del Reglament del Domini Públic Hidràulic, d'altra banda, els límits d'abocament mai no poden superar els límits fixats per la taula 1, del mateix annex, a excepció de causes justificades.

- Abocaments al mar: Els límits de contaminació admesos per aquests tipus d'abocaments s'hauran de fixar amb l'administració competent, l'A.C.A.

1.4 Els colorants

El color de les aigües residuals, especialment les tèxtils, és causat per colorants. En aquest apartat es defineixen i classifiquen els colorants i s'expliquen les causes de la seva presència en les aigües residuals.

1.4.1 Definició i classificació

Els colorants són substàncies químiques capaces d'absorbir radiació electromagnètica entre 400 nm i 700 nm (rang de la llum visible per a l'home) propietat que els atorga color. S'apliquen sobre materials tèxtils, paper, pèl, etc. a partir d'un líquid en el qual són completament o parcialment solubles i presenten una afinitat específica cap als substrats que tenyeixen [1.12] dotant-los de color de manera estable front factors físics i/o químics com poden ser la llum, els rentats, agents oxidants, etc.

Els colorants es poden classificar segons la seva estructura química. Estan compostos per un grup d'àtoms responsables del seu color, anomenat cromòfor així com de substituents donadors i acceptors d'electrons que provoquen o intensifiquen el color del cromòfor, anomenats auxocroms. Els grups cromòfors més importants són els azo (-N=N-), carbonil (-C=O), polimetínics $(\text{-CH=})_n$ i nitro (-NO_2). Els auxocroms més importants són els amino (-NH_3), carboxil (-COOH), sulfònics ($\text{-SO}_3\text{H}$) i hidroxil (-OH).

Es calcula que la producció mundial de colorants està al voltant de les 8×10^5 tones anuals i les 10×10^5 tones anuals [1.13, 1.14] les quals majoritàriament són colorants azo [1.15]. Els colorants azo s'utilitzen principalment per colors com el groc, taronja i el vermell. Els colorants antraquinònics representen el segon grup més important després dels azo. Malgrat que aquest tipus de colorant presenta colors a gairebé tot l'espectre, s'utilitzen principalment per colors com el violeta, blau i verd.

Els colorants naturals i els primers colorants sintètics tenen noms propis acceptats de forma general. No obstant això, des de finals del segle XIX els colorants s'introdueixen al mercat amb noms comercials. Al 1924, la British Society of Dyers and Colourists (SDC) va publicar un índex de totes les matèries colorants amb el nom de "**COLOUR INDEX"**. Les següents edicions es van publicar amb contribució de la American Association of Textile Chemists and Colorists (AATCC).

El Colour Index és l'obra de referència més important i completa en el camp dels colorants. Atorga a cada colorant o pigment, ja sigui natural o sintètic, dues referències: una basada en la classe tintòria, "*C.I. Generic Name*", i l'altra corresponent a la seva estructura química "*C.I. Constitution Number*". Per tant, cada colorant comercial es pot identificar pel seu nom de Colour Index i segons el seu número de constitució si han estat publicats. No obstant això, dos colorants comercials amb les mateixes referències de Colour Index no s'han de considerar "idèntics", ja que alguns aspectes no recollits en aquesta obra de consulta poden ser determinants a l'hora de valorar el seu comportament (tamany de partícula, estructura cristal·lina, additius, impureses, etc.) [1.16, 1.17].

1.4.2 Reaccions dels colorants amb la fibra

Un grup particular de colorants són els colorants reactius. Aquests colorants es caracteritzen per tenir grups reactius que formen enllaços covalents amb els grups -OH, -NH o -SH de les fibres (cotó, llana i seda). El grup reactiu determina el comportament químic del colorant. Alguns colorants contenen dos grups reactius o bé un o dos grups reactius bifuncionals [1.18]. Les tintures obtingudes amb aquest tipus de colorant es caracteritzen pels seus colors brillants i la seva elevada solidesa [1.19].

El grup reactiu del colorant està format per una estructura d'anells N-heterocíclics amb halògens. La reacció amb la fibra té lloc en medi bàsic [1.20] on els grups hidroxils d'aquesta s'ionitzen i, per un mecanisme de substitució nucleòfila, s'uneixen al colorant gràcies a l'eliminació de l'halogen (reacció 1):

$$\text{Col-X} + \text{Cel-O}^- \longrightarrow \text{Col-O-Cel} + X^- \qquad \text{(reacció 1)}$$

Com que l'aigua també és un nucleòfil feble, apareix, simultàniament, una reacció secundària d'hidròlisi del colorant, afavorida pel pH bàsic del bany de tintura (reacció 2):

$$\text{Col-X} + H_2O \longrightarrow \text{Col-OH} + \text{HX} \qquad \text{(reacció 2)}$$

El colorant hidrolitzat perd la capacitat de formar enllaços covalents amb la fibra. La fracció de colorant hidrolitzat se situa entre el 10% i el 30%, essent per tant el grau d'esgotament d'aquests colorant entre el 70% i el 90%.

En els darrers anys ha crescut la utilització de colorants amb dos grups reactius (bifuncionals) per tal d'obtenir tintures amb majors solideses i al mateix temps augmentar el tant per cent d'esgotament d'aquesta família de colorants.

1.4.3 Sistemes d'avaluació del color en les tintures

La reproducció del color en diverses tintures es calcula determinant les diferències de color entre les mostres tenyides amb aigua reutilitzada i les mostres de referència (teixit tenyit amb aigua de xarxa descalcificada). Les diferències de color s'obtenen amb un colorímetre i defineixen les coordenades cromàtiques de cada tintura. Aquestes coordenades són definides per tres eixos que corresponen a tres paràmetres:

- **L** representa la lluminositat, pren valors des de 0 (negre) fins a 100 (blanc).
- **a** es divideix en valors positius i negatius. Els valors positius indiquen la quantitat de vermell mentre que valors negatius indiquen la quantitat de verd.
- **b** presenta també valors positius i negatius. Un valor positiu representa el groc i un valor negatiu representa el blau.

Els paràmetres a i b que es representen en coordenades axials poden ser substituïts per altres paràmetres representats en coordenades polars:

- **C** correspon al croma o saturació, representa la propietat que permet diferenciar des d'un color pur a un to gris.
- **h** correspon al to o matís. Els seus valors van des de 0 a 360º, començant i acabant amb el color vermell, passant pel groc, el verd i el blau, a més de tots els colors intermedis com el taronja, el violeta, etc.

A partir dels diferents valors obtinguts per cada paràmetre entre dues tintures diferents es calculen els valors de DL, Da, Db, DC i DH que indiquen les diferències en les coordenades cromàtiques entre les reutilitzacions i la tintura de referència. Amb aquests valors es calculen les diferències de color CIELab (DE_{CIELab}) [1.21]. Les diferències de color entre dues tintures es determinen a partir de les diferències calculades en les coordenades cromàtiques segons les fórmules següents:

$$DE_{CIELab} = [(DE)^2 + (Da)^2 + (Db)^2]^{1/2} \text{ en coordenades axials}$$

$$DE_{CIELab} = [(DL)^2 + (DC)^2 + (DH)^2]^{1/2} \text{ en coordenades polars}$$

A més de les coordenades CIELab, una altra forma per calcular les diferències de color entre dues mostres de teixit es DE CMC (l:c) que ofereixen una millor correlació i fiabilitat que la fórmula DE_{CIELab} respecte la sensació visual de les diferències de color. A la indústria tèxtil els valors de l i c són 2 i 1 respectivament, $DE_{CMC(2:1)}$ [1.22]:

$$DE_{CMC(2:1)} = [(DL/2S_L)^2 + (DC/S_c)^2 + (DH/S_H)^2]^{1/2}$$

a on: $S_L = 0{,}040975\ L_R/(1 + 0{,}01765\ L_R)$
si $L_R < 16$ $S_L = 0{,}511$
$S_C = 0{,}0638\ C_R (1 + 0{,}0131\ C_R) + 0{,}638$
$S_H = S_C\ (Tf + 1 – f)$
$f = \{(C_R)^4 / [C_R)^4 + 1900]\}^{1/2}$
$T = 0{,}36 + [0{,}4 \cos(35+h_R)]$ si $h_R \geq 345º$ o $h_R < 164º$
$T = 0{,}56 + [0{,}2 \cos(168+h_R)]$ si $164º < h_R < 345º$

L_R, C_R i h_R són les coordenades cromàtiques de les tintures de referència [1.23].

1.4.4 Problemàtica dels colorants reactius

Com s'ha comentat anteriorment, part del colorant reactiu queda hidrolitzat en el bany de tintura provocant efluents acolorits. Malgrat que els colorants reactius no són nocius per al medi ambient, no permeten el pas de la llum solar a través de l'aigua que els conté provocant així la seva eutrofització. Una petita quantitat de colorant reactiu de l'ordre de mg/L pot causar un problema visual en l'aigua. Per aquest motiu, és necessària la destrucció total o parcial del colorant hidrolitzat en les aigües de tintura.

1.5 Tractaments d'aigües residuals

Actualment s'apliquen diversos tractaments per a l'eliminació del color de les aigües residuals. Aquests tractaments es poden classificar en quatre grups principals. *Tractaments d'oxidació*: oxidació electroquímica, peròxids, ozó, etc. *Tractaments fisicoquímics*: adsorció, intercanvi iònic, coagulació/floculació. *Membranes*: nanofiltració, òsmosi inversa, etc. i *Tractaments biològics*: processos enzimàtics de decoloració [1.24].

1.5.1 Tractaments electroquímics

Un procés redox és una transferència electrònica entre dos reactius. En un procés electroquímic, la transferència electrònica té lloc entre el substrat i un elèctrode metàl·lic, normalment inert, per mitjà d'un corrent elèctric [1.25].

Els tractaments electroquímics es porten a terme en reactors que tenen una o vàries cel·les electroquímiques. Una cel·la electroquímica de corrent continu consta de dos conductors elèctrics denominats elèctrodes, cadascun d'ells submergit en una dissolució adequada d'electròlit. Per a que circuli un corrent en una cel·la, és necessari (1) que els elèctrodes es connectin externament mitjançant un conductor metàl·lic, (2) que les dues dissolucions d'electròlit estiguin en contacte per tal de permetre el moviment dels electrons d'una a l'altre, i (3) que pugui tenir lloc una reacció de transferència d’electrons en cada un dels dos elèctrodes [1.26].

Les cel·les electroquímiques poden ser de dos tipus:

- *Galvàniques*: quan les reaccions electroquímiques es produeixen espontàniament després de connectar els elèctrodes mitjançant un conductor (piles).

- *Electrolítiques*: quan les reaccions són provocades per l’aplicació d’un corrent extern més gran que el voltatge reversible de la cel·la.

Aquest darrer tipus és el que s’utilitza per produir reaccions electroquímiques a expenses de l’energia, el que dóna lloc a un consum energètic [1.27]. Aquestes reaccions impliquen una transferència d’electrons entre la superfície d’un elèctrode i les substàncies de la dissolució, per mitjà del corrent elèctric. Poden ser ions o molècules dissoltes, àtoms de metall procedents de l’elèctrode, o fins i tot molècules del propi dissolvent. Les substàncies formades poden passar a la dissolució, desprendre’s com a gas o precipitar. D’altra banda, els productes formats a l’ànode per oxidació poden passar a la dissolució i ser reduïts al càtode, i viceversa (a no ser que l’ànode i el càtode estiguin separats per una membrana).

Les principals aplicacions dels tractaments electroquímics als efluents tèxtils són l’eliminació de color [1.28, 1.29] i la destrucció de compostos orgànics tòxics o no biodegradables [1.30].

Aquestes tècniques ofereixen l’avantatge d’operar en condicions suaus: pressió atmosfèrica i temperatura ambient (presenten poca influència en un rang ampli de temperatura de treball entre 20 i 60 ºC) [1.31- 1.33]; tenen un ampli rang de pH de treball [1.34], utilitzen un reactiu net: l'energia elèctrica i no necessiten d'addició de productes químics a l'aigua [1.35].

Els tractaments electroquímics també s'apliquen a les aigües residuals d'indústries com la del paper [1.36], pintures [1.37] o per al tractament dels lixiviats d'abocador [1.38].

1.5.2 Tractament electroquímic de les aigües residuals tèxtils

Generalment el tractament electroquímic de destrucció dels colorants i d'altres compostos orgànics presents en les aigües residuals es porta a terme per oxidació, encara que també hi ha estudis de decoloració per reducció electroquímica dels colorants azo presents en aigües residuals de tintura i rentat [1.39-1.42].

Les espècies orgàniques poden ser descompostes de forma parcial o total fins a CO_2 i aigua (mineralització). El rendiment del tractament electroquímic depén tant de la intensitat de corrent aplicada com de l'estructura química del colorant [1.43]. Acostuma a ser més interessant una oxidació parcial de la molècula que la seva destrucció completa, ja que d'aquesta forma el consum d'energia és menor. El resultat ideal és obtenir compostos fàcilment biodegradables que s'eliminen en un tractament biològic posterior [1.44]. Cal recordar que alguns efluents tèxtils poden ser difícilment biodegradables [1.45]. D'un estudi realitzat amb 87 colorants, el 53% no són biodegradables [1.46].

El procés d'oxidació es pot portar a terme tant de forma directa com indirecta. L'oxidació directa té lloc sobre la superfície del propi elèctrode, en el mateix reactor electroquímic, amb o sense separació de compartiments. Per contra, l'oxidació indirecta té lloc per reacció d'especies oxidants generades anòdicament (parells redox: ClO^-/Cl^-, Cr(VI)/Cr(III), etc.). L’oxidació es pot produir tant in situ com en un reactor diferent [1.47, 1.48]. En general, l’oxidació directa no és tan eficaç com la indirecta [1.49]. Per altra banda, també poden tenir lloc els dos fenòmens en un procés d’oxidació combinada [1.50].

En l’oxidació directa, el grau d’oxidació depén, entre d’altres variables, de l’elèctrode utilitzat. Alguns estudis proposen l’ús d’elèctrodes de bor dopats amb diamant com a material constituent de l’ànode. La utilització d’aquests elèctrodes comença a ser possible des de que es poden preparar ànodes amb àrees suficientment grans. Aquests elèctrodes han demostrat bona resistència química, mecànica i tèrmica; un ampli rang de treball de potencial electroquímic en solucions aquoses, una extremada estabilitat electroquímica i no es corroeixen encara que es treballi a densitats de corrent elevades [1.51].

L’oxidació mitjançant reactius generats (oxidació indirecta) és un important recurs en el tractament d’aigües residuals que contenen clorurs ja que l’oxidació electroquímica d’aquests ions produeix clor i hipoclorit, els quals oxiden els compostos orgànics en solució. El principal inconvenient d’aquesta tècnica és la possible formació de compostos orgànics halogenats que s’ha de controlar i procurar minimitzar. En aquest cas, es poden emprar materials anòdics que siguin catalitzadors pobres en la formació d’aquests compostos i afavoreixin, per contra, l’oxidació directa sobre l’ànode (per exemple, l’òxid d’estany) [1.52].

Pel que fa al paper dels radicals hidroxil, diversos autors coincideixen en destacar-lo com l’espècie oxidant més convenient de la matèria orgànica. També es fan servir per trencar els enllaços azo (-N=N-), els quals després d’una obertura electrofílica inicial són oxidats per radicals hidroxil [1.53].

En aquest sentit, Zanoni i col. realitzen un extens estudi utilitzant el colorant Reactive Blue 4 en el qual es demostra que l'oxidació indirecta via radicals hidroxils és un camí molt convenient per a la degradació i mineralització d'aquest tipus de colorant antraquinònics [1.54]. Brillas i col. conclouen en el seu estudi que aquest mètode de decoloració és prou potent com per destruir pràcticament la totalitat de compostos orgànics en un rang de pH entre 3 i 6, essent 4 el seu òptim. A pH 2, el poder d'oxidació és molt inferior, segurament motivat per la poca producció de radicals $OH^{\bullet}$ [1.55]. Altres autors recolzen aquesta afirmació [1.56, 1.57].

Per la seva banda, Kim i col. van estudiar l'eficàcia dels tractaments electroquímics en funció dels grups cromòfors dels colorants. En el seu estudi es demostra que tots els colorants reactius tractats varen ser totalment decolorats mitjançant processos electroquímics d'oxidació i conclouen que els colorants que tenen grups diazo decoloren més lentament que els mono azo o antraquinònics [1.58].

1.5.3 Tractaments amb radiació UV

L'aplicació de radiació ultraviolada (UV) en el tractament d'aigües residuals sol ser complement d'altres tècniques. Els colorants són resistents a la irradiació d'UV directe i per tant no es pot aplicar com a mètode únic de decoloració. En canvi, s'ha comprovat que és un mètode eficaç amb un catalitzador.

Els primers usos de la radiació UV se centraven en la desinfecció d'aigües de subministrament. En els darrers anys, la seva aplicació al tractament d'aigües residuals ha experimentat un gran interès. S'ha comprovat que una correcta dosificació de dels rajos ultraviolats és eficaç contra bacteris i virus, a més de disminuir la formació de compostos tòxics com poden ser els compostos organoclorats obtinguts en la cloració [1.59, 1.60].

La interacció de la fotocatàlisi amb la radiació per sota de 400 nm produeix especies d'oxigen actiu, els quals poden oxidar la matèria orgànica [1.61]. Segons alguns investigadors, per tal que aquesta oxidació tingui lloc, s'han de complir tres condicions: (1) la molècula s'ha d'adsorbir a sobre el catalitzador o al seu voltant, (2) llum amb la longitud d'ona adequada ha d'interaccionar a la part activa del catalitzador i (3) hi ha d'haver oxigen dissolt per reemplaçar les espècies d'oxigen actives desplaçades per la radiació [1.62].

Actualment el principal mètode de generació de radiació ultraviolada per a aigües residuals és la làmpada d'arc de mercuri de baixa pressió. Un dels avantatges que presenta la làmpada de mercuri és que el 85% de la llum emesa és monocromàtica amb una longitud d'ona de 253,7 nm. Per produir energia UV, la làmpada, que conté vapor de mercuri, es carrega en contacte amb un arc elèctric. L'energia generada per l'excitació del vapor de mercuri contingut a la làmpada produeix l'emissió dels rajos ultraviolats. En l'aplicació pràctica d'aquests elements, les làmpades poden estar suspeses fora del líquid o bé submergides en ell. En aquest darrer cas, es recobreixen amb tubs de quars per evitar l'efecte refrigerant del líquid que es troba al seu voltant.

Un dels principals avantatges de la fotocatàlisi és que degrada els compostos orgànics contaminants en condicions moderades. En un estudi realitzat per a la degradació del Rhodamina 6G, durant 0.5 h de tractament continu, la DQO i DBO_5 van ser reduïdes en un 93.9% i 87.6% respectivament utilitzant TiO_2 com a fotocatalitzador. Aquests resultats mostren que el mètode pot fer-se servir per la degradació de colorants orgànics.

Altres estudis també proposen l'ús del TiO_2 juntament amb la radiació UV per degradar compostos orgànics [1.63, 1.64] així com la part aromàtica dels colorants [1.65]. Malgrat l'extens ús del TiO_2 com a fotocatalitzador, una elevada concentració de colorant a tractar, augmenta la quantitat d'aquest adsorbida sobre la superfície del catalitzador, provocant una reducció en l'absorció de llum per part del catalitzador i conseqüentment una menor activitat catalítica [1.53, 1.59, 1.66].

Com alternativa a la fotocatàlisi, s'està estudiant l'aplicació de radiació UV després d'un tractament electroquímic. Amb aquest acoblament de tècniques, es millora el procés global de decoloració i degradació de les aigües residuals tèxtils tant en efectivitat com en cost [1.67-1.69].

Motheo i col., realitzen un ampli estudi comparatiu de tres processos: fotocatalític (interacció de radiació UV amb la superfície d'un elèctrode), electroquímic (aplicar una densitat de corrent constant) i fotoelectroquímic (aplicació simultània d'un corrent constant i radiació UV). Es va investigar l'efecte de la densitat de corrent, entre 5 mA/cm i 89 mA/cm. Es va observar que a densitats de corrent baixes, entre 5 mA/cm i 30 mA/cm, les eliminacions de color i TOC en el procés fotoelectroquímic resulten ser la suma dels processos fotocatalític i electroquímic. No obstant això, a mesura que la densitat de corrent augmenta, el grau de decoloració pel mètode fotoelectroquímic és molt millor. L'explicació d'aquest fenomen la trobem en la major producció d'O_2 que interactua amb la radiació UV i causa l'oxidació del colorant [1.70]. Altres publicacions recolzen aquesta afirmació [1.71].

Com a alternativa a les làmpades UV, alguns treballs estudien l'ús de la llum solar. Aquesta llum resulta ser atractiva des del punt de vista mediambiental i econòmic, però no es pot oblidar que resulta difícil controlar la seva densitat de corrent, que varia segons l'hora del dia i l'estació de l'any. D'altres autors han comparat decoloracions obtingudes entre llum UV i llum solar, arribant ambdós experiments a decoloracions altes però en temps diferents, essent més ràpids els experiments realitzats amb làmpades de llum UV [1.69-1.71].

A més de les tècniques fotoelectroquímiques, n'hi ha altres que també utilitzen la irradiació UV. Les més destacades són els processos Fenton i Fotofenton [1.72-1.75]. Aquests processos treballen a pH àcid, per tant, quan s'apliquen a efluents amb colorants reactius, és necessari baixar el pH de l'efluent fet que implica augmentar la seva salinitat.

La irradiació UV també es combina però en menor mesura amb ozó, ultrasons [1.76] i peròxid d'hidrogen [1.77, 1.78].

1.5.4 Tractaments amb ozó

L'ozó és una molècula produïda a partir de l'oxigen elemental. La reacció general de formació és la següent (reacció 3):

$$3\ O_2 \leftrightarrow 2\ O_3\ (\Delta H^{o}\ \text{a 1 atm} = +\ 284{,}5\ \text{kJ/mol}) \qquad \text{(reacció 3)}$$

és per tant una reacció endotèrmica que es porta a terme en un ozonitzador, equip capaç de generar ozó a partir d'una tensió elèctrica.

L'ozó és un dels oxidants més potents. Presenta un elevat potencial d'oxidació, $E^o = 2{,}07$ V i caràcter electrofílic, per tant tendeix a reaccionar en zones d'elevada densitat electrònica, com els dobles enllaços carboni-carboni [1.79].

Les tècniques d'ozonització s'han fet servir en el tractament d'aigües potables des de fa temps, i s'han desenvolupat significativament en els últims 25 anys a França, Alemanya i Suïssa.

Els tractaments amb ozó segueixen unes cinètiques de pseudo-primer ordre respecte el colorant [1.80-1.82] i es poden obtenir graus de decoloració elevats, superiors al 95% en un ample rang de pH (entre 4-12) per a colorants reactius, directes i per colorants utilitzats per tenyir pell [1.83-1.85]. Per contra, proporcionen resultats pobres quant a la disminució de DQO [1.86, 1.87]. Per aquest motiu, és freqüent la combinació de l'oxidació amb ozó amb altres tècniques que proporcionin bons resultats en l'eliminació de DQO. En aquest sentit, es troben estudis que combinen el tractament d'ozó amb l'electroforesi [1.88] o amb dos tractaments més com poden ser la coagulació per eliminar més DQO seguida d'un tractament amb fangs activats de l'efluent resultant, que ja és fàcilment biodegradable [1.89]. D'altres el combinen amb ultrasons però els resultats no milloren significativament [1.84].

1.5.5 Processos de membrana

Aquests processos fan servir una membrana per separar components d'una solució en funció de la seva mida, massa i càrrega.

Els principals rangs i tipus de filtració es mostren a la figura 1.3.

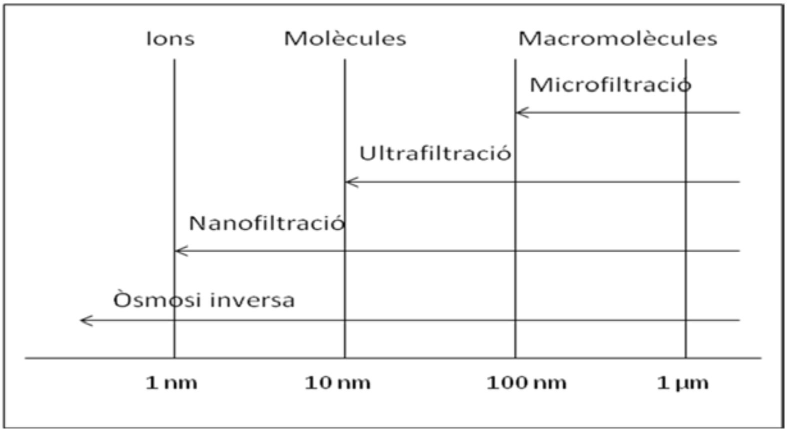

Figura 1.3 Rangs de filtració i tips de compostos filtrats en microfiltració, ultrafiltració, nanofiltració i òsmosi inversa. (Elaboració pròpia).

A partir de la figura 1.3 es poden definir els següents conceptes:

- **Microfiltració**: permet la separació de compostos majors de 100 nm. S’utilitzen per a la retenció de bacteris.

- **Ultrafiltració**: separa compostos de fins a 10 nm. Fent ús de la ultrafiltració en el tractament d’aigües residuals, l’eliminació de compostos contaminants i del color mai és completa (entre el 31% i 76%) i inclús en els millors casos, la qualitat de l’aigua tractada no permet la seva reutilització en processos com els de tintura [1.90].

- **Nanofiltració**: permet la separació de compostos orgànics de baix pes molecular i de fins a 1 nm així com de sals divalents i monovalents. Les sals dels colorants reactius hidrolitzats i els auxiliars del procés de tintura es poden separar per nanofiltració [1.90] possibilitant així la reutilització de l’aigua [1.91] per exemple en nous processos d’acabat [1.92].

- **Òsmosi inversa**: permet l’eliminació de totes les sals minerals, colorants reactius hidrolitzats i additius químics [1.93]. L’òsmosi inversa, permet concentrar el permeat de la nanofiltració i separar-lo en aigua pura i solució concentrada de sals [1.94].

Des dels primers experiments a principis de la dècada dels 90, diversos autors han mostrat la possibilitat de concentrar colorants, estalviar aigua, additius (sobretot sals) i energia mitjançant la utilització de membranes de nanofiltració [1.95] possibilitant així la reutilització de l’aigua de procés de la indústria tèxtil tant des del punt de vista ambiental, econòmic com industrial [1.96].

El problema que presenten els tractaments amb membrana és que a major concentracions de sals, la pressió osmòtica augmenta necessitant així una major aportació energètica i provocant la ràpida colmatació de les membranes.

Hi ha dos paràmetres importants que afecten l’eficiència de la membrana: la disminució en el flux i les incrustacions a la superfície de la membrana [1.97-1.99].

S’han estudiat diverses combinacions d’aquestes tècniques. La més documentada és la formada per nanofiltració i la òsmosi inversa, que millora substancialment els resultats respecte les aplicacions per separat [1.100]. En aquests processos la nanofiltració produeix un permeat que pot ser reutilitzat i la òsmosi inversa millora la seva qualitat [1.101-1.104]. Segons Barredo-Damas, la combinació de la ultrafiltració i nanofiltració no proporciona tant bons resultats [1.105].

Altres combinacions que es poden trobar a la bibliografia són la ultrafiltració amb òsmosi inversa que pot donar suficientment bons resultats en funció de l’aplicació final de l’aigua i la combinació de processos de membrana previs a un tractament biològic.

A part de combinar-se entre sí, les tècniques de filtració també es combinen amb altres tècniques per tal d’obtenir bons resultats finals. En aquest sentit, una de les tècniques més habituals aplicada abans de la filtració és l’adsorció sobre carbó activat [1.106]. Els principals inconvenients d’aquesta combinació és l’elevat preu de la regeneració del carbó activat [1.107] i el fet que no sigui un adsorbent selectiu [1.108].

1.5.6 Processos de Coagulació – Floculació

Els processos de coagulació-floculació faciliten la retirada de les substàncies en suspensió i de les partícules col·loïdals presents en les aigües residuals.

La coagulació consisteix en la desestabilització de les partícules col·loïdals causada per l'addició d'un reactiu químic anomenat coagulant, normalment sals de ferro o clorurs d'alumini, que neutralitzen les càrregues electrostàtiques d'aquestes partícules fent que tendeixin a unir-se. Per la seva banda, la floculació és l'aglomeració de les partícules desestabilitzades en microflòculs i després en flòculs més grans que tendeixen a dipositar-se al fons de la solució. Per millorar la formació dels flòculs, es pot afegir un polielectròlit durant la fase de floculació [1.109].

Diversos factors influeixen en la coagulació de l'aigua, els principals són:

1) Tipus de coagulant.

2) Quantitat de coagulant que es requereix per portar l'aigua a l'òptim de coagulació. Encara que existeix una certa relació entre la turbidesa de l'aigua bruta i la dosi de coagulant apropiada, la quantitat exacte sols es pot determinar mitjançant assajos de Jar-Test.

3) pH de l'aigua. Existeix una zona de pH per a cada coagulant en la qual es produeix una bona floculació i amb una dosi baixa de coagulant.

4) Temps de barreja i floculació. Es defineix com el temps transcorregut entre l'addició del coagulant a l'aigua i el final de l'agitació de l'aigua a

una velocitat que impedeixi la decantació de les matèries floculades. Abans de l'entrada al decantador, es pot estimar entre 10 i 30 minuts.

5) Temperatura. Afecta al temps necessari per a una bona formació del flòcul, generalment quant més freda és l'aigua major és el temps d'estabilització.

6) Velocitat d'agitació. Una velocitat d'agitació massa alta durant l'etapa de floculació pot trencar el flòcul.

7) Presència de nuclis. Les partícules sòlides en suspensió actuen com a nuclis per a la formació inicial de flòculs.

La coagulació-floculació és un dels processos més utilitzats per al tractament d'aigües residuals tèxtils. Pot ser utilitzat com a pre-tractament, post-tractament o inclús com a tractament principal [1.110, 1.111] per a l'eliminació del color de colorants sulfurosos i dispersos i en menor mesura dels colorants àcids, directes i reactius així com la reducció de la DQO [1.112-1.114].

També es fa servir combinat amb altres tècniques com poden ser el carbó activat [1.115] o termòlisi (Catalytic thermal treatment) [1.126].

El principal inconvenient dels processos de coagulació-floculació és la formació de fangs que han de ser tractats posteriorment [1.117, 1.118].

1.6 Microencapsulació

Actualment no existeix un tractament per a l'eliminació del color de les aigües residuals que sigui totalment satisfactori, per aquest motiu, els investigadors cerquen alternatives en altres tecnologies. En aquest sentit, en la present tesi es va iniciar un estudi de microencapsulació com un intent d'obrir noves vies per a la degradació de colorants.

La microencapsulació no és una tècnica nova i altres sectors industrials porten temps utilitzant-la. La indústria farmacèutica la utilitza en noves formes d'aplicar medicaments [1.119, 1.120], com a repel·lent d'insectes [1.121] i en l'encapsulació de col·lagen [1.122] entre d'altres, mentre que la indústria alimentària aplica microcàpsules contenint conservants, potenciadors de sabor, aromes, etc. [1.123-1.128]. Altres usos habituals són la microencapsulació de pesticides [1.129] i herbicides [1.130].

1.6.1 Definicions: microencapsulació i microcàpsula

La microencapsulació es pot definir com el procés de recobriment de reactius o productes en forma de partícules amb materials de diferent naturalesa per obtenir partícules de mida micromètrica que permetin l'alliberació controlada del seu contingut.

A més de definir la microcàpsula, es considera oportú definir també la micropartícula i la microesfera. Aquests tres termes sovint es confonen però es refereixen a tres conceptes molt diferents.

Es consideren ***micropartícules*** aquelles partícules sòlides que tenen diàmetres en l'ordre dels microns. Tenen origen divers i entre elles podem trobar: grans de pol·len, espores, diatomeas, grans de midó i una gran varietat de pols industrials com poden ser els asbestos i derivats minerals.

La ***microesfera*** està formada per la barreja de dos materials, l´un actua com a suport i l'altre és la matèria activa. En una microesfera no existeix una diferenciació entre la composició del nucli i de la membrana. Solen adoptar forma esfèrica i la distribució de la matèria activa en la matèria suport no té perquè ser homogènia.

Finalment, la ***microcàpsula*** es pot definir com un contenidor microscòpic format per una membrana externa que recobreix, aïlla i protegeix un principi actiu situat al nucli de la càpsula. La principal funció de les microcàpsules és la de l'alliberació controlada del seu contingut [1.130].

La dispersió de mides de les microcàpsules és molt gran, poden oscil·lar entre 0,1 – 100 µm de diàmetre entre 0,5 – 150 µm de finor de la membrana i el nucli constitueix entre el 20 i el 95% de la massa total. La figura 1.4 correspon a l'esquema d'una microcàpsula.

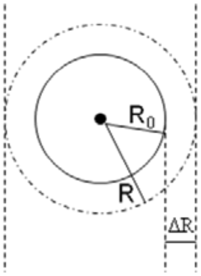

Figura 1.4 Representació d'una microcàpsula. A on R_0 és el radi del nucli, R el radi total de la càpsula i ΔR simbolitza increment del radi a causa de la membrana. (Elaboració pròpia).

Existeixen diversos mètodes d’alliberament de la matèria activa per part d’una microcàpsula. Aquests mètodes són la resposta a un estímul extern, els més importants són:

- Estímuls físics: principalment pressió o fricció.

- Estímuls químics: normalment per dissolució de la membrana causada per l’acció d’un agent químic.

- Estímuls tèrmics: augment o disminució de la temperatura.

- Difusió: equilibri entre medis diferents sempre i quan la membrana ho permeti.

1.6.2 Mètodes d’obtenció de compostos microencapsulats

Existeixen moltes i diverses tècniques per a l’obtenció de compostos microencapsulats depenent de les característiques de la matèria activa que es desitgi encapsular.

Es poden definir dues vies principals d’obtenció de microcàpsules:

1) atenent a l’estat de la matèria activa a encapsular,

2) atenent a la naturalesa del procés utilitzat [1.130].

En la primera via d’obtenció, atenent a l’estat de la matèria activa a encapsular, es poden distingir dues situacions: quan la matèria activa és líquida i quan aquesta matèria és sòlida. Malgrat aquesta diferenciació, es poden establir unes etapes comunes en el procés global d’obtenció:

- La primera etapa consisteix en la dispersió de la matèria activa, pot ser per dissolució o emulsió si és líquida o per aglomeració o recobriment si és sòlida.

- En la segona etapa, té lloc la transformació de la dispersió en microcàpsules que de la mateixa manera que abans, es fa amb unes tècniques o altres depenent de l’estat de la matèria activa.

- Finalment, a la tercera etapa s’apliquen tècniques d’estabilització de les microcàpsules formades a l’etapa anterior.

En la segona via d’obtenció, atenent a la naturalesa del procés utilitzat, es poden distingir els següents processos [1.130]:

- Processos físics: basats en sistemes de combinació de matèries de forma que es força al material de recobriment a formar un dipòsit sobre el material del nucli. Alguns processos físics són el goteig, l’extrusió, el pulveritzat i assecat.

- Processos fisico-químics i químics: basats en les interaccions de les macromolècules i polímers que constitueixen les membranes. Per exemple la coacervació simple, els liposomes com a processos fisico-químics i la polimerització interficial com a procés químic.

1.6.3 Tècniques d’emulsió, preparació de microcàpsules

Les tècniques d’emulsió són àmpliament utilitzades en la primera etapa d’obtenció de microcàpsules, gràcies en gran part a la seva senzillesa d’operació i facilitat per dispersar la matèria activa a encapsular formant així precursors de les microcàpsules.

Una emulsió és una mescla estable i homogènia de dos líquids que tendeixen a separar-se i que són immiscibles entre ells. Una substància, la fase dispersa, és dispersada en l'altra, la fase contínua.

Es distingeixen tres tipus d’emulsions: *directes*, formades per fases oli/aigua, *inverses* aigua/oli i les *emulsions múltiples*, aigua/oli/aigua (en anglès O/W, W/O i W/O/W respectivament) entenent com a oli una fase orgànica [1.131-1.136]. Les tècniques d’emulsió són per tant molt versàtils i permeten emulsionar tant líquids orgànics com inorgànics així com substàncies solubles en aquests líquids. Donen també la possibilitat d’estabilitzar un producte en un determinat medi gràcies a les emulsions múltiples.

Les principals variables de les emulsions són:

- **Tensioactiu**: la seva funció és estabilitzar les emulsions. Es classifiquen segons el seu balanç hidrofílic-lipofílic (HLB), amb valors de 0 a 20. Segons aquesta escala, es pot escollir el tensioactiu més adient per a cada tipus d’emulsió. Per a estabilitzar emulsions O/W, calen agents tensioactius més solubles en aigua que en oli, per tant, HLB alts: 8-16/18. Per contra, per estabilitzar emulsions W/O: calen agents tensioactius més solubles en oli que en aigua, per tant, HLB baixos: 4 – 6.

- **Relació dels reactius:** un dels reactius sol estar en excés i l'altre determina el gruix de la càpsula. Per exemple, en una emulsió O/W el monòmer soluble en aigua sol estar en excés i la difusió del monòmer soluble en oli marcarà la reacció i per tant el gruix de la membrana de la càpsula.

- **Velocitat i tipus d'agitació:** és un factor crític. En general l'agitació ha de ser vigorosa per tal d'obtenir càpsules de petit tamany. Una de les agitacions més utilitzades és la generada per equips d'alta potència, com són els agitadors Ultra Turrax. El tipus de pala també afecta al tamany de la càpsula.

- **Temperatura:** les tècniques d'emulsió es poden dur a terme a temperatura ambient i a diferència d'altres tècniques, no requereixen d'un exhaustiu control de la temperatura.

A més d'aquests quatre factors també és important comentar-ne d'altres que malgrat semblar evidents, s'han de tenir en compte especialment si després de l'emulsió es porta a terme una polimerització interficial (procediment molt habitual):

- Les temperatures de fusió i ebullició dels dissolvents han de ser diferents.

- La matèria activa a encapsular no ha de ser reactiva ni amb els monòmers ni amb el polímer.

- La precipitació del polímer dificulta la difusió dels monòmers i per tant la reacció de polimerització i els límits de la membrana protectora.

1.6.4 Polimerització interficial

La polimerització interficial és una de les tècniques més utilitzades per a l'obtenció de microcàpsules [1.137-1.141].

És un procés de naturalesa química que estabilitza els precursors de les microcàpsules prèviament formats, normalment per emulsió.

Aquesta tècnica forma les membranes de les microcàpsules mitjançant una reacció de polimerització que té lloc a la interfase de l´emulsió, és a dir, entre la fase orgànica i l'aquosa. En aquesta reacció intervenen els monòmers dissolts en cada fase.

En el següent esquema (figura 1.5) es mostra el procés global de formació de microcàpsules utilitzant primer tècniques d'emulsió i posteriorment polimerització interficial. L'esquema correspon a matèries actives solubles en aigua.

En l'esquema s'aprecia com una matèria activa dissolta en la fase aquosa que també conté un dels monòmers, s'emulsiona amb una fase orgànica (W/O) sota forta agitació i en presència d'un tensioactiu.

Una vegada estabilitzada l'emulsió formada, s'afegeix el segon monòmer present en la fase majoritària. D'aquesta manera, es recobreixen els precursors de la microcàpsula. Finalment, s'aplica alguna tècnica que permeti separar les microcàpsules del medi.

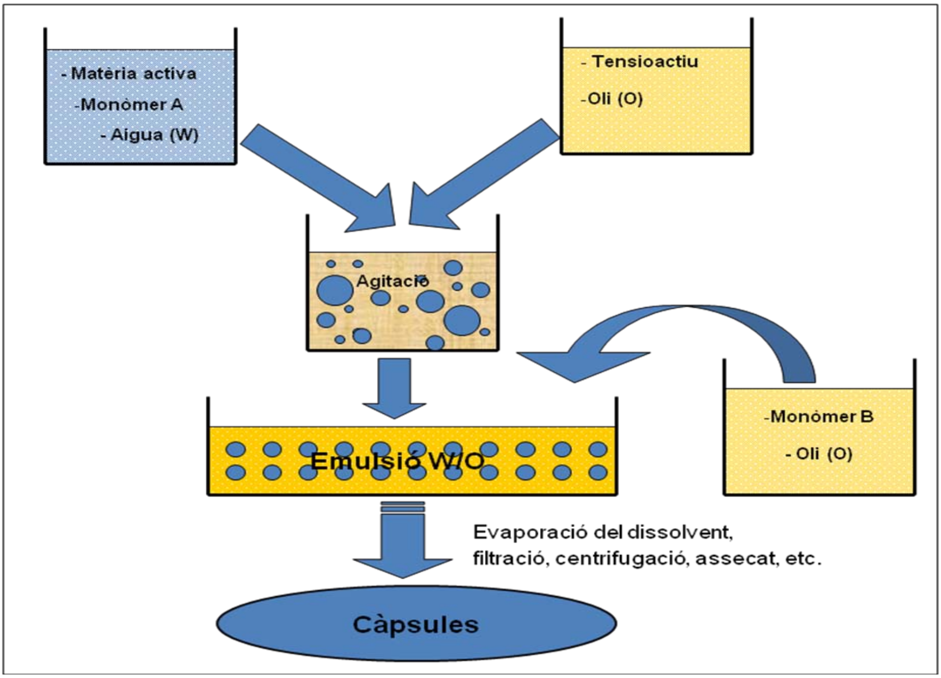

Figura 1.5 Obtenció de microcàpsules mitjançant tècniques d'emulsió i posterior polimerització interficial. (Elaboració pròpia).

En les tècniques de polimerització interficial un dels principals productes utilitzats per a la reacció de polimerització són els cianoacrilats. Aquests productes reaccionen ràpidament amb els grups hidroxils de l'aigua formant un polímer resistent. El seu ús està àmpliament documentat a la bibliografia [1.142-1.144]. El fet que reaccionin amb l'aigua permet prescindir d'un segon monòmer en el medi de reacció i facilita el recobriment de la matèria activa quan aquesta està dissolta en medi aquós.

Els acrilats també es fan servir per a l'obtenció de nanocàpsules, nanopartícules i làtex [1.145-1.147].

1.6.5 Mètodes de seguiment i caracterització de les microcàpsules

Diverses tècniques permeten determinar la formació de microcàpsules. La més ràpida és la microscopia òptica, essent ràpida i senzilla. Altres tècniques, com l'espectroscopia infrarroja amb transformada de Fourier (FTIR), permet per exemple comparar espectres d'infrarroig del polímer format amb els dels monòmers per separats així com detectar compostos incorporats al sistema. La comparació del punt de fusió del polímer format amb el punt de fusió teòric és també una opció interessant.

Unes de les proves de caracterització més habituals de microcàpsules són els estudis d'estabilitat, diàmetre de partícula i potencial zeta. En aquesta categoria, cal destacar les imatges obtingudes per microscòpia electrònica (SEM) que permeten l'observació de partícules micromètriques i nanomètriques amb gran detall. Es pot trobar tècniques d'IR acoplades a SEM (SEM/EDS) que permenten l'anàlisi espectroscòpic de les mostres. A més d'aquests estudis, també és necessari determinar la capacitat de la càpsula per alliberar el seu contingut. El seguiment adequat d'aquest alliberament dependrà en cada cas del tipus del material alliberat i de la membrana principalment.

1.6.6 Aplicacions de la microencapsulació al sector tèxtil

Les primeres aplicacions de microencapsulació al sector tèxtil van ser els colorants dispersos microencapsulats [1.148, 1.149]. Posteriorment s'ha utilitzat la microencapsulació per a l'aplicació de liposomes per millorar la tintura de la llana [1.150], incorporació de retardants de flama a teixits especialitzats [1.151, 1.152] o la incorporació de perfums [1.153]. Una de les aplicacions més importants són els materials de canvi de fase (de l'anglès Phase-Change Materials) i coneguts com

PCMs especialment per teixits destinats a ús exterior (jaquetes, equips de neu, pantalons de protecció, etc.) i productes de la llar (mantes, edredons, matalassos i coixins) [1.154-1.156]. A més de ser dissenyats per combatre el fred, els teixits que incorporen els PCMs ajuden a combatre el sobreescalfament, per tant, el seu efecte es pot descriure com termoregulador. Els PCMs reaccionen molt ràpidament als canvis externs de temperatura [1.157].

1.6.7 Aplicacions de la microencapsulació al tractament d'aigües

Les referències a l'ús de material microencapsulat per al tractament d'aigües residuals són molt escasses. Ross i col. [1.158] han estudiat l'encapsulació del permangat potàssic per a la degradació de compostos orgànics volàtils i semivolàtils donada la seva capacitat oxidant. Els resultats obtinguts en la degradació del tricloroetè (TCE) van ser molt positius. Wang i col. han tractat el dinitro butil fenol (DNBP) de les aigües residuals industrials a partir de microcàpsules de K_2FeO_4 [1.159]. Altres autors han encapsulat antioxidants solubles en aigua per mantenir l'estabilitat de les substàncies solubles dissoltes [1.160]. Els resultats semblen prometedors, però encara queda un llarg camí d'investigació a recórrer.

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Chapter 2

Objectives and justification

Chapter 2. Objectives and justification

2.1 Objectives

This thesis deals with colour removal of reactive dyebath effluents proposed as a prior step to the biological depuration or for the reuse of effluents in new dyeing processes.

The main objectives of this thesis are:

- Study of diverse decolourization methods applied to reactive dye bath effluents:
  - application of UV irradiation after an electrochemical treatment,
  - other techniques: nanofiltration, coagulation-flocculation and ozonation.

- Reuse of decolourized electrochemical treated textile reactive dye effluents for new dyeing processes.

- Proposal of a new method based in encapsulated material.

These general objectives are detailed in specific objectives as follows:

- **First objective: Decolourization**

a) Electrochemical treatment and UV irradiation:

  - Evaluation of the UV irradiation influence after an electrochemical treatment on textile reactive dyebath effluents decolourization.

  - Optimization of the UV irradiation conditions after an electrochemical treatment.

- Evaluation of the possible formation of hazardous materials during the electrochemical treatment: organic halogenated compounds and aromatic amines. Establishment of chromatographic methods for the separation, identification and quantification of these compounds.

b) Other decolourization techniques:

- Dye removal with coagulation-flocculation and nanofiltration treatments.

- Combined and separate application of these techniques.

- Ozonation.

- **Second objective: Reuse**

  - Reuse of dye bath effluents after an electrochemical treatment. Determination of the dye degradation extent.

  - Evaluation of the new dyeings quality with respect to a reference.

- **Third objective: Encapsulation**

  - Encapsulation of aqueous NaClO solution.

  - Evaluation of different encapsulation methods. Capsules characterization.

  - Application of aqueous NaClO microcapsules for the decolourization of reactive dye bath effluents.

2.2 Justification

The experimental work presented in this thesis is structured as follows:

- **Chapter 3**: *Chromatography*.

  In this chapter, chromatographic methods for the separation, identification and quantification of organic halogenated compounds and aromatic amines were established. These methods were applied to analyze the possible formation of these compounds during the electrochemical treatment of effluents containing reactive azo dyes.

- **Chapter 4:** *Article on decolourization I: Colour removal of three reactive dyes by UV light exposure after electrochemical treatment.*

  In this work, the influence of UV irradiation applied to effluents containing reactive azo dyes after a low current density electrochemical treatment was studied. It was concluded that the combination of these two techniques improves the results of colour removal of the treated effluents with respect to only an electrochemical treatment. Moreover, the results showed that with a very small Cl^- concentration in water, the combined techniques provide full decolourization of the effluents and this also minimizes the formation of organic halogenated compounds.

  This work was published in the Chemical Engineering Journal 156 (2010) 114-120.

- **Chapter 5:** *Article on decolourization II: Optimization of UV irradiation after an electrochemical pre-treatment to remove colour of textile effluents*.

  The goal of this work was to optimize the working conditions of the combined treatment, from the results obtained in chapter 4, in order to obtain a higher colour removal of the effluents. For that purpose, different UV irradiation conditions after an electrochemical pre-treatment of textile effluents were studied. The results show that total colour removal of reactive dyes effluents can be achieved with UV irradiation after an electrochemical pre-treatment. The type of UV lamp and its way of application were found to have a strong influence on the colour removal. In this chapter, ozonation was also applied to decolourize the same effluents and the mechanisms of both treatments were discussed.

  This work is currently under the second revision at Dyes and Pigments journal.

- **Capítol 6:** *Article on decolourization III: Combination of coagulation–flocculation and nanofiltration techniques for dye removal and water reuse in textile effluents*.

  In this work, some other decolourization techniques applied to remove colour from reactive dyebath effluents were evaluated. In this sense, nanofiltration, coagulation–flocculation and their combination were studied. From the results, it was demonstrated that the combination of these two treatments dramatically improve the results of both techniques separately in terms of dye removal.

  This work was published in the Desalination Journal 252 (2010) 53-59.

- **Chapter 7:** *Article on reuse: Influence of electrochemical pre-treatment in dyeing wastewater reuse for five reactive dyes.*

  In this chapter, the influence of an electrochemical pre-treatment applied to dyebath effluents before been reused was evaluated. From the results, it can be concluded that DE (CMC (2:1)) values are improved up to 75% with respect to direct bath reuse by applying an electrochemical pre-treatment to the dyeing wastewater before reuse.

  This work was accepted to be published in the Textile Research Journal.

- **Chapter 8:** Patent: *NaClO encapsulation*.

  The aim of this chapter was the encapsulation of NaClO aqueous solutions and their application to the decolourization of reactive dye solutions. The work was performed during a staying (March 2008 – August 2008) at the Max Planck Institute of Colloids and Interfaces. The results showed promising indication that the encapsulation of NaClO aqueous solutions was achieved by interfacial polymerization method. The application of the obtained microcapsules to C.I. Reactive Black 5 dye solutions reached the 61,5% of colour removal after 5h of UV light exposure under the studied conditions.

  This work was registered as a Spanish patent by the “Oficina Española de Patentes y Marcas”. Patent code 201000011.

In summary, this thesis is structured in four main experimental parts: chromatography (chapter 3), decolourization of reactive dye effluents (chapters 4, 5 and 6) dyebtah reuse (chapter 7) and microencapsulation of NaClO aqueous solutions and its application to the decolourization of reactive dye solutions (chapter 8).

Capítol 3

Cromatografia

Capítol 3. Cromatografia

3.1 Introducció

Un dels inconvenients que presenten les tècniques electroquímiques aplicades al tractament d’aigües residuals és la possible formació de compostos orgànics halogenats, principalment clorats [3.1]. Per tal de minimitzar la seva formació, es poden aplicar algunes mesures com poden ser l’ús de Na_2SO_4 com a electròlit de tintura en lloc de NaCl [3.2], l’ús de Pt com a material anòdic [3.3] o l’aplicació de llum UV durant o després del tractament electroquímic [3.4 – 3.6]. La combinació d’aquests tractaments permet reduir a més, la DQO dels efluents [3.7 – 3.9]. Habitualment s’havia proposat el tractament anaeròbic dels efluents que contenien compostos orgànics halogenats per tal de degradar-los [3.10, 3.11].

És per la importància en el control dels compostos orgànics halogenats, que s’han desenvolupat diversos mètodes per a la seva determinació, la majoria basats en cromatografia de gasos - espectrometria de masses (GC-MS) [3.12 – 3.16]. Altres, per exemple, utilitzen nous sistemes basats en sensors polimèrics [3. 17].

D’altra banda, quan se sotmet a un tractament electroquímic de reducció als efluents que contenen colorants azo, podria tenir lloc la formació d’amines aromàtiques [3.18] algunes d’elles cancerígenes.

A causa de la creixent preocupació pel risc potencial d’aquests compostos en els consumidors, el parlament europeu va acceptar l’esmena 19 de la directiva 76/769/CEE i va emetre la directiva europea 2002/61/CE [3.19]. Aquesta directiva restringeix específicament la comercialització i l’ús dels colorants azoics que després d’una fragmentació reductora poguessin alliberar alguna de les vint-i-dues amines aromàtiques perjudicials en concentracions superiors a 30 ppm en productes tèxtils o de pell que puguin entrar en contacte directe i prolongat amb la pell humana o la cavitat bucal [3.20].

A la bibliografia es troben diverses tècniques analítiques per a la determinació d'amines aromàtiques tant en mostres ambientals [3.21 - 3.24] mostres aquoses d'aliments [3.25], fluids biològics [3.26] i amines aromàtiques derivades de colorants azoics [3.27 – 3.30].

En aquesta tesi, es varen posar a punt mètodes cromatogràfics que permeten la determinació i quantificació tant de compostos orgànics halogenats com d'amines aromàtiques. Les tècniques cromatogràfiques són molt variades, però en totes elles hi ha una fase mòbil que consisteix en un fluid (gas, líquid o fluid supercrític) que arrossega la mostra a través d'una fase estacionària que es tracta d'un sòlid o un líquid fixat sobre un sòlid. Els components de la mescla interaccionen amb la fase estacionària a diferents velocitats provocant la seva separació.

En el cas dels compostos orgànics halogenats, es va posar a punt un nou mètode cromatogràfic per cromatografia de gasos - espectrometria de masses (GCMS) que permetia millorar el mètode existent. Les millores se centren en la utilització d'un nou equip que permet una major sensibilitat i automatització en l'anàlisi de mostres respecte l'equip anterior.

Pel que fa a les amines aromàtiques, es varen posar a punt dos mètodes cromatogràfics diferents: un per cromatografia líquida d'alta resolució (HPLC) acoblada a un detector DAD i l'altre per cromatografia de gasos – espectrometria de masses (GCMS). Amb la primera tècnica (HPLC), es va determinar el mètode d'extracció més adient de les amines aromàtiques. La segona tècnica (GCMS) va resultar més fàcil i més senzilla. Aquesta tècnica es va fer servir per tant, per a la determinació i quantificació de les 26 amines aromàtiques estudiades en aquesta tesi.

Així doncs, en l'apartat 3.3 d'aquest capítol es va treballar en la posada a punt dels mètodes cromatogràfics anteriorment esmentats i en l'etapa d'extracció de les amines.

En la posada a punt dels mètodes cromatogràfics tant d'HPLC com de GCMS, es va agafar com a base de partida la norma EN 14362 "Métodos para la determinación de ciertas aminas aromáticas derivadas de colorantes azoicos".

Aquesta norma consta de tres etapes experimentals: alliberament d'amines aromàtiques, extracció i concentració:

- La primera etapa, que té lloc en medi reductor, té com a finalitat la reducció de les amines aromàtiques dels colorants azoics presents en teixits. Aquesta etapa no es durà a terme en aquesta tesi ja que les amines a analitzar estarien en solució aquosa.

- La segona etapa consisteix en l'extracció de les amines formades durant la primera etapa des del medi aquós a medi orgànic.

- La tercera etapa consisteix en la concentració de l'extracte orgànic que conté les amines anteriors.

3.2 Compostos orgànics halogenats

3.2.1 Material i mètodes

La determinació i quantificació dels compostos orgànics halogenats es va portar a terme per cromatografia de gasos-espectrometria de masses (GCMS) basats en la norma UNE-EN ISO 10301 i el mètode EPA 624. Es va fer servir un equip GCMS Shimadzu QP 2010 i la tècnica de head-space en la injecció de les mostres. Es va treballar amb una solució patró de 25 compostos orgànics halogenats de 0.2 mg L^{-1} (AccuStandard) i p-bromofluorobenzè (AccuStandard) com a patró intern (d'ara en endavant, P. I.). El dissolvent utilitzat en la preparació dels patrons va ser metanol.

A continuació es detallen les condicions tant de la tècnica de head-space com del mètode cromatogràfic.

Mètode qualitatiu

- Head-space: s'escalfen 20 mL de mostra a 80ºC durant 45 minuts en un vial segellat amb un septum de silicona/PTFE. S'injecta al GCMS 1 mL de l'aire en cap.
- Condicions del GCMS:

- GC:
  - El gradient de temperatura de la columna s'indica a la figura 3.1.
  - Columna: TRB-5MS (Tecknocroma)
  - Temperatura d'injecció: 230 ºC
  - Gas portador: He
  - Mode d'injecció: Split 1/20

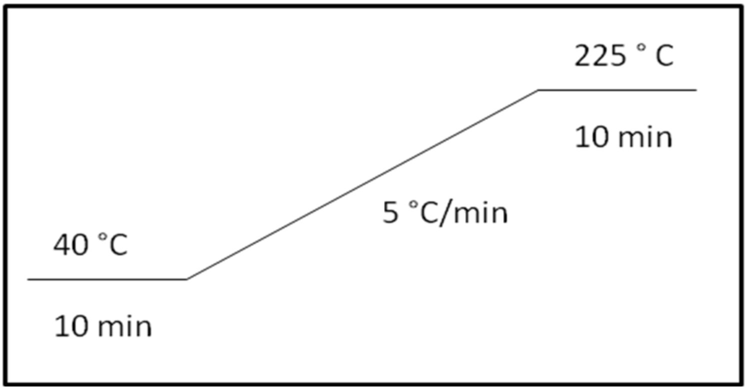

Figura 3.1 Programa de la temperatura de columna per a la determinació de compostos orgànics halogenats.

- MS: - Temperatura de la font: 200 ºC
  - Temperatura de la interfase: 250ºC
  - Rang de masses analitzat: 40 m/z 350 /z

La identificació dels compostos es va realitzar a partir de les següents bases de dades: Nist 147, Nist 27 i Wiley 229.

Mètode quantitatiu

La quantificació dels compostos orgànics halogenats es va fer injectant per quintuplicat patrons de concentració 1 ppb; 2 ppb; 5 ppb i 10 ppb respectivament dels compostos. La concentració de P.I. es va fixar a 5 ppb.

3.2.2 Resultats

En les condicions establertes en el mètode qualitatiu, es va aconseguir la separació i identificació de tots els compostos orgànics halogenats estudiats. La figura 3.2 mostra el cromatograma d'aquests compostos.

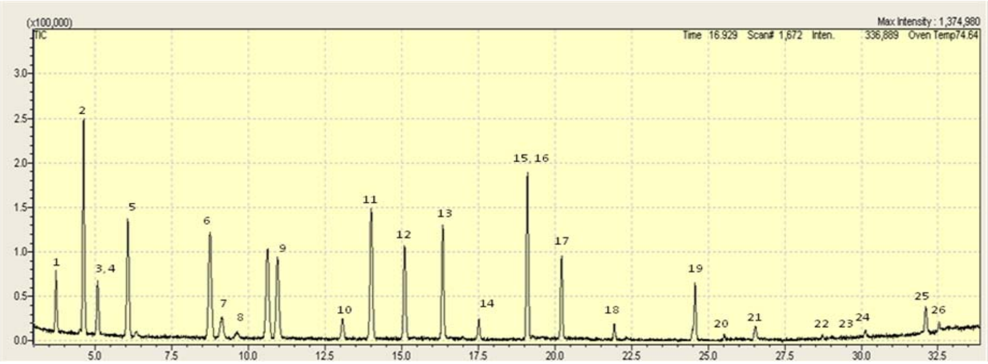

Figura 3.2 Cromatograma de la separació i identificació dels compostos orgànics halogenats. El llistat dels compostos orgànics halogenats es troba a la taula 3.1.

La identificació dels compostos es va realitzar mitjançant la comparació dels espectres de masses obtinguts experimentalment per cada pic cromatogràfic respecte els espectres de masses de les bases de dades especificades anteriorment. A la figura 3.3 es mostren ambdós espectres de masses pel cas del cloroform.

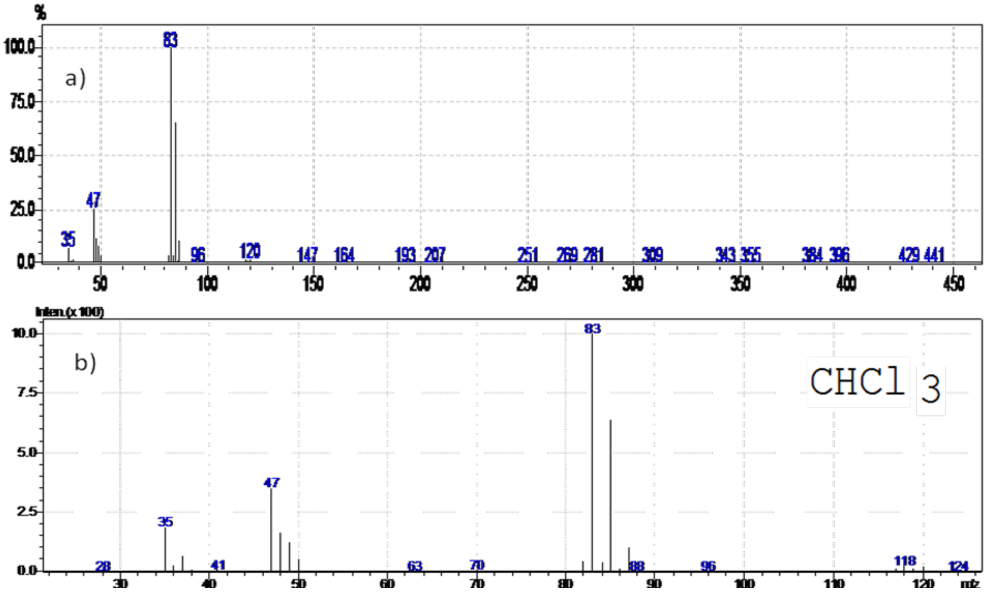

Figura 3.3 Espectres de masses del cloroform: a) espectre experimental i b) espectre de la base de dades.

A la taula 3.1 es mostren les equacions de les corbes de calibració i els límits de detecció obtinguts per els compostos orgànics halogenats. Els límits de dectecció es varen calcular segons el mètode UC Code of Federal Regulations (US-CFR, 2005), mètode corresponent a la relació senyal/soroll = 3 amb nivell de confiança del 99%.

Taula 3.1 Número CAS, equacions corbes calibració i límits de detecció dels compostos orgànics halogenats.

Núm	**Compost**	**Núm. CAS**	**Eq. corba cal.**	**R^2**	**L. D. (ppb)**
1	1,1-dicloroetè	75-35-4	y=1,269x – 5,01exp(-2)	0,9998	2,5
2	Diclorometà	75-9-2	y=0,936x – 1,09exp(-2)	0,9986	1,0
3	t-1,2-dicloroetè	156-60-5	y=2,027x – 7,33exp(-3)	0,9993	2,5
4	c-1,2-dicloroetè	540-59-0	y=3,084exp(-2)x + 6,41exp(-5)	0,9989	2,5
5	Clorofom	67-66-3	y=1,143x – 2,16exp(-3)	0,9988	1,0
6	1,1,1-tricloroetà	71-55-6	y=2,363x – 4,51(exp-2)	0,9989	2,5
7	Tetraclorometà	56-23-5	Y=2,588x – 0,107	0,9998	2,5
8	1,2-dicloroetà	107-6-2	y=0,819x – 2,67exp(-2)	0,9984	10
9	Tricloroetilè	79-1-6	y=1,957x + 2,28exp(-2)	0,9993	1,0
10	1,2-dicloropropà	78-87-5	y=1,187x – 2,34exp(-2)	0,9995	5
11	Bromodiclorometà	75-27-4	y=1,273x + 5,22exp(-2)	0,9985	5
12	c-1,3-dicloropropè	10061-1-5	y=0,501x + 1,38exp(-3)	0,9929	10
13	t-1,3-dicloropropè	10061-2-5	y=0,264x + 2,24exp(-2)	0,9898	10
14	1,1,2-tricloroetà	79-0-5	y=0,631x – 2,39exp(-3)	0,9992	10
15	Tetracloroetè	127-18-4	Y=2,211x + 0,166	0,9998	1,0
16	Dibromoclorometà	124-48-1	y=0,710x + 8,98exp(-2)	0,9979	10
17	Clorobenzè	108-90-7	y=4,184x + 1,48exp(-2)	0,9973	1,0
18	Bromoform	75-25-2	Y=0,196x + 0,143	0,9991	10
19	p-bromofluorobenzè	460-00-4	P.I.		
20	1,3-diclorobenzè	541-73-1	y=3,088x + 3,33exp(-2)	0,9969	1,0
21	1,4-diclorobenzè	106-46-7	y=2,936x + 5,50exp(-2)	0,9963	0,5
22	1,2-diclorobenzè	95-50-1	y=2,399x + 2,29exp(-2)	0,9975	0,5
23	1,3,5-triclorobenzè	108-70-3	y=1,327x – 2,74exp(-3)	0,9983	1,0
24	1,2,4-triclorobenzè	120-82-1	y=1,327x – 2,74exp(-3)	0,9969	1,0
25	Hexaclorobutadiè	87-68-3	*		0,5
26	1,2,3-triclorobenzè	87-61-6	y=1,327x – 2,74exp(-3)	0,9978	1,0

*No es va poder determinar la corresponent equació de la corba de calibració per falta de reproductibilitat de les dades.

Aquest mètode es va fer servir per determinar i quantificar la presència de compostos orgànics halogenats en efluents després d’un tractament electroquímic a baixa densitat de corrent amb posterior irradiació UV. Els resultats formen part de l’article “COLOUR REMOVAL OF THREE REACTIVE DYES BY UV LIGHT EXPOSURE AFTER ELECTROCHEMICAL TREATMENT” publicat a la revista Chemical Engineering Journal 156, (2010) 114–120.

3.3 Amines aromàtiques: Extracció i anàlisi per HPLC

3.3.1 Material i mètodes

En aquesta part del treball experimental es va utilitzar un equip de cromatografia líquida Perkin-Elmer Advanced LC Sample Processor ISS200 amb detector DAD 235C. La columna cromatogràfica utilitzada va ser TR-011970 (Lichorsorb) RP-18 5.0µm 4,60x250 mm. Es van seleccionar quatre amines aromàtiques: anilina (Riedel-de Haën), 4-aminobifenil (Sigma-Aldrich), 1, 4-fenilendiamina (Fluka), 4-cloroanilina (Riedel-de Haën) i com a P.I. 4-aminoquinaldina (Sigma-Aldrich). Els diferents grups substituents dels anells benzènics d’aquestes amines aromàtiques provoquen una diferent interacció amb la fase estacionària facilitant aixi la seva separació.

Les condicions cromatogràfiques varen ser les següents:

- Gradient d’elució: indicat a la figura 3.4.
- Volum d’injecció de mostra: 15 µL.
- Longitud d’ona de detecció: 240 nm.
- Flux: 1mL min^{-1}.

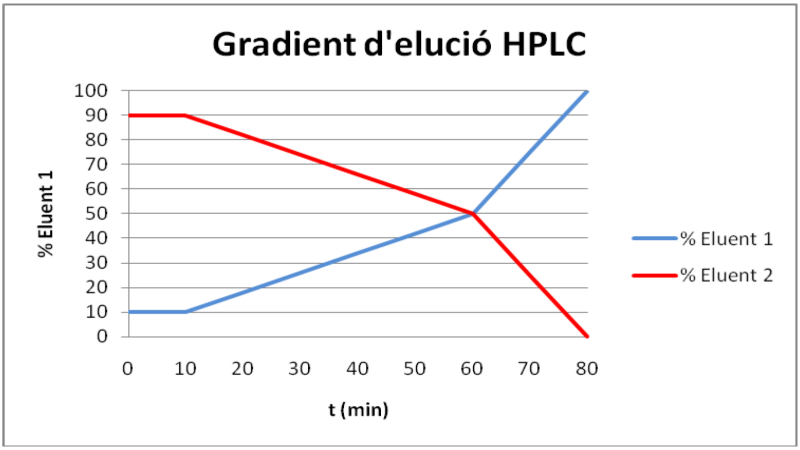

Figura 3.4 Gradient elució HPLC.

A on:

- Eluent 1: metanol (Fluka).
- Eluent 2: barreja de 0,575 g dihidrogenofostat amònic (Sigma-Aldrich) + 0,7 g hidrogenofosfat disòdic (Sigma-Aldrich) + 100 mL metanol (Fluka) en 1L d'aigua, pH 6,9.

Es va seguir la norma EN 14362, al qual indica l'ús d'una columna de terres diatomees per retenir i concentrar les amines aromàtiques. En aquesta etapa es fa un canvi de medi aquós a orgànic i posteriorment es concentra l'eluat en el dissolvent apropiat (metanol, acetat d'etil o t-butil metil èter) segons la norma anterior.

Les característiques requerides de la columna, segons la norma EN 14362 són les següents:

- Diàmetre intern: de 25 a 30 mm.
- Longitud: de 140 a 150 mm.
  - 20 g de terres de diatomees (90% SiO_2) (Myta) amb fibra de vidre al fons de la columna.

D'acord amb la norma EN 14362 es va utilitzar el t-butil metil èter com a eluent.

Per tal de calcular el tant per cent de recuperació del mètode, 1 mL de mostra d'amines de concentració 120 ppm, s'addiciona a la columna juntament amb 4 mL de metanol i 15 mL de solució tampó (hidròxid de sodi/citrat) pH 6 (Fluka). Posteriorment s'elueix amb 80 mL de t-butil metil èter i es concentra l'eluat fins a 1 mL aproximadament en un rotavapor (Buchi R-200). Finalment, s'enrasa a 2 mL amb t-butil metil èter.

A més de l'ús de la columna de terres de diatomees, es van provar dos mètodes alternatius per a la extracció de les amines aromàtiques: columnes Sep-Pak C18 (Waters Associates) i extracció líquid-líquid en embut de decantació. En ambdós mètodes es va treballar amb la mateixa concentració d'amines que amb la columna de terres de diatomees (120 ppm).

- **Columnes Sep-Pak (C-18)**: es prepara la columna amb 2 mL de metanol i 5 mL d'aigua destil·lada; s'afegiex 1 mL de solució d'amines i seguidament 4 mL de metanol, 15 mL de solució tampó hidròxid de sodi/citrat pH 6 i 1 mL de t-butil metil èter per eluir les amines.

- **Extracció líquid-líquid en embut de decantació**: la fase aquosa, formada per 1 mL de solució d'amines, 4 mL de metanol i 15 mL de solució tampó hidròxid de sodi/citrat pH 6 s'afegeix a l'embut de decantació juntament amb la fase orgànica formada per 20 mL de t-butil metil èter. El procés consta de tres extraccions amb t-butil metil èter.

Finalment, i d'igual manera que amb l'ús de la columna de terres de diatomees, l'eluat es concentrava al rotavapor fins a 1 mL i enrasava posteriorment a 2 mL amb t-butil metil èter.

Per a la quantificació de les amines aromàtiques es varen determinar les corbes de calibració injectant per triplicat cinc concentracions patró diferent: 1 ppm, 10 ppm, 20 ppm, 30 ppm i 50 ppm amb concentració de patró intern constant i igual a 20 ppm.

3.3.2 Resultats

En les condicions cromatogràfiques descrites anteriorment, es va aconseguir la separació i identificació de les quatre amines estudiades.

A la figura 3.5 es mostra el cromatograma d'HPLC obtingut per les quatre amines i el patró intern en les condicions esmentades.

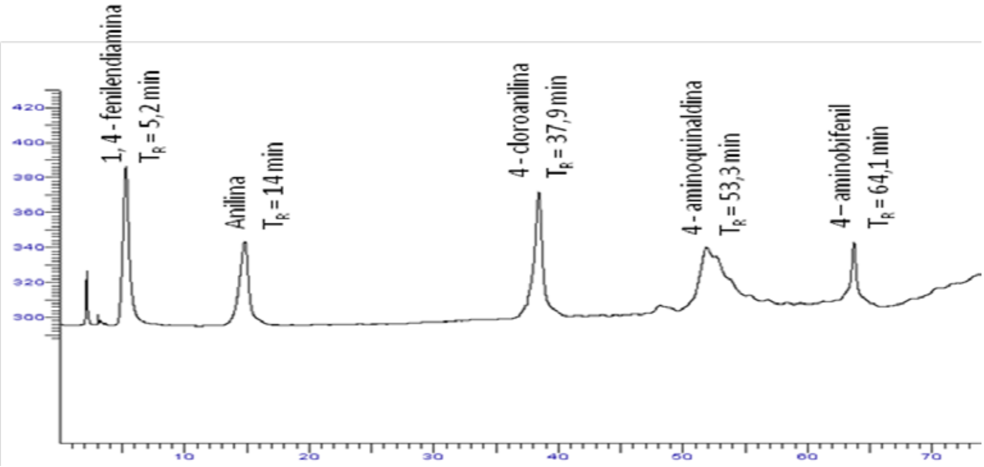

Figura 3.5 Cromatograma HPLC corresponent a una solució de 30 ppm de cada amina: 1,4-fenilendiamina, anilina, 4-cloroanilina, 4-aminoquinaldina i P. I. 4-aminobifenil, 20 ppm.

Una vegada resolta la separació i identificació de les amines aromàtiques estudiades, es va procedir a la seva quantificació segons el mètode quantitatiu.

A la taula 3.2 es mostren les equacions de les corbes de calibració respecte el P. I.

Taula 3.2 Equacions de les corbes de calibració de 1, 4-fenilendiamina, anilina, 4-cloroanilina i 4-aminobifenil. (P. I. 20 ppm).

Amina aromàtica	**Eq. corba calibració**	**R^2**
1,4-fenilendiamina	$y^{(1)} = 0{,}5435x^{(2)} - 0{,}0636$	0,9999
Anilina	$y = 0{,}4165x - 0{,}01$	0,9999
4-cloroanilina	$y = 0{,}6206x - 0{,}0478$	0,9998
4-aminobifenil	$y = 0{,}1324x + 0{,}1769$	0,9999

(1)y = Àrea pic amina/àrea pic P.I.; (2) x = Conc. Amina/conc. P.I.

Amb les corbes de calibració corresponents a les amines seleccionades, es va procedir a comparar els tres mètodes d’extracció.

A la taula 3.3 es mostren els percentatges de recuperació mitjans obtinguts per a cada mètode. Tots els experiments es varen fer per duplicat.

Taula 3.3 Percentatges de recuperació de les amines per als diferents mètodes d’extracció.

Amina	**% de recuperació**			
	Columna terres diatomees	Columna Sep-Pak	Extracció líquid-líquid	EN 14362*
1,4-fenilendiamina	15,7	3,1	51,9	No especifica**
Anilina	96,4	7,2	96,7	No especifica**
4-cloroanilina	73,9	24,4	99,8	70
4-aminobifenil	94,9	70,8	73,8	70

* Mínim requerit per la norma EN 14362.

** La norma EN 14362 no especifica els percentatges de recuperació d’aquestes amines aromàtiques ja que provenen de la descomposició de la 4-aminoazobenzè.

A partir de la taula 3.3 es pot concloure que tant la columna de terra de diatomees com l'extracció líquid-líquid proporcionen en general bons resultats de recuperació per tres amines aromàtiques. En el cas de l'anilina, 4-cloroanilina i 1,4-fenilendiamina l'extracció líquid-líquid proporciona els millors resultats de recuperació excepte per la 4-aminobifenil que s'extreu millor amb la columna de terra de diatomees. Només per aquesta última amina, 4-aminobifenil, la columna Sep-Pak va proporcionar resultats de recuperació acceptables.

A la taula 3.3 també apareixen els percentatges de recuperació que la norma EN 14362 proposa per a cada amina. Tant en el cas de la 1,4-fenilendiamina com de l'anilina, la norma no especifica aquests valors. Aquestes amines es generen a partir de la 4-aminoazobenzè (producte que alguns colorants azo poden formar) en les condicions d'alliberament d'amines de la norma EN 14362. Els factors de recuperació proposats per la norma per la 4-cloroanilina i la 4-aminobifenil són 70% per ambdós casos, valors que s'aconsegueixen tant amb la columna de terra de diatomees com amb l'extracció líquid-líquid.

A partir d'aquests resultats, i tenint en compte la seva facilitat d'operació i senzillesa, es va proposar l'extracció líquid-líquid com a mètode més adient per portar a terme l'extracció i concentració de les amines.

3.4 Amines aromàtiques: Extracció i anàlisi per GCMS

3.4.1 Material i mètodes

En aquesta part del treball experimental es va utilitzar un equip de GCMS Shimadzu QP 2010, un patró comercial de 24 amines (Cromlab) de 10 ppm i dos patrons d'amines individuals no incloses en aquest patró mixte: anilina (Riedel-de Haën), 1,4-fenilendiamina (Fluka). Patró intern: 2,4,5-tricloroanilina (Cromlab).

Les condicions cromatogràfiques són les següents:

Mètode qualitatiu

- GC:
  - El gradient de temperatura de la columna s'indica a la figura 3.6
  - Columna: DB-35 MS; (Tecknocroma)
  - Temperatura d'injecció: 260 ºC
  - Gas portador: He
  - Mode d'injecció: Splitless

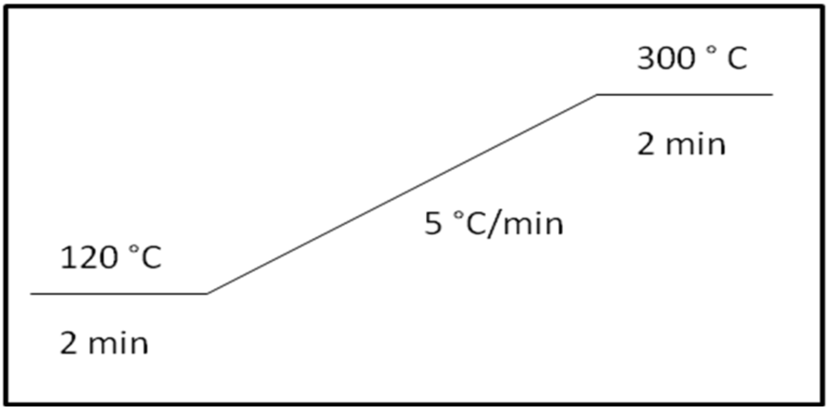

Figura 3.6 Programa de la temperatura de columna per a la determinació d'amines aromàtiques.

- MS:
  - Temperatura de la font: 200 ºC
  - Temperatura de la interfase: 260 ºC
  - Rang de masses analitzat: 40 m/z – 350 m/z

La identificació dels compostos es va realitzar a partir de les següents bases de dades: Nist 147, Nist 27 i Wiley 229.

Mètode quantitatiu

La quantificació de les amines aromàtiques es va realitzar amb patrons de concentració 0,1 ppm; 0,25 ppm; 0,5 ppm; 1 ppm i 2 ppm de cada compost. La concentració del patró intern utilitzada va ser de 0,5 ppm. Tots els patrons es varen injectar per quintuplicat.

3.4.2 Resultats

En les condicions cromatogràfiques descrites anteriorment, es va aconseguir la separació i identificació de les 26 amines estudiades.

A la figura 3.7 es mostra el cromatograma obtingut per les 26 amines i P.I. en les condicions esmentades. A la següent taula (taula 3.4), es mostren els noms, números CAS i temps de retenció de les mateixes amines segons els seu ordre d'elució.

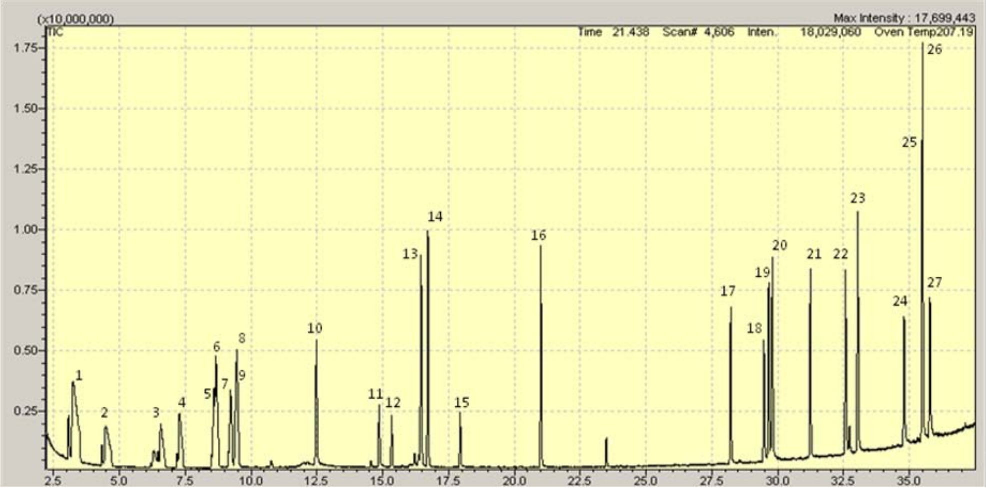

Figura 3.7 Cromatograma GCMS corresponent a la separació de les 26 amines estudiades i al P.I. La concentració d'amines és 1 ppm i la de P. I. 0.5 ppm. El llistat d'amines analitzades es troba a la taula 3.4.

En els casos de les amines que elueixen solapades (similars o mateixos temps de retenció) l'espectrometria de masses permet la seva discriminació per quantificació d'una massa específica de l'amina aromàtica a analitzar.

Taula 3.4 Ordre d'elució, nom, núm. CAS i temps de retenció de les amines corresponents a la 3.7.

Número	**Amina**	**Núm. CAS**	**t_R (min)**
1	Anilina	62-53-3	3,228
2	o-toluidina	95-53-4	4,475
3	o-anisidina	90-04-0	6,575
4	4-cloroanilina	106-47-8	7,283
5	2-metoxi-5-metilanilina	120-71-8	8,592
6	2,4,5-trimetilanilina	137-17-7	8,662
7	4-cloro-2-metilanilina	95-69-2	9,221
8	3-cloro-o-toluidina	87-60-5	9,250
9	1,4-fenilendiamina	106-50-3	9,454
10	2,4-diaminoanisole	615-05-4	12,479
11	2,4-diaminotoluè	95-80-7	14,863
12	2,4,5-tricloroanilina (P.I.)	636-30-6	15,342
13	2-aminonaftalè	91-59-8	16,454
14	2-aminobifenil	90-41-5	16,717
15	2-metil-5-nitroanilina	99-55-8	17,942
16	4-aminobifenil	92-67-1	21,004
17	4-fenilazoanilina	60-09-3	28,217
18	4,4'-oxidianilina	101-80-4	29,479
19	4,4'-diaminodifenilenmetà	101-77-9	29,663
20	Benzidina	92-87-5	29,796
21	o-aminoazotoluè	97-56-3	31,238
22	3,3'-dimetil-4-4'-diaminodifenilmetà	838-88-0	32,575
23	3,3'-dimetilbenzidina	119-93-7	33,042
24	4,4'-tiodianilina	139-65-1	34,796
25	3,3'-diclorobenzidina	91-94-1	35,500
26	4,4'-metilenbis(2-cloroanilina)	101-14-4	35,520
27	3,3'-dimetoxibenzidina	119-90-4	35,779

Per dur a terme la quantificació de les amines aromàtiques, es varen determinar tant les corbes de calibració absolutes com les corresponents als factors de resposta respecte la concentració de P. I. En tots dos casos, va ser necessari prescindir de la mostra de concentració més elevada (2 ppm) per tal d'obtenir bona linealitat en les corbes.

A la taula 3.5 es mostren les equacions de les corbes de calibració respecte el patró intern de les amines aromàtiques i els límits de detecció obtinguts. Els límits de detecció es varen calcular segons el mètode UC Code of Federal Regulations (US-CFR, 2005), mètode corresponent a la relació senyal/soroll = 3 amb nivell de confiança del 99%.

Els mètodes anteriors es varen aplicar per estudiar la possible alliberació d'una o més d'una de les amines aromàtiques després d'una fragmentació reductora, segons indica la directiva europea 2002/61/CE, en els següents colorants azo: Procion Crimson H-EXL, Procion Navy H-EXL i Procion Yellow H-EXL. Aquests colorants són una tricromia habitual en l'ús industrial.

Les següents taules (taules 3.6, 3.7 i 3.8) mostren els resultats obtinguts després d'efectuar diversos tractaments de decoloració electroquímica a 3, 24 i 40 mA/cm^2. Posterior al tractament de 24 mA/cm^2 es va irradiar amb llum UV la mostra.

Taula 3.5 Equacions de les corbes de calibració respecte el P.I. de les amines aromàtiques.

Núm.	Amina	Eq. corba calibrat respecte P.I.	R^2	L. D.(ppm)
1	Anilina	y=0,2165x – 0,0219	0,9999	0,058
2	o-toluidina	y=0,2538x – 0,0646	0,9989	0,077
3	o-anisidina	y=0,1409x - 0,0373	0,9898	0,013
4	4-cloroanilina	y=0,1731x – 0,0376	0,9978	0,008
5	2-metoxi-5-metilanilina	y=0,1579x – 0,0388	0,9988	0,011
6	2,4,5-trimetilanilina	y=0,1825x – 0,0394	0,9999	0,008
7	4-cloro-2-metilanilina	y=0,1516x – 0,0302	0,9989	0,009
8	3-cloro-o-toluidina	y=0,1461x – 0,0330	0,9987	0,009
9	1,4-fenilendiamina	y=0,1243x – 0,0032	0,9999	0,032
10	2,4-diaminoanisole	y=0,0111x – 0,004	0,9999	0,023
11	2,4-diaminotoluè	y=0,1566x – 0,0184	0,9997	0,027
12	2-aminonaftalè	y=0,2420x - 0,0187	0,9996	0,064
13	2-aminobifenil	y=0,1955x – 0,0082	0,9986	0,003
14	2-metil-5-nitroanilina	y=0,0284x – 0,0040	0,9981	0,004
15	4-aminobifenil	y=0,2393x – 0,0219	0,9989	0,043
16	4-fenilazoanilina	y=0,1325x + 0,0001	0,9998	0,010
17	4,4’-oxidianilina	y=0,0938x – 0,019	0,9877	0,111
18	4,4’-diaminodifenilenmetà	y=0,0837x – 0,0208	0,9899	0,009
19	Benzidina	y=0,1649x – 0,0355	0,9934	0,113
20	o-aminoazotoluè	y=0,1556x – 0,0302	0,9988	0,053
21	3,3’-dimetil-4-4’-diaminodifenilmetà	y=0,0761x – 0,0173	0,9999	0,003
22	3,3’-dimetilbenzidina	y=0,2371x – 0,0617	0,9879	0,142
23	4,4’-tiodianilina	y=0,0041x – 0,0036	0,9981	0,103
24	3,3’-diclorobenzidina	y=0,1537x – 0,0267	0,9985	0,011
25	4,4’-metilenbis(2-cloroanilina)	*		*
26	3,3’-dimetoxibenzidina	*		*

*No es va determinar la corresponent equació de la corba de calibració per falta de reproductibilitat de les dades.

Taula 3.6 Concentració d'amines detectades al Procion Crimson H-EXL.

Amina	Col. inicial	Tract. electr. (3 mA/cm2)	Tract. electr. (24 mA/cm2)	Tract. electr. (24 mA/cm2) + UV	Tract. electr. (40 mA/cm2)
o-toluidina (ppm)	0,002	0	0	0,002	0,014
4-cloroanilina (ppm)	0	0,024	0,055	0,031	0,021
2,4-diaminotoluè (ppm)	0	0	0,064	0,068	0
4-aminobifenil (ppm)	0,960	0,860	0,060	0,060	0,055
Total (ppm)	0,962	0,984	0,179	0,161	0,090

Taula 3.7 Concentració d'amines detectades al Procion Navy H-EXL.

Amina	Col. inicial	Tract. electr. (3 mA/cm2)	Tract. electr. (24 mA/cm2)	Tract. electr. (24 mA/cm2) + UV	Tract. electr. (40 mA/cm2)
o-toluidina (ppm)	0,015	0,015	0,015	0,015	0,018
4-cloroanilina (ppm)	0,036	0,022	0,024	0,023	0,019
4-aminobifenil (ppm)	0,920	0,550	0,050	0,050	0,053
4,4'-oxidianilina (ppm)	0,160	0,160	0,160	0,160	0,160
Total (ppm)	1,131	0,747	0,249	0,248	0,25

Taula 3.8 Concentració d'amines detectades al Procion Yellow H-EXL.

Amina	Col. inicial	Tract. electr. (3 mA/cm2)	Tract. electr. (24 mA/cm2)	Tract. electr. (24 mA/cm2) + UV	Tract. electr. (40 mA/cm2)
Anilina (ppm)	0,55	0,069	0,070	0,061	0,062
o-toluidina (ppm)	0,014	0,023	0,017	0,014	0,015
4-cloroanilina (ppm)	0,55	0,024	0,042	0,022	0,020
4-aminobifenil (ppm)	1,34	0,084	0,056	0,060	0,056
Total (ppm)	2,454	0,200	0,185	0,157	0,153

A la figura 3.8 es mostra l’evolució de la concentració total d’amines per als tres colorants estudiats respecte la densitat de corrent aplicada durant el tractament electroquímic i posterior irradiació UV (cas de 24 mA/cm^2).

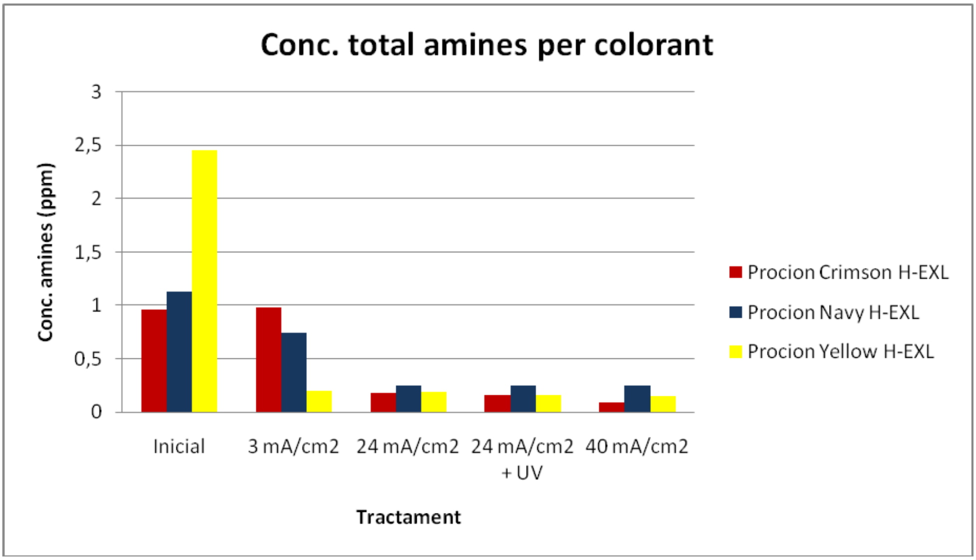

Figura 3.8 Evolució de la concentració total d’amines per Procion Crimson H-EXL, Procion Navy H-EXL i Procion Yellow H-EXL respecte la densitat de corrent aplicada durant el tractament electrolític i posterior irradiació UV (cas de 24 mA/cm^2).

A partir d’aquests resultats, es conclou que els colorants estudiats contenen molt petites quantitats d’amines aromàtiques en la seva composició en valors molt inferiors als permesos per la normativa vigent. Aquest fet es pot justificar tenint en compte que la síntesi dels colorants azo es dóna per reacció entre una amina que conté dos grups azo i una amina aromàtica o un fenol [3.31].

Es pot apreciar també, que l’aplicació d’un tractament electroquímic disminueix la concentració d’aquestes amines respecte la concentració inicial. Aquesta influència és tant més gran quant major és la densitat de corrent aplicada durant el tractament electroquímic. Només en el cas del Procion Crimson H-EXL, el tractament a 3 mA/cm^2 provoca la formació d'amines que inicialment no havien estat detectades: 4-cloroanilina i 2,4-diaminotoluè. En tots els casos, les concentracions obtingudes són molt inferiors als valors indicats a la norma EN 14362 (30 ppm).

La irradiació UV posterior al tractament electroquímic de les mostres, pot resultar beneficiosa en la disminució de la concentració total d'amines aromàtiques. En aquest sentit, la 4-cloroanilina és el compost més degradat per aquesta irradiació, arribant gairabé a reduir a la meitat la seva concentració en el cas del Procion Yellow H-EXL.

3.5 Conclusions

Les principals conclusions d'aquest capítol són:

- Es va aconseguir la posada a punt de mètodes cromatogràfics que permeten la separació, identificació i quantificació de compostos orgànics halogenats i amines aromàtiques respectivament.

- El mètode cromatogràfic establert és adequat per a la determinació i quantificació de compostos orgànics halogenats en mostres tractades. Els resultats s'inclouen al capítol 4 d'aquesta tesi "COLOUR REMOVAL OF THREE REACTIVE DYES BY UV LIGHT EXPOSURE AFTER ELECTROCHEMICAL TREATMENT" treball publicat a la revista Chemical Engineering Journal, 156 (2010) 114–120.

- Els colorants estudiats contenen amines aromàtiques en la seva composició. La seva concentració és molt baixa, de l'ordre d'1-2 ppm.

- El tractament electroquímic afavoreix l'eliminació de les amines aromàtiques presents en la composició dels colorants. Aquesta influència és tant més gran quant major és la densitat de corrent aplicada durant el tractament electroquímic.

- El mètode d'extracció líquid-líquid de les amines aromàtiques proporciona similars o millors resultats que la columna de terra de diatomees proposat per la norma EN 14362. A més, aquest mètode resulta més fàcil i senzill.

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Chapter 4

Article on decolourization I:

Colour removal of three reactive dyes by UV light exposure after electrochemical treatment

COLOUR REMOVAL OF THREE REACTIVE DYES BY UV LIGHT EXPOSURE AFTER ELECTROCHEMICAL TREATMENT

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Abstract

This study applies UV light irradiation after a low current density electrochemical treatment to degrade reactive dyes to remove wastewater colour. The combination of these two techniques improves the quality of the treated effluent with respect to only an electrochemical treatment. Synthetic dyeing effluents containing a reactive dye (C.I. Reactive Orange 4, C.I. Reactive Black 5 or Procion Navy H-EXL) and Na_2SO_4 were studied. Ti/Pt oxides electrodes and UV irradiation lamp (6 W, 254 nm maximum emission) were used. Kinetic constants of the UV irradiation step were calculated. The influence of chloride ion at 3 and 6 mA/cm^2 was evaluated. Results showed that, with a very small Cl^- concentration (in the order of the net water content) the combined techniques provided full decolourization. The possible presence of 25 organic halogenated compounds was studied by Gas Chromatography-Mass Spectrophotometry (GCMS). Only four of them were detected after the electrochemical treatment at low intensity, mainly chloroform. Its concentration was found to be highly dependent of the Cl^- concentration, being much lower when reducing the amount of chloride ion. In all cases, the chloroform concentration was dramatically reduced by further UV irradiation which destroyed it up to a 75%.

Keywords: reactive dye, decolourization, UV light, textile wastewater, dyeing bath, GCMS.

1. Introduction

Worldwide increasing demand of new fabrics increases the consumption of dyes that is estimated in 800,000 t annually [1]. Reactive dyes represent an important fraction of the commercialized synthetic dyes used (approximately 12% of the worldwide production) [2]. The main environmental problem associated with the reactive dyes is their low exhaustion. Frequently, the fixation efficiency of these dyes range between 60% and 90% [3] consequently substantial amounts of unfixed dyes are released in the wastewater.

Several technologies to remove colour of wastewater have been studied and some of them are applied nowadays. These technologies can be classified in four main groups. *Oxidation techniques*:

electrochemical oxidation, peroxides, ozone, etc. *Physicochemical techniques*: adsorption, ion exchange, coagulation/flocculation. *Membranes*: nanofiltration, reverse osmosis, etc, and *Biologic techniques*: enzymatic decolourization processes. Sometimes the combined use of two techniques provides better results and it is more and more frequent. This work focuses in a combined process based on UV light exposure after an electrochemical treatment.

Electrochemical processes are electronic transferences between two compounds where these transferences take place between the substratum and the metallic electrodes, usually inert, by means of the electrical current [4]. Generally, these techniques work under soft conditions (room temperature and atmospheric pressure) but their main advantage is that they do not need the addition of any chemical reagent [5].

Some authors have applied the electrochemical techniques to the destruction of toxic or non biodegradable organic compounds in wastewater (phenols, cyanides, PCB's…). In the case of textile organic dyes, the electrochemical treatment has been mainly proposed for the colour removal [6] although the mineralization of residual dyes has also been reported [7]. From a practical point of view, the electrochemical treatment is only useful to remove effluents color, discarding the complete mineralization to CO_2 and H_2O because of its high cost [8].

Reactive dyes are usually difficult to biodegrade [9] but if they undergo an electrochemical treatment, they can be broken into colourless smaller molecules which can be removed in a further biological treatment. Most of dyes contain azo groups (-N=N-) that can be oxidized to nitrocompounds when oxidation occurs or reduced to amines when reduction occurs [10]. Although some reduction electrochemical treatments of colour removal of textile effluents have been reported [11], the oxidation treatments are more common.

Oxidation processes can be classified in two types: those which take place on the electrode surface, known as *direct oxidation* and those which take place due to the action of molecules formed in the anode, known as *indirect oxidation*. Both processes can occur either in the same reactor or in a different one [12] and simultaneously or not [13]. The most common species in indirect oxidation are: hydroxyl radical ($OH^{\bullet}$), chlorine and hypochlorite in water purifying, ozone in sterilization and oxidation of organic matter, and redox pairs species such as Cr(VI)/Cr(III).

Many authors establish that $OH^{\bullet}$ is the most appropriate to degrade effluents when using indirect oxidation [14, 15]. Alternatives such as HCl for the degradation of organic compounds in textile effluents have been proposed by others [16].

One of main inconvenients of electrochemical treatments is their high energy cost which can be reduced by using indirect electrochemical treatments in the presence of Cl^-. In this case the formation of haloforms or other halogenated compounds is observed when the chloride oxidation products react with organic matter. The haloforms concentration was dependent on the current density applied during the electrochemical treatment [10]. For this reason, in this work we propose its combined use with UV exposure. Combination of both techniques allows the decolourization of residual dyes at a lower current density which implies a lower cost. Electrochemical treatment is used only to initiate the degradation of the dyes. In this first step, different radical species are formed, able to react with organic compounds by an indirect oxidation reaction which is further catalysed by applying UV light. Simultaneously, this UV treatment achieves the decomposition of the small amount of halogenated compounds generated during the electrochemical treatment.

UV radiation alone is not capable to destroy reactive dyes as they are resistant to direct UV light exposure [17]. Some authors have reported the use of UV light exposure with electrochemical treatment as a proper way to reduce COD, BOD_5 and NH_3 content in wastewater [18]. Other authors have applied UV light using TiO_2 as a photocatalizer to degrade dyes [19]. Although colour removal by electrochemical treatment followed by UV exposure has already been reported [7], studies about their combined use are still very scarce and some aspects must be clarified before the application of this process at an industrial level.

The two main goals of this study are the optimization of the electrochemical and further UV light irradiation whole treatment to achieve good colour removal of simulated textile effluents at a low cost and to find the conditions in which halogenated compounds content is minimized.

2. Materials and methods

In this work three reactive dyes, kindly provided by DyStar, were selected: Procion Orange MX-2R (Colour Index Reactive Orange 4), reactive group dichlorotriazine and chromophore azo; Remazol Black B 133 (Colour Index Reactive Black 5), double reactive group sulfatoethylsulfone and chromophore diazo; Procion Navy H-EXL, with a double monochlorotriazine reactive group and chromophore azo. From this section, these dyes will be referred in the text as: RO4, RB5 and PN H-EXL respectively. Figure 1.a and 1.b shows the two available structures of the dyes. The formula corresponding to PN H-EXL has not been published.

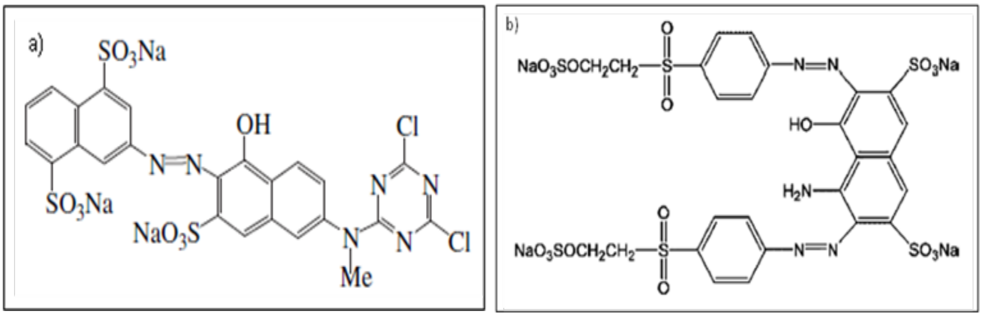

Figure 1. Chemical structure of: a) C.I. Reactive Orange 4 and b) C.I. Reactive Black 5.

2.1. Reactive dyebath effluent preparation

The dyeing process with reactive dyes is usually carried out at alkaline pH (10-12) with a high concentration of salts (generally NaCl or Na_2SO_4) to accomplish the proper fixation of the dyes. During this step, dyes are linked to the fibre by a chemical reaction. But, simultaneously, there is competitive hydrolysis reaction with the solvent and the hydrolysed dyes (10-40% of the initial amount) must be removed in the wastewater.

Simulated dyebath effluents were prepared in the laboratory in distilled water at 0.1 g L^{-1} of the commercial dyes, previously hydrolyzed to simulate an industrial effluent. The hydrolysis was carried out as follows: the pH was adjusted to 12 with NaOH (Flucka) and then the solution was heated at 80 ºC for two hours. After the hydrolysis, it was let cool down to room temperature and the pH was adjusted to 9 with sulphuric acid (Scharlau).

Different concentrations of NaCl, between 0 and 5 g L^{-1}, were added to the effluent to study the effect of Cl^- in decolourization and halogenated compounds formation. As indicated previously, a high concentration of salts is used in the dyeing process. To simulate the conductivity of an industrial effluent, the required amount of sodium sulphate (Scharlau) was finally added to each solution in order to reach a final conductivity of 35.000 µS cm^{-1}.

2.2. Experimental wastewater treatment plant

The experimental plant consists in two different parts: an electrochemical cell (continuous process) followed by an UV exposure device (batch process).

2.2.1. Electrochemical cell

Electrochemical treatments were performed in an undivided electrolytic cell based on the commercial cell ECO 75 (ELCHEM, Germany), which was initially designed to obtain hypochlorite for disinfection. Cathodes were constituted by titanium and anodes were made of titanium covered by platinum oxides. The total surface area of each electrode was 486 cm^2. The volume of the vessel was 1L. The cell was able to treat up to 25 L h^{-1} which allows its use at industrial scale.

The experimental plant was constituted by the electrochemical cell, the pump to feed the system and the deposit to store the treated wastewater. This plant operated continuously, and the flow rate was fixed at 20 L h^{-1}. The source supply allowed regulating the current among 0 and 25 A. The voltage was variable among 0 and 40 V, depending on the current applied and on the conductivity fixed for the treatment.

A range of synthetic effluents containing different chloride ion concentration, from 0 to 5 g L^{-1} of NaCl, were treated in this plant, each of them at two different current densities (3 and 6 mA/cm^2).

2.2.2. UV Device

After the electrochemical treatment, aliquots of 250 mL of effluents were collected, placed in a recipient 8 cm under the UV lamp and irradiated while stirring. For the irradiation, a 6W fluorescent UV light source with a maximum emission spectrum at 254 nm (Vilber Lourmat) was used.

2.3. Analytical measurements

2.3.1 Decolourization measurements

Decolourization was calculated from the initial concentration and dye concentrations at time t (c_i and c_t respectively) by measuring the absorbance at the visible maximum dye absorption wavelength (488 nm for RO4, 583 nm for RB5 and 606 nm for PN H-EXL). Measurements were carried out on the effluent, just after electrochemical treatment and along the UV treatment. During UV exposure, samples were taken and measured every 5 minutes. Decolourization (D) was reported in %:

$$D\ (\%) = \frac{(c_i - c_t)}{(c_i)} \times 100 \qquad (1)$$

Absorbance measurements were carried out with a UV-visible spectrophotometer (Shimadzu UV-2401 PC). Dye absorbance has a linear behaviour versus the concentration in the range between 0.001 and 0.020 g L^{-1} according to the equations:

$Abs = 29.413c - 0.002$ ($R^2 = 0.9999$) for RO4
$Abs = 30.858c - 0.002$ ($R^2 = 0.9999$) for RB5
$Abs = 26.149c - 0.004$ ($R^2 = 0.9999$) for PN H-EXL

where c is the dye concentration expressed in g L^{-1}.

2.3.2. Organic matter removal measurements

The organic matter removal was calculated from COD measurements [20] as follows:

$$COD\ removal\ (\%) = \frac{(COD_i - COD_t)}{(COD_i)} \times 100$$

where COD_i corresponds to the initial value and COD_t is the value at time t.

2.4. Halogenated compounds study

The formation and further removal of halogenated compounds in treated effluents were evaluated. Analyses were carried out in a Shimadzu QP 2010 (GCMS) with head space technique for the injection of the samples.

- *Head space injection*: 20 mL of the samples were heated to 80ºC for 45 min in a 30 mL vial sealed with silicon/PTFE septum and 1 mL of air was injected into the GCMS.

- *GCMS conditions:*

- GC:
  - Column program T: initial 40ºC (10 min), increasing gradient rate 5ºC min^{-1}, final 225ºC (10 min)
  - Injection T: 230ºC
  - Carrier gas: He, flow 22.1 mL min^{-1}
  - Injection mode: Split
  - Split ratio: 1/20
  - Column flow: 0.95 mL min^{-1}

- MS:
  - Ion source T: 200ºC
  - Interface T: 250ºC
  - Solvent cut time: 2 minutes
  - Acquisition mode: SIM

Identification of the compounds was performed using Nist 147, Nist 27 and Wiley 229 as reference libraries.

In this study, 25 halogenated compounds were analyzed in each sample. A standard solution from Accustandard 0.2 mg L^{-1} was used to determine a calibration curve. Compounds and detection limits (D.L.) are listed in Table 1. As internal standard (I.S.) p-bromofluorobenzene was selected and used for the quantification of all compounds.

2.5. Kinetic evaluation

After the electrochemical treatment, an increase of decolourization was observed depending on NaCl concentration and UV exposure time.

For this step, first-order reactions were assumed and the decolourization rate constants were calculated from the slope of the semilogarithmic plot colour (peak absorbance at λ_{max}= 488 nm for RO4) versus exposition time, in accordance with the kinetic equation:

$$\ln(Abs_t/Abs_0) = k_d \cdot t$$

Table 1. Organic halogenated compounds and their detection limits.

Compound	CAS Number	D.L. (µgL^{-1})
1,1-Dichloroethene	75-35-4	2.5
Dichloromethane	75-09-2	1.0
t-1,2-Dichloroethene	156-60-5	2.5
c-1,2-Dichloroethene	156-59-2	2.5
Chloroform	67-66-3	1.0
1,1,1-Trichloroethane	71-55-6	2.5
Tetrachloromethane	56-23-5	2.5
1,2-Dichloroethane	107-06-2	10
Trichloroethene	79-01-6	1.0
1,2-Dichloropropane	78-87-5	5
Bromodichloromethane	75-27-4	5
c-1,3-Dichloropropene	10061-01-5	10
t-1,3-Dichloropropene	10061-02-6	10
1,1,2-Trichloroethane	79-00-5	10
Tetrachloroethene	127-18-4	1.0
Dibromochloromethane	124-48-1	10
Chlorobenzene	108-90-7	1.0
Bromoform	75-25-2	10
1,3-Dichlorobenzene	541-73-1	1.0
1,4-Dichlorobenzene	106-46-7	0.5
1,2-Dichlorobenzene	95-50-1	0.5
1,3,5-Trichlorobenzene	108-70-3	1.0
1,2,4-Trichlorobenzene	120-82-1	1.0
Hexachlorobutadiene	87-68-3	0.5
1,2,3-Trichlorobenzene	87-61-6	1.0

where k_d is the first-order decolourization kinetic constant expressed in min^{-1}; Abs_t and Abs_0 are the absorbances at time t and initial respectively.

3. Results and discussion

Results are structured in two parts: sections 3.1, 3.2, 3.3 and 3.4 are focused on the study of the dye RO4. In the second part (section 3.5) RB5 and PN H-EXL were selected to verify the behaviour of other reactive dyes.

3.1. Decolourization study

Figure 2 shows the evolution of the UV-visible spectra of the dye RO4 solution (containing 0.5 g L^{-1} NaCl) during the different steps of treatment.

It can be seen that the absorbance in the visible region was partially reduced after the electrochemical experiment (performed at 6 mA/cm^2) and completely removed later by applying UV light.

During the UV irradiation step, the absorbance evolution in the visible spectrum region (evaluated at the dye maximum wavelength) was found to be mainly influenced by the current density applied in the electrochemical treatment and chloride ion concentration in the solution (figure 3).

The electrochemical treatment was performed at two different current densities, 3 and 6 mA/cm^2. From Figures 3.a and 3.b it can be appreciated that colour removal due to electrochemical treatment (time t = 0 min. of UV light exposure) was greater when current density was also greater.

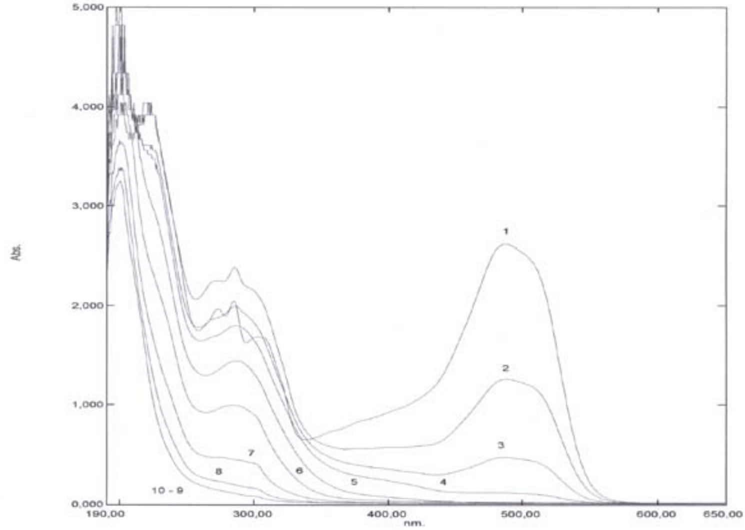

Figure 2. Evolution of decolourization of Reactive Orange 4 (0.1 g L^{-1}) after electrochemical treatment (20 L h^{-1}, 6 mA/cm^2) and during UV light irradiation (254 nm, 6 W). Curves: (1) initial, (2) immediately after electrochemical treatment at 6 mA/cm^2, (3) 15 min UV, (4) 30 min UV, (5) 45 min UV, (6) 60 min UV, (7) 2 hours UV, (8) 3 hours UV, (9) and (10) 4 and 10 hours UV respectively (same line).

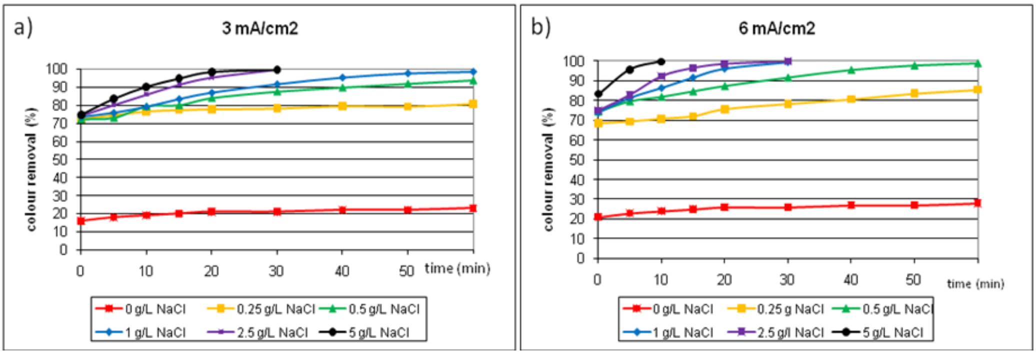

Figure 3. Influence of different NaCl concentrations on color removal of Reactive Orange 4 (0.1 g L^{-1}) due to UV light exposure (254 nm, 6 W) after electrochemical treatment (20 L h^{-1}). Current density: a) 3 mA/cm^2 and b) 6 mA/cm^2.

The highest differences in the colour removal behaviour were clearly attributed to action of chloride ion. The electrochemical treatment showed poor results of decolourization and the later UV exposure was also ineffective in the absence of chlorine.

In Figure 3.a, it can be seen that more than 95% of decolourization was reached in solutions containing between 0.5 to 5 g L^{-1} NaCl after 60 minutes of UV light exposure. Even when using only 0.25 g L^{-1} of NaCl an 80% of colour removal was reached for the same exposure time.

In figure 3.b, values of colour removal were higher than in figure 3.a, as the current density was also higher but a similar general behaviour was observed. Again 0.25 g L^{-1} of NaCl provided slightly lower colour removal results: 85% of colour removal after 60 minutes of UV exposure. In this experiment, all other NaCl concentrations reached at least 98% of colour removal before 60 min of UV exposition.

Textile wastewater contains large quantities of inorganic salts, usually $NaSO_4$ or NaCl used as dyeing electrolyte. These salts increase the conductivity of the effluent [21, 22], which improves the efficiency of the electrochemical reaction. The case where the only electrolyte used in the effluent was Na_2SO_4 (that is 0 g L^{-1} NaCl) is very unlike in dyehouse effluents, as usually dyeing is carried out with decalcified tap water which always contains a certain amount of chloride. A NaCl concentration between 0.25 and 0.5 g L^{-1} corresponds to a Cl^- concentration in water between 153 and 306 ppm. In the case of Barcelona area, the main line tap water contains about 200 ppm Cl^- (approximately 0.3 g L^{-1} NaCl). This implies that when $NaSO_4$ is used as dyeing electrolyte, the Cl^- present in the main line tap water is enough to provide a high decolourization level without the further addition of NaCl to carry out the treatment.

From the experimental results performed on dye solutions containing NaCl between 0.25 and 0.5 g L^{-1}, it can be concluded that after an electrochemical treatment at 3 mA/cm^2 and a later UV radiation treatment during 60 minutes, at least an 80% of colour removal is achieved. This discolouration of the effluent is sufficient and treatments more intensive are not required. We must consider that the contribution of the coloured effluents to the total plant wastewater is only about a 10%. The dilution with the rest of process effluents and the subsequent biological treatment ensure that final wastewater will be able to accomplish regulations.

3.2. Decolourization kinetic constants (K_d)

In the dye decolourization process, the breakage of azo bound (-N=N-) leads to the elimination of colour [23].

The decolourization catalysed by UV light follows a pseudo-first order reaction, in other words, a first-order law with respect to dye concentration. Decolourization kinetic constants (k_d) were calculated at different NaCl concentrations and current densities, in order to determine the optimal conditions for electrochemical treatment-UV exposure colour removal (table 2).

From k_d results it is possible to state that decolourization kinetic constants values depend on the NaCl concentration as well as current density: decolourization is greater when applying higher current densities and greater NaCl concentration.

When Na_2SO_4 is used as only electrolyte (NaCl concentration 0 g L^{-1}) decolourization constants values are very low and consequently, colour removal in the effluent is very slow.

In general, for each current density, k_d values double when NaCl concentration is increased two times, except for 0.25 and 0.5 g L^{-1} where the relationship between constants values are five. This fact permit to confirm this NaCl concentration as the minimum required to use electrochemical treatment followed by UV exposure as a colour removal method.

3.3. Influence of the UV light in organic matter removal

Organic matter removal of the effluent due to electrochemical treatment and UV exposure was evaluated by COD measurements [24, 25].
At the lower current density (3 mA/cm^2) and immediately after electrochemical treatment, the COD decreased an 11% and it reached a 15% after 60 minutes of UV irradiation. When current density applied was 6 mA/cm2, the COD removal was a 17% in the first step and a 20% in the combined process after 60 minutes of UV treatment. The maximum organic matter removal accomplished was a 38%. It was reached at 6 mA/cm^2, after four hours of UV light exposure (COD values are listed in section 3.5).

A full mineralization could be reached with a higher intensity electrochemical treatment [26, 27] and probably also with a more intense UV exposition (or a combination of both) but economical cost of the process would be very high what makes it a non attractive method to be applied at industrial scale for the mineralization of dyeing effluents. Complete degradation of textile effluents can be achieved by several other methods, such as conventional activated sludge biological treatments, at lower economical costs.

Table 2. Decolorization kinetics constants (k_d) of Reactive Orange 4.

K_d (min^{-1})												
Current density (mA/cm^2)	NaCl conc. (g/L)											
	0		0.25		0.5		1		2.5		5	
	k_d	R^2	k_d	R^2	k_d	R^2	k_d	R^2	k_d	R^2	k_d	R^2
3	0.0012	0.99	0.0051	0.98	0.0261	0.98	0.0469	0.99	0.867	0.99	0.1404	0.99
6	0.0031	0.99	0.0136	0.99	0.0558	0.99	0.0927	0.98	0.2089	0.98	0.4256	0.99

For this reason, the combination of electrochemical techniques with UV treatment is proposed as a previous step to the biological treatment, where the coloured effluents (about the 10% of the total plant effluents) are treated separately and, once the dyes molecules have been broken and converted in smaller size and more biodegradable compounds, they can be easily treated in the biological plant with the rest of effluents (scouring, bleaching, washing, etc.). The colour removal by electrochemical treatment-UV irradiation after the biological treatment is also possible, although it is less in advantageous as a much higher volume of water must be treated.

More details about dye degradation when applying UV light can be obtained from figure 2 where the evolution of the effluent absorbance during its exposition to UV light versus time is shown. There are three important regions to be studied. The first one is centred at 488 nm and shows how the effluent is decolourized, mainly attributed to the azo bounds breakages. The second area is the band at λ_{max} 290 nm which corresponds to the aromatic rings of the dye. The intensity of this band decreases in time during UV exposure, due to the degradation of the aromatic dye fragments. Finally, the third region, absorption under 200 nm, can be attributed to carboxylic acid accumulated at the final stage of the oxidation. This represents the residual COD present in the effluent [28].

The evolution of these three bands shows clearly that the combination of electrochemical and UV light exposure produces a breakage of the molecular bonds of the dye. Although the mineralization obtained is not too high under these experimental conditions, it is predictable that the production of simpler molecules would facilitate the further mineralization by biological methods.

3.4. Influence of the UV light in organic halogenated compounds

Although the use of electrochemical treatment to decolourize effluents has been recognized as a very effective technique, the main disadvantage of the method is the formation of small amounts of organic halogenated compounds when chloride ion is the solution [29]. But the evolution on these compounds when subsequent UV irradiation is applied to the effluent has not still been reported. For this reason, an extensive study about the formation of volatile organic halogenated compounds was performed by GCMS. Figure 4 shows a typical chromatogram obtained.

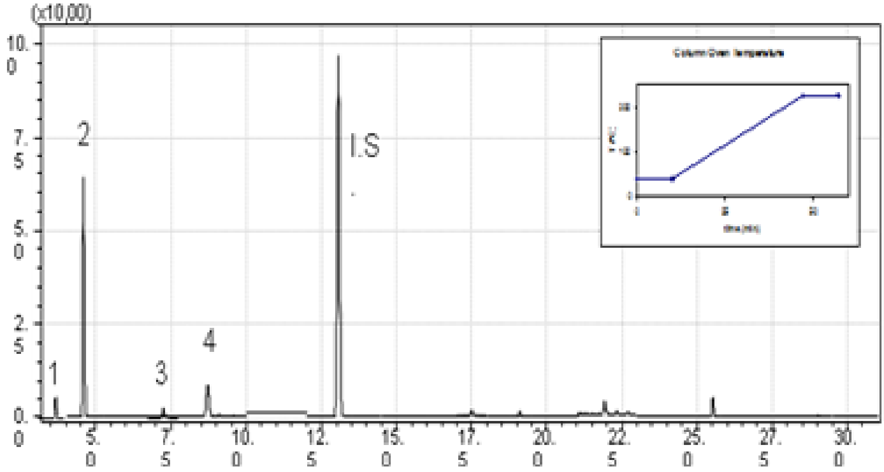

Figure 4. Chromatogram of Reactive Orange 4 treated at 3 mA/cm^2 and containing 0.5 g L^{-1} of NaCl. [1] Dichloromethane, [2] Chloroform, [3] Trichloroethylene and [4] Bromodichloromethane. I.S. is the Internal Stanrdard, p-Bromofluorobenzene.

The compounds formed are dichloromethane, chloroform, trichloroethylene, bromodichloromethane mainly at ppb concentrations, as indicated in Figure 4 and in Table 3.

Table 3. Concentrations (mg/L) of halogenated compounds generated during the treatment of Reactive Orange 4, current density 3 mA/ cm^2 at different NaCl concentration.

NaCl Conc. (g/ L)	Treatment	Dichloromethane (ppm)	Chloroform (ppm)	Trichloroethylene (ppm)	Bromodichloromethane (ppm)
0	After electrochem.	0.001	0.06	0.002	< D.L.
0.5	Initial (before electrochem.)	< D.L.	0.02	0.003	< D.L.
	After electrochem.	0.004	0.27	0.004	0.002
	After 60 min. of UV exposure	0.004	0.11	0.003	< D.L.
10	After electrochem.	0.006	2.83	0.02	0.06

The formation of bromodichloromethane is attributed to the bromide trace impurities of the NaCl.

This table shows the organic halogenated compounds evolution along the combined treatment and the influence of NaCl concentration in the effluent in the formation of these compounds.

From the results in Table 3, it can be concluded that the greater the NaCl concentration is, the greater the organic halogenated compounds generation is. Because of this fact, when an electrochemical treatment should be performed to the effluent, Na_2SO_4 must be selected as the only dyeing electrolyte in order to minimize the organic halogenated compounds formation.

An important result of section 3.1 is that in the case of dyeing effluents, the small Cl^- concentration present in the decalcified main line tap water is enough to reach a good decolourization level. Consequently, no additional NaCl is required to obtain of good decolourisation of the residual dyebaths.

Current density applied during the electrochemical treatment is also an important factor in organic halogenated compounds generation. Low current densities produce less organic halogenated compounds. Chloroform is the compound formed in greater extension. After electrochemical treatment, the concentration of this compound is quite higher than initially, but UV exposure achieves a significant reduction of its concentration. It is possible to state that UV exposure of the effluent after the electrochemical treatment removes up to a 75% of organic halogenated compounds generated during the electrochemical treatment.

3.5. Other dyes

In this section, two other reactive dyes, RB5 and PN H-EXL, were studied to evaluate their behaviour versus RO4. For this purpose, studies of decolourization, organic matter removal and organic halogenated compounds were performed.

Figure 5 shows the decolourization of dye effluents containing 0.5 g L^{-1} NaCl after applying an electrochemical treatment at 6 mA/cm^2 followed by UV light irradiation.

Comparing the evolution of the three dyes, it is possible to state that RB5 and PN H-EXL effluents can be treated in the same way that RO4 to remove colour, as their decolourization is even faster for the same conditions.

With respect to the influence of the UV light degradation on the organic matter removal, the three dyes showed a similar degradation, being even more alike in the case of RO4 and RB5 (table 4). After electrochemical treatment at 6 mA/cm^2, RO4 degradation was a 17%, reaching a 25% after 60 minutes of UV light exposure. For RB5 results were 15% and 29% respectively; whereas 18 and 28% were obtained for PN H-EXL, respectively (table 4).

Finally, the influence of the UV light in organic halogenated compounds degradation for RB5 and PN H-EXL is reported in Table 5. The same compounds that in the case RO4 were identified.

The quantitative results showed again a similar behaviour that RO4. Electrochemical process increased the concentrations of these compounds, especially chloroform, and UV light exposure removed them in a great extent.

g/L NaCl. In this range, decolourization kinetic constants values (k_d) are much greater than expected and a 95% of colour removal can be reached in short expositions times.

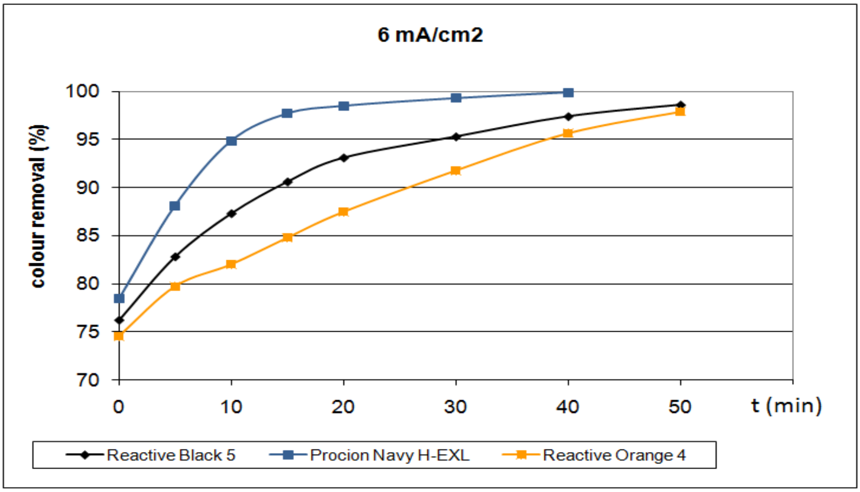

Figure 5. Evolution of color removal for Reactive Orange 4, Reactive Black 5 and Procion Navy H-EXL after electrochemical treatment (6 mA/cm^2) plus UV light irradiation of effluents containing 0.5 g L^{-1} NaCl.

4. Conclusions

The application of UV light irradiation after electrochemical treatment improves the yield of the first process in the degradation of reactive dyes in terms of colour removal and organic matter removal. The combination of the two techniques allows to perform the electrochemical treatment at lower current densities.

A small amount of Cl$^-$ ion is recommended in order to obtain an effective combination of electrochemical treatment and UV exposure, the optimum was found to be between 0.25 and 0.5

During the electrochemical treatment, some halogenated compounds can be formed due to the chloride reactions. When working at low current densities, as the selected in this study, only four halogenated compounds were detected after the electrochemical treatment, being the chloroform the only one significant. Their concentrations were dramatically reduced when the NaCl concentration decreased. In addition, the UV irradiation showed a chloroform destruction up to a 75%.

Acknowlegdements

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Chapter 5

Article on decolourization II:

Optimization of UV irradiation after electrochemical pre-treatment to remove colour of textile effluents

OPTIMIZATION OF UV IRRADIATION AFTER AN ELECTROCHEMICAL PRE-TREATMENT TO REMOVE COLOUR OF TEXTILE EFFLUENTS

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Abstract

Different UV irradiation conditions after an electrochemical pre-treatment of textile effluents were studied in order to improve the colour removal of wastewater. Synthetic dyeing effluents containing a reactive dye (C.I. Reactive Black 5, Procion Crimson H-EXL, Procion Navy H-EXL, Procion Yellow H-EXL and Procion Blue H-EXL) and Na_2SO_4 as dyeing electrolyte were studied. Ti/Pt oxides electrodes and three UV irradiation lamps (6 and 9 W; 254, 360 and 365 nm maximum emission) were used. Results showed that total colour removal was achieved by UV irradiation after electrochemical pre-treatment. A strong influence of the type of UV lamp on colour removal was found, being the submerged lamps into the dye solution the most efficient. Ozonation treatments (0.1841 mg O_3 min^{-1}) of the effluents were also performed and compared with the previous treatment. Kinetic constants of the UV irradiation step and ozonation were calculated. The mechanisms of both treatments were discussed.

Key words: reactive dye, colour removal, electrochemical treatment, UV irradiation, ozonation, wastewater.

1. Introduction

Textile industries generate effluents at an average of 100-170 L kg^{-1} of cloth processed, which are characterized by strong colour, rather high COD and wide variation in pH [1]. When colour is due to the presence of reactive dyes, it represents an environmental problem as they are usually difficult to biodegrade [2] and its colour can remain in the environment for an extended period of time [3]. For instance, the half-life of hydrolysed Reactive Blue 19 (RB19) is about 46 years at pH 7 and 25 ºC [4].

In the last few years, the use of double reactive group dyes has increased in cotton dyeing. These dyes present higher exhaustion what implies less residual hydrolyzed dye in solution after the dyeing process.

Currently, treatment technologies for colour removal of textile wastewater involve physical and/or chemical processes, but them all present advantages and disadvantages [5].The major methods are: *oxidation treatments*, which are rapid but present high energy consumption and possible formation of by-products; *adsorption methods*, which provide good removal of a wide range of dyes although the adsorbent requires regeneration or disposal; *membrane technologies*, which can remove the majority of dyes but produce concentrated effluents and *coagulation-flocculation*, which produce sludge.

Among the oxidation treatments, electrochemical processes are one of the most important in wastewater treatment because of their versatility, environmental compatibility and potential cost effectiveness for the degradation of different organic pollutants [6]. Electrochemical treatments are proposed as a pre-treatment stage prior to biological treatment or as complementary treatment of textile effluents [7-9]. They can also be applied to other industries such as paint [10], paper [11] or for the treatment of landfill leachates [12].

During the electrochemical treatment, oxidation processes can take place on the electrode surface, *direct oxidation,* or due to the action of molecules formed in the anode, *indirect oxidation*. Usually, indirect oxidation is more effective than direct oxidation [8]. The most common species in indirect oxidation are: hydroxyl radical ($OH^•$), chlorine and hypochlorite, ozone, and redox pairs species such as Cr(VI)/Cr(III) [13]. Indirect oxidation is usually more effective than direct oxidation [14].

Thanks to these considerations, electrochemical processes can be widely used to treat textile coloured wastewater containing different types of dyes [15-19] although its effectiveness largely depend on the chemical structure of the dye [20]. In order to minimize the drawbacks of the electrochemical technique or improve its results, some possibilities have been proposed. The use of DSA-type electrodes [21], metals such as Pt and Pt-Ir and graphite has been positively checked for treating organic dye solutions mediated with active chlorine to minimize halogenated organic compounds generation [22]. Results of both, decolourization and COD removal can be improved by combination of electrochemical treatments with UV light [13, 23-28].

Another important oxidation treatment is ozonation. Ozone is also used in colour removal of textile wastewater [29-32]. Studies performed with two reactive dyes, Reactive Orange 122 and C. I. Reactive Blue 15, showed that the ozonation of the aqueous reactive dyes follows a pseudo-first order reaction with respect to the dye [33, 34]. COD removals with ozonation are lower than the obtained with electrochemical previous to UV irradiation [35]. To improve COD removal, ozonation can be combined with coagulation-flocculation processes [36, 37].

The main objectives of this work are the establishment of the optimum UV irradiation conditions to achieve the decolourization of some reactive dyes, using a previous electrochemical treatment to initiate the degradation reaction. The required electrochemical conditions before the UV irradiation were also studied.

2. Experimental

Material and methods

Five reactive dyes, kindly provided by DyStar, were selected: Remazol Black 133 B (C. I. Reactive Black 5), with two reactive groups sulfatoethylsulfone and chromophore diazo; Procion Crimson H-EXL, Procion Navy H-EXL, Procion Yellow H-EXL and Procion Blue H-EXL, all of them with two monochlorotriazine reactive groups and chromophore azo.

From this section, these five dyes will be referred in the text as: RB5, PC, PN, PY and PB respectively.

All the dyes have double reactive groups hence they represent one of the most used reactive dye types in currently cotton dyeing. Figure 1 shows the available structures of the dyes [38-41]. PN and PY are mixtures of two compounds. The formula corresponding to PB has not been already published.

2.1. Reactive dyebath effluent preparation

Simulated dyebath effluents were prepared in the laboratory in distilled water at 0.1 g L $^{-1}$ of the commercial dyes previously hydrolyzed. The hydrolysis was carried out as follows: pH of the solution was adjusted to 12 with NaOH (Flucka) and then heated at 80ºC for two

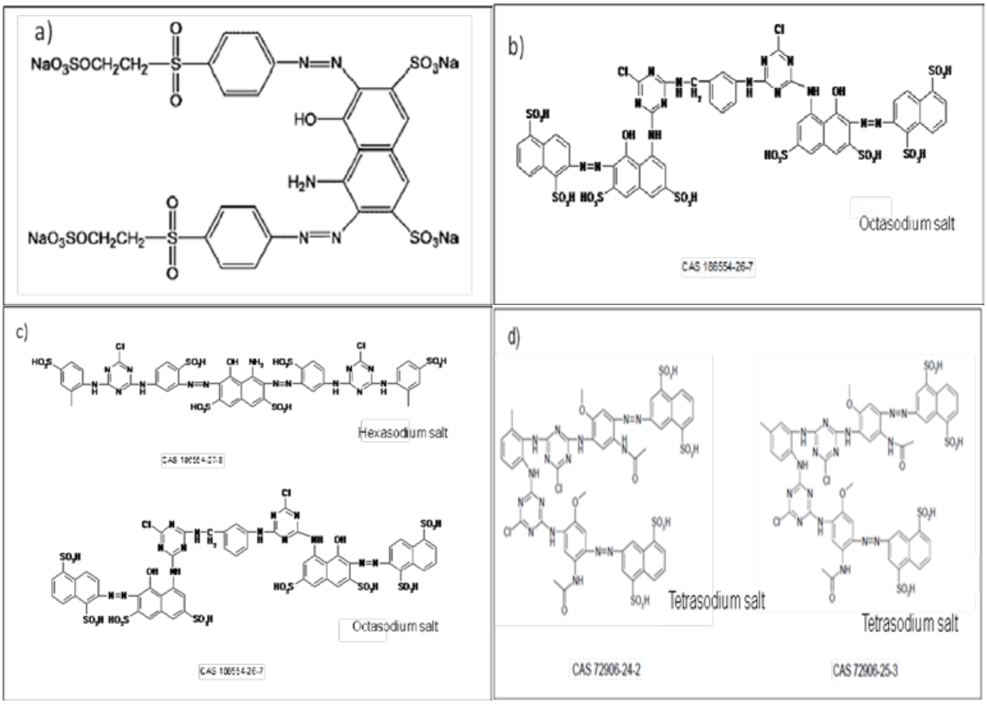

Figure 1. Chemical structure of (a) C. I. Reactive Black 5, (b) Procion Crimson H-EXL, (c) Procion Navy H-EXL and (d) H-EXL, Procion Yellow H-EXL.

hours. After the hydrolysis, it was let cool to room temperature and the pH was adjusted to 9 with sulphuric acid (Scharlau).

In order to simulate the industrial effluents conditions, NaCl (Flucka) was added to the solution at a concentration of 0.3 g L^{-1} to reach the chloride concentration present in net water. The addition of this amount was necessary as the yield of electrochemical treatment was found to be dependent on the chloride concentration [25]. Sodium sulphate (Scharlau), 40 g L^{-1}, was also added to the solution to simulate the conductivity of industrial effluents after dyeing process with reactive dyes. Sodium sulphate is one of the most common electrolytes in reactive dyes dyeing.

2.2 Experimental wastewater treatment plant

The experimental plant consists in two different parts: an electrochemical cell (continuous process) followed by an UV exposure device (batch process).

2.2.1 Electrochemical cell

Electrochemical treatments were performed in an undivided electrolytic cell based on the commercial cell ECO 75 (ELCHEM), which was initially designed to obtain hypochlorite for disinfection. Cathodes were constituted by titanium and anodes were made of titanium covered by platinum oxides. The total surface area of each electrode was 486 cm^2. The volume of the vessel was 1L. The cell was able to treat up to 25 L h^{-1} which allows its use at industrial scale.

The experimental plant was constituted by the electrochemical cell, the pump to feed the system and the deposit to store the treated wastewater. This plant operated continuously, and the flow rate was fixed at 20 L h^{-1}. The source supply allowed regulating the current among 0 and 25 A. The voltage was variable among 0 and 40 V, depending on the current applied and also on the conductivity fixed for the treatment.

2.2.2 UV lamps

Three different UV lamps were used in order to evaluate the influence of the wavelength applied and the way of application. The UV lamps were the following:

- Lamp A: 9 W, maximum emission spectra centred at 254 nm, applied in vertical position inside the solution (Phillips),

- Lamp B: 9 W, maximum emission spectra centred at 360 nm, applied in vertical position inside the solution (Phillips),

- Lamp C: 12 W, constituted by two horizontal fluorescents (C1 and C2) with maximum emission spectra centred at 254 nm and 365 nm, respectively (Vilber Lourmat), applied over the solution.

After the electrochemical treatment, aliquots of 300 mL and 600 mL of effluents were collected and irradiated with UV light. Lamps A and B were submerged into the solution in a protecting quartz container (d = 3.6 cm, h = 14 cm) and lamp C was placed 8 cm over the solution. In total, eight different experiments were performed under magnetic stirring, as indicated in table 1.

Table 1. Experiments run for PC.

Position	Conditions		
	Lamp	λ lamp irradiation (nm)	Volume (mL)
submerged, vertical	A	254	300
submerged, vertical	B	360	300
over the solution, horizontal	C1	254	300
over the solution, horizontal	C2	365	300
submerged, vertical	A	254	600
submerged, vertical	B	360	600
over the solution, horizontal	C1	254	600
over the solution, horizontal	C2	365	600

2.3 Ozone

Ozone was generated from air by a lab-scale ozone generator (TECOZON) and supplied into the dye solution at a dose of 0.1841 mgO_3 min^{-1}. Ozone generation was determined by titration with KI (Scharlau) where the ozone reacted with the potassium iodide according to equation 1:

$$O_3 + 2KI + H_2O \rightarrow I_2 + 2KOH + O_2 \qquad (1)$$

The resulting iodine was titrated using a standard sodium thiosulfate solution in the presence of starch as indicator.

Dye solutions were ozonated for 5 h at room temperature and atmospheric pressure.

2.4. Analytical measurements

2.4.1 Decolourization measurements

Decolourization was calculated from the initial concentration and dye concentrations at time t (c_i and c_t respectively) by measuring the absorbance at the visible maximum dye absorption wavelength (583 nm for RB5, 545 nm for PC, 606 nm for PN, 418 nm for PY and 604 nm for PB). Measurements were carried out on the effluent, just after electrochemical treatment and along the UV treatment. During UV exposure, samples were taken and measured every minute. Decolourization (D) was reported in %:

$$D\ (\%) = \frac{(c_i - c_t)}{(c_i)} \times 100 \qquad (2)$$

Absorbance measurements were carried out with a UV-visible spectrophotometer (Shimadzu UV-2401 PC). Dye absorbance has a linear behaviour versus the concentration in the range between 0.001 and 0.020 g L^{-1} according to the equations:

Abs = 30.858c – 0.002 (R^2 = 0.9999) for RB5 (3)
Abs = 27.784c – 2exp-5 (R^2 = 0.9999) for PC (4)
Abs = 26.149c – 0.004 (R^2 = 0.9999) for PN (5)
Abs = 14.315c – 0.003 (R^2 = 0.9999) for PY (6)
Abs = 16.816c – 0.999 (R^2 = 0.9999) for PB (7)

where c is the dye concentration expressed in g L^{-1}.

2.4.2. Organic matter removal measurements

The organic matter removal was calculated from COD measurements [42] as follows:

$$COD\ removal\ (\%) = \frac{(COD_i - COD_t)}{(COD_i)} \times 100 \qquad (8)$$

where COD_i corresponds to the initial value and COD_t is the value at time t.

2.5 Kinetic evaluation

Decolourization kinetic constants were calculated for UV and ozonation treatments. First-order reactions were assumed and the decolourization rate constants were calculated from the slope of the semilogarithmic plot colour (at the maximum absorbance wavelength of each dye) versus exposition time, in accordance with the kinetic equation number 9:

$$\ln(Abs_t/Abs_0) = k_d \cdot t \qquad (9)$$

where k_d is the first-order decolourization kinetic constant expressed in min^{-1}; Abs_t and Abs_0 are the absorbances at time t and initial respectively.

3. Results and discussion

3.1 Selection of UV light irradiation conditions

After a fixed electrochemical treatment at 6 mA/cm^2, the influence of UV wavelength irradiation on the dye solutions and the lamp position were studied. For this purpose, PC dye was selected.

Three UV lamps were tested at two different ways of applying the UV light irradiation (submerged into the dye solution and over the dye solution), all of them at two different wavelengths. Detailed conditions of experiments are in indicated in table 1. The volume of irradiated dye solution was also tested. The results of these eight experiments are shown in figure 2.

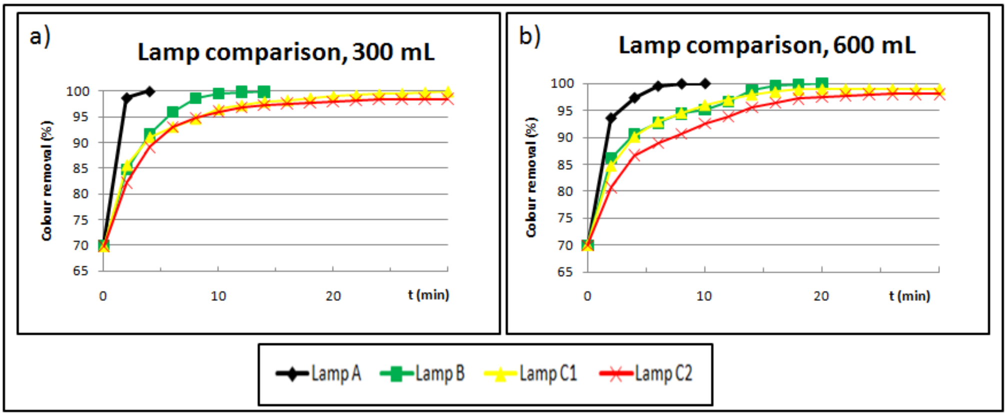

Figure 2. Colour removal of PC solutions for UV lamps A, B, C1 and C2. a) 300 mL and b) 600 mL.

From Figure 2 it can be appreciated that all experiments reached colour removal over 98% in less than 30 min of UV irradiation after the fixed electrochemical pre-treatment.

It is also possible to state that for the same volume and the same wavelength, the submerged lamps (A and B) reached the full colour removal in shorter periods of time than the UV lamps placed over the solution (C1 and C2). Moreover, as can be seen in figure 2a or 2b, the wavelength 254 nm (A and C1) was more efficient for colour removal than 360 nm (B) or 365 nm (C2).

Consequently, the best results of colour removal were obtained for the UV lamp A (submerged, 254nm). With respect to the volume of dye solution, the colour removal of 300 mL was faster than 600 mL, as expected.

Once determined the proper UV lamp and conditions to irradiate dye effluents after an electrochemical treatment, the minimum current density needed to be applied in the electrochemical step to reach a high colour removal was determined. For this purpose, five current densities, from 3 mA/cm^2 to 40 mA/cm^2, were applied to the dye solutions as a previous step to the UV irradiation treatment.

Figure 3 shows the results of colour removal for PC solutions with UV light irradiation after an electrochemical pre-treatment at different current densities.

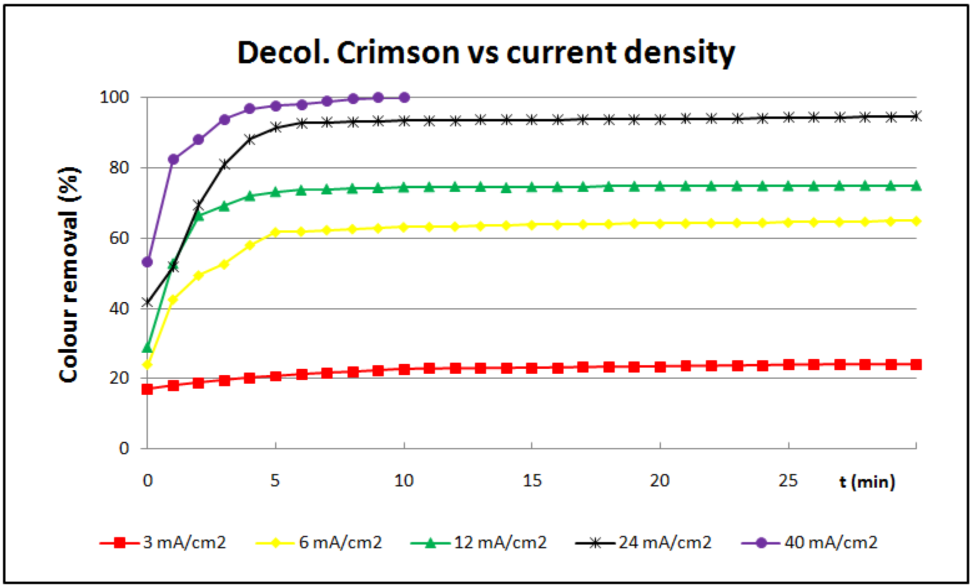

Figure 3. Colour removal of PC under UV irradiation at different current densities. UV lamp A, 300 mL.

Figure 3 shows that the higher the current density applied was, the higher the colour removal achieved after the electrochemical pre-treatment was. This value is plotted in Figure 3 as t=0 min because it corresponds to the initial point with respect to the UV treatment. Consequently, the current density applied at the electrochemical treatment also influence the further colour removal of the PC solution due to the UV irradiation. In this sense, at the end of the UV treatment, the faster and the higher colour removal was obtained for the PC solutions preteated with electrochemical at 40 mA/cm^2. When the current density was 24 mA/cm^2, the colour removal reached the 95%. This value can be considered high enough as the coloured effluents constitute only about a 10% of the total plant wastewater. The dilution with the rest of process effluents and a subsequent biological treatment ensure a final wastewater uncoloured and able to accomplish the Spanish regulations [43].

It must also be taken into account that a current density of 3 mA/cm^2 is not enough to initiate the colour removal process. The UV light irradiation is almost unefficient in this case, as the colour removal could only reach the 24%. From the results discussed in this section, it can be stated that best colour removal of PC solutions was obtained when an UV lamp was submerged in 300 mL of dye solution irradiating at 254 nm wavelenght. For this dye, current densities of at least 24 mA/cm^2 should be applied to reach the 95% of colour removal.

3.2 Selection of the current density for the electrochemical pre-treatment

In the above section, the colour removal was found to be highly dependent on the current density applied during the electrochemical pre-treatment. For this reason, the influence of the initial electrochemical treatment on the rest of dyes was also studied. Dye solutions (RB5, PN, PY and PB) were tested at five current densities, from 3 mA/cm^2 to 40 mA/cm^2, before undergo the UV irradiation under the previously fixed conditions (lamp A submerged in 300mL of dye solution). Results are shown in Figure 4.

As can be observed from Figure 4, general tendencies obtained for the four dyes are similar than the obtained for PC. That is to say, higher current density applied in the electrochemical pre-treatment leads to higher colour removal in the UV exposure. However, it is important to notice that UV colour removal achieved when the initial electrochemical treatment was performed at 3 mA/cm^2 or at 6 mA/cm^2 was very different, being much lower in the first case. Electrochemical pre-treatments carried out at current densities higher than 6 mA/cm^2 reached similar percentage of colour removal after UV irradiation, but the period of UV exposure required was rather different.

When comparing the different behaviour of dyes with respect to the initial electrochemical treatment, it is interesting to comment the case of RB5 and PN. At the lower current densities, 3 mA/cm^2 and 6 mA/cm^2, RB5 colour removal was lower than PN colour removal. But from 12 mA/cm^2, this situation changed and both, the initial colour removal due to the electrochemical treatment and the further UV irradiation, were higher for RB5 than for PN.

The PY had peculiar results. It can be seen that the solutions of this dye did not

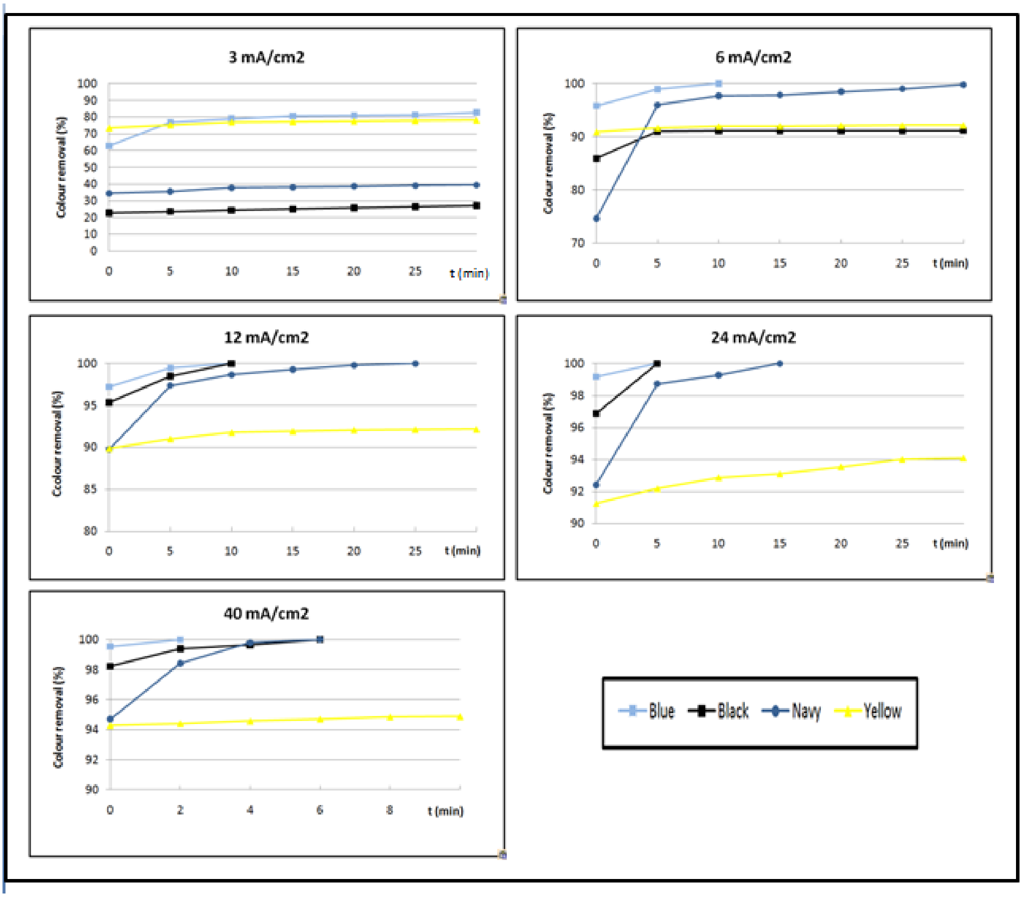

Figure 4. Colour removal due to the UV light exposure (254 nm, 6W): influence of the current density (3, 6, 12, 24 and 40 mA/cm^2) applied in the electrochemical pre-treatment (20 L h^{-1}).

reach 100% of colour removal at any current density after 30 min of UV irradiation.

One possible explanation is the formation of slightly coloured intermediates during the electrochemical treatment which produce a yellowish colour and interfere in the absorbance of the PY.

In table 2 are summarized the percentages of colour removal reached after the initial electrochemical treatment and the final UV irradiation, as well as the difference of both, which is attributed to the UV irradiation.

Table 2. Effect of UV irradiation in colour removal (%) of RB5, PC, PN, PY and PB dye solutions: influence of the current density applied in the electrochemical pre-treatment.

% of colour removal											
Current density (mA/cm^2)	Treat.	RB5		PC		PN		PY		PB	
		%	ΔUV %	%	ΔUV %	%	ΔUV %	%	ΔUV %	%	ΔUV %
3	Electr.	23	4	17	7	34	5	73	5	63	20
	UV	27		24		39		78		83	
6	Electr.	86	5	24	41	75	25	91	1	96	4
	UV	91		65		100		92		100	
12	Electr.	95	5	29	46	90	10	90	2	97	3
	UV	100		75		100		92		100	
24	Electr.	97	3	42	53	92	8	91	3	99	1
	UV	100		95		100		94		100	
40	Electr.	98	2	53	47	95	5	94	1	99	1
	UV	100		100		100		95		100	

As previously discussed in Figure 4, the yield of colour removal after the electrochemical treatment was greater at higher current density. At 3 mA/cm^2, the contribution of the electrochemical treatment in the colour removal was low for RB5, PC and PN while it was higher for PY and PB that reached the 73% and the 63% respectively. The further UV irradiation of the partially decoloured dye solution increased the final colour removal of the solution but results were still low for RB5, PC and PN and the 78% and 83% was reached for PY and PB respectively.

The influence of the UV irradiation was enough to reach the 100% of colour removal for PN and PB and the 91% and 92% for RB5 and PY respectively after an electrochemical treatment at 6 mA/cm^2. At higher current densities the electrochemical treatment removed over 90% of colour for these dyes and the later UV irradiation treatment achieved total colour removal for RB5, RB and PN.

The PC solutions were the most difficult to discolour, but the influence of UV irradiation on colour removal was the greatest. Maximum UV irradiation influence was achieved after an electrochemical treatment at 24 mA/cm^2, which increased the 53% of colour removal. In this case, the total colour removal reached was the 95%.

The PY solutions were the less affected by the UV irradiation. The possible explanation is that PY solutions were easely treated by the electrochemical treatment and therefore high colour removal were achived after this treatment.

As a whole, it can be stated that colour of dye solutions can be satisfactorily removed by the application of UV irradiation after an electrochemical treatment at low current density for the majority of tested dyes.

3.3. Influence of the UV light in organic matter removal

Organic matter removal of the dye solutions due to the electrochemical treatment and UV exposure was evaluated by COD measurements as others authors do [44, 45]. These results are indicated in Table 3.

From the results indicated in Table 3, it can be seen that COD removal is strongly dependent on the current density applied in the electrochemical treatment COD removal of the dye solutions is higher when higher current densities were applied in the electrochemical treatment. The greater COD removals, bold in the table, were achieved at 40 mA/cm^2. Slightly higher COD removal were obtained due to the exposure of the treated dye solutions to UV irradiation.

PB is the most sensitive dye to electrochemical pre-treatment with respect to COD removal. It reached the 65% of COD removal after an electrochemical pre-treatment at 40 mA/cm^2. In contrast, PC is the most resistant dye to the electrochemical pre-treatment. It only reached the 28% of COD removal after an electrochemical treatment at 40 mA/cm^2. Despite this, PC dye showed a peculiar behaviour versus the current density applied in the electrochemical treatment. At low current densities, between 3 mA/cm^2 and 12 mA/cm^2, PC was slightly degraded by the electrochemical treatment; only a 7% and 11% of COD removal were achieved at 3 mA/cm^2 and 12 mA/cm^2 respectively. However, at high current densities, 24 mA/cm^2 and 40 mA/cm^2, PC doubled this COD removal, and reached the 22% and 28% respectively. Similar tendencies were obtained for this dye with the UV exposure.

Results of COD removal presented in this study did not achieve the 100%, although electrochemical treatments can be applied to obtain a full degradation of the dye solutions (mineralization of the dye) [46, 47]. But it would require higher electrochemical current density or a longer treatment time which implies a higher and unnecessary additional cost. Complete degradation of biodegradable organic matter of textile effluents can be achieved by several other methods, such as conventional activated sludge biological treatments. Also, as demonstrated in this study, the further exposure to UV irradiation of dye solutions pre-treated by electrochemical, improved colour removal at a lower cost.

For this reason, the combination of electrochemical techniques with UV treatment is proposed as a previous step to the biological treatment, where the coloured effluents (about the 10% of the total plant effluents) are treated separately and, once the dyes molecules have been broken and converted into more biodegradable compounds, they can be easily treated in the biological plant with the rest of effluents (scouring, bleaching, washing, etc.). The colour removal by electrochemical pre-treatment-UV irradiation can also be applied after the biological treatment, although it is less advantageous as a much higher volume of water must be treated.

Table 3. COD values (mg O_2 L^{-1}) and % of COD removal of 0.1 g L^{-1} dye solutions (RB5, PC, PN, PY and PB). Electrochemical pre-treatment from 3 mA/cm^2 to 40 mA/cm^2 followed by UV irradiation.

Dye	Current density (mA/cm^2)	COD values (mg O_2 L^{-1})			COD removal (%)	
		Initial dye sol.	After electr. treatment	After 60 min of UV exposure	After electr. treatment	After 60 min of UV exposure.
RB5	3	154	143	119	7	23
	6		132	109	15	29
	12		114	86	26	44
	24		94	68	39	56
	40		**71**	**60**	**54**	**61**
PC	3	32	30	27	7	16
	6		29	27	9	16
	12		28	26	11	19
	24		25	19	22	41
	40		**23**	**17**	**28**	**47**
PN	3	33	28	26	15	21
	6		26	23	18	28
	12		24	22	27	33
	24		21	18	36	45
	40		**20**	**17**	**39**	**48**
PY	3	36	34	32	6	11
	6		32	31	11	14
	12		31	30	14	17
	24		29	27	19	25
	40		**24**	**22**	**33**	**39**
PB	3	175	154	121	12	26
	6		131	107	25	39
	12		112	87	36	50
	24		93	56	47	68
	40		**61**	**51**	**65**	**71**

3.4 Ozone decolourization

Ozonation treatments were conducted for the five reactive dyes studied in this work. In Figure 5 are shown the colour removal results.

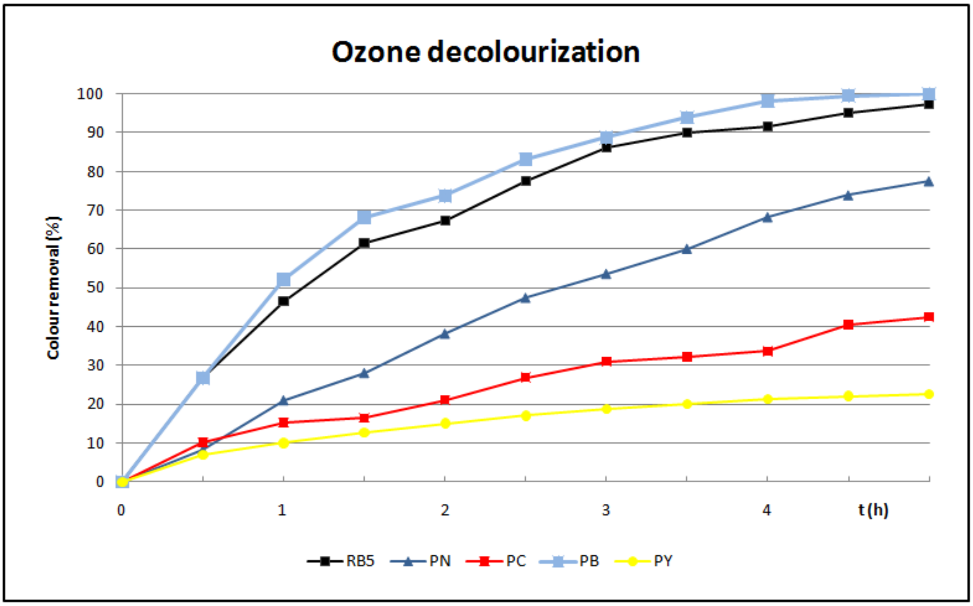

Figure 5. Ozone decolourization treatments for RB5, PC, PN, PY and PB at 0,1841 $mgO_3\ min^{-1}$.

Figure 5 shows that in the case of PB, the100% of colour removal was achieved after 4.5 h of ozonation. RB5 reached the 97% after 5h while PN reached the 77% of colour removal for the same time. The other two dyes, PC and PY reached only the 42% and 23% respectively after 5h of ozonation.

As can be seen, under the tested conditions, the percentages of colour removal were much lower for ozonation than for electrochemical combined with UV irradiation for all dyes.

On the basis of ozonation provide lower COD removals than the obtained with electrochemical followed by UV irradiation [35], the COD of the ozonation experiments were not conducted.

3.5 Decolourization kinetic constants (k_d) and mechanism discussion

The decolourization kinetic constants (k_d) were calculed for the two types of treatments: ozonation and UV irradiation (initiated by electrochemical) . In both cases, the k_d followed a pseudo-first-order reaction [33, 34], that is a first-order law with respect to the dye concentration (table 4).

Table 4. Decolourization kinetic constants (k_d) of RB5, PC, PN, PY and PB for UV irradiation (initiated by an electrochemical treatment from 3 mA/cm^2 to 40 mA/cm^2) and ozonation, 0.1841 mgO$_3$ min^{-1}.

k_d (min^{-1}) *						
Dye	Treatment					
	UV (initiated by electrochemical)					O$_3$
	3 mA/cm^2	6 mA/cm^2	12 mA/cm^2	24 mA/cm^2	40 mA/cm^2	0.1841 mgO$_3$ min^{-1}
RB5	0.0865	0.7272	1.0069	1.2011	1.2538	8.2×10^{-4}
PC	0.0144	0.1572	0.1795	0.2037	0.4016	4.4×10^{-4}
PN	0.1418	0.4531	0.7617	0.8311	0.8927	6.1×10^{-4}
PY	0.5391	0.8021	0.8062	0.818	0.8533	3.6×10^{-4}
PB	0.0906	1.2179	1.3435	1.7369	**	9.1×10^{-4}

* R^2 were 0,9999 in all cases except for k_d corresponding to PY at 6 mA/cm^2, PN at 12 mA/cm^2 and all the UV treatments initiated at 40 mA/cm^2.

** It was not possible to calculate the k_d of PB as 99.5% of colour removal was already reached after the electrochemical treatment at 40 mA/cm^2.

The behaviour of the different dyes with respect the two treatments, previously exposed in section 3.2 can be confirmed when comparing the k_d. It can be appreciated that general tendencies are similar for both treatments, being the PB the most sensitive dye. Moreover, the k_d values confirm that the PY colour removal is almost stabilized from 6 mA/cm^2.

It is also possible to state that colour removal due to the UV irradiation is faster after electrochemical treatments at high current densities and also that the combination of electrochemical treatment followed by UV irradiation is also faster than ozonation for colour removal at the studied conditions.

With respect to the initial electrochemical treatment, k_d increased when the current density increased. However, this increase was much higher from 3 mA/cm^2 to 6 mA/cm^2. This fact permit to state that the optimum current density to be applied at the electrochemical pre-treatment is 6 mA/cm^2 for the majority of dyes. From current densities higher than 6 mA/cm^2, the energy consumption increases more than the yield of colour removal. For intance, for PB the ratio between k_d at 3 mA/cm^2 and k_d at 6 mA/cm^2 is 13 whereas only a ratio of 1.1 is obtained between 12 mA/cm^2 and 24 mA/cm^2 experiments.

On the basis of these results, a general mecanism for the degradation of the dyes is proposed. It is well known that the azo bonds (-N=N-) of the dyes are the main responsible of their colour. The breakage of this bond causes the decolourization of the dye solution [48]. A general decolourization reaction is shown in equation 10. The extent of the degradation depends on the intensity of each treatment.

$$\text{Dye (R-N=N-R') + OH}^{\bullet}\text{ (or other radicals)} \rightarrow \text{dye-intermediates} \rightarrow CO_2 + H_2O + N_2 \quad (10)$$

Although the kinetics were much slower in the case of ozone, no significant differences on the dyes behaviour were found between both methods, the UV irradiation after the electrochemical treatment and ozonation.

In one hand, in the ozonation treatment the decomposition rate of ozone is directly affected by pH and temperature [49, 50]. Ozone can oxidise a variety of compounds directly or via radical species formed during its initiation reaction (11), propagation reactions (12) - (17) and termination reactions (18) and (19), all of them resulting in a generation of free radicals [51, 52]:

$$O_3 + OH^- \rightarrow HO^{\bullet}_2 + O_2^{-\bullet} \tag{11}$$

$$HO^{\bullet}_2 \leftrightarrow O_2^{-\bullet} + H^+ \tag{12}$$

$$O_3 + O_2^{-\bullet} \rightarrow O_3^{-\bullet} + O_2 \tag{13}$$

$$O_3^{-\bullet} + H^+ \leftrightarrow HO^{\bullet}_3 \tag{14}$$

$$HO^{\bullet}_3 \rightarrow HO^{\bullet} + O_2 \tag{15}$$

$$HO^{\bullet} + O_3 \rightarrow HO^{\bullet}_4 \tag{16}$$

$$HO^{\bullet}_4 \rightarrow HO_2^{\bullet} + O_2^{\bullet} \tag{17}$$

$$HO^{\bullet}_4 + HO^{\bullet}_4 \rightarrow H_2O_2 + 2O_3 \tag{18}$$

$$HO^{\bullet}_4 + HO^{\bullet}_3 \rightarrow H_2O_2 + O_3 + O_2 \tag{19}$$

Among the formed radicals, the hydroxyl radical is the most oxidizing agent (Eº = 2.8 V) [53] and it is able to attack the dye molecule [54]. These radicals are formed form decomposition at high pH values, as it is our case, while the molecular ozone remains as the main oxidant at low pH values. The extent of colour removal is favoured by the direct ozone attack, at low pH values, since molecular ozone is selective for the destruction of chromophore groups. The hydroxyl radicals have a higher oxidizing potential, indirect oxidation, and are less selective than molecular ozone, and their influence is greater at high pH values [55]. The efficiency of the indirect oxidation at high pH values is proved to be somewhat superior than the direct oxidation for colour removal [33].

The treated dye solutions were prepared at pH 9, in order to simulate industrial wastewater, and therefore the influence of the indirect oxidation due to the action of $OH^{\bullet}$ radical is much higher than the influence of ozone.

On the other hand, in the electrochemical treatment, the direct and the indirect oxidation of the dye molecule were also involved.

The following reactions are assumed to take place [35]:

- In anodic reaction

Main reaction

$$2\,Cl^- \rightarrow Cl_2 + 2e^- \tag{20}$$

Side reaction

$$4\,OH^- \rightarrow O_2 + H_2O + 4e^- \tag{21}$$

$$Cl_2 + H_2 \rightarrow OH^+ + Cl^- + HClO \tag{22}$$

$$HClO \rightarrow H^+ + ClO^- \tag{23}$$

$$Dye + ClO^- \rightarrow CO_2 + H_2O + Cl^- \tag{24}$$

- At cathodic reaction

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (25)

Hydrogen peroxide can be electrochemically produced by reducing oxygen at cathode at acidic medium:

$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ (26)

This shows hydrogen peroxide to be the product of a two-electron transfer to oxygen. However, if oxygen is reduced by a for-electron process, water is formed as the end product:

$O_2 + 4H^+ + 4e^- \rightarrow H_2O$ (27)

Hydrogen peroxide can reduce further to water:

$H_2O_2 + 2H^+ + 2e^- \rightarrow H_2O$ (28)

In alkaline media, the reaction stoichiometry is given by:

$O_2 + H_2O + 2e^- \rightarrow OH^- + HO_2^-$ (29)

$HO_2^- + H_2O + 2e^- \rightarrow 3OH^-$ (30)

The per-hydroxyl ion (HO_2^-) is formed by hydrogen peroxide dissociation in base:

$H_2O_2 \rightarrow H^+ + HO_2^-$ (31)

In presence of UV lamp:

$H_2O_2 + \lambda \upsilon \rightarrow 2\ OH^\bullet$ (32)

$OH^\bullet$ + dye → dye-intermediate (33)

$OH^\bullet$ + dye-intermediate → CO_2 + H_2O + mineralization-products (34)

From the above reactions, it can be appreciated that in the electrochemical oxidation treatment many radicals are involved. Among them, the hydroxyl radical, which has the most strong oxidizing strength, and others such as hydrogen peroxide (E^o = 1.87 V), hypochlorite (E^o = 1.49 V), chlorine (E^o = 1.36 V) and chlorine dioxide (E^o = 1.27 V) [56].

Therefore, the proposed general mechanism for the electrochemical treatment of the dye is the following:

Dye + $OH^\bullet$ / chlorine radicals→ dye-intermediates → CO_2 + H_2O (35)

where the chlorine radicals play a very important role, as the presence of chlorine is needed for the electrochemical treatment to be efficient [13, 25].

In summary, from the mechanisms of both treatments, it can be assumed that hydroxyl radical is the most oxidizing radical in indirect oxidation. For this reason, similar behaviour in colour removal were obtained for the studied dyes. The different kinetiks of both treatments can be explained by the fact that, in the electrochemical treatment, chlorine radicals are also involved.

4. Conclusions

The main conclusions of this study are the following:

- The application of UV irradiation after an electrochemical treatment of dye solutions improved the yields of colour removal and COD removal.

- The optimum conditions to apply UV irradiation to the dye solutions were with a lamp, vertically placed and submerged into the solution, with maximum emission spectra centred at 254 nm.

- The application of UV irradiation after an electrochemical pre-treatment at only 6 mA/cm^2 provided satisfactorily results of colour removal for the majority of dyes. Higher current densities did not improve significantly the final colour removal results except for Procion Crimson H-EXL.

- The best COD removals of the dye solutions were obtained after an electrochemical treatment at 40 mA/cm^2. However, lower current densities can be applied in order to obtain biodegradable compounds able to undergo a biological treatment.

- Similar mechanisms are proposed for the UV irradiation after an electrochemical treatment and ozonation of alkaline dye solutions. In the combination of electrochemical treatment and UV irradiation, free chlorine and radicalarian species such as $Cl^{\bullet}$, $Cl_2^{\bullet -}$, $HClO^-$ play also a very important role.

5. Acknowledgements

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Chapter 6

Article on decolourization III:

Combination of coagulation-flocculation and nanofiltration techniques for dye removal and water reuse in textile effluents

COMBINATION OF COAGULATION-FLOCCULATION AND NANOFILTRATION TECHNIQUES FOR DYE REMOVAL AND WATER REUSE IN TEXTILE EFFLUENTS

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Abstract

Color is one of the main problems in wastewater and many techniques can be applied to remove it. In this work, nanofiltration, coagulation-flocculation and their combination were studied to remove color from five reactive dyes. Nanofiltration was carried out using an Energy Saving nanofiltration membrane in a 0.5 L pilot plant at 10 bar. Coagulation-flocculation experiments were performed in a Jar test apparatus using an anionic polyelectrolyte flocculant, $FeCl_3$ as coagulant agent and two different resins: melamine-urea-formaldehyd and polyamine resin. From the results it was concluded that nanofiltration removed in the order of 40 and 80% of color for the five dyes while cogulation-flocculation reached between 85-95% of color removal for four dyes except in the case of polyamine resin for RB5. The combination of these techniques dramatically improved the removals reaching over 98% of color removal for all dyes except for RB5 that achieved a 90%. The combined process also decreases COD values as it implies the use of lower resin concentration than coagulation-flocculation.

Keywords: Nanofiltration, coagulation-flocculation, color removal, COD, wastewater.

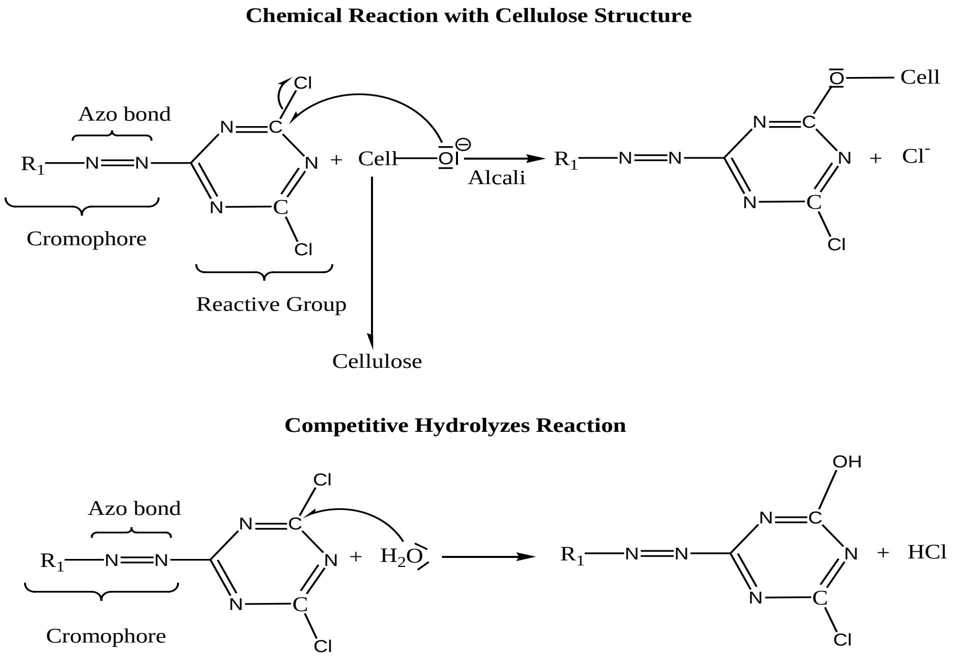
1. Introduction

It is estimated that more than 100.000 synthetic dyes are available in the world with over 7 x 10^5 tons of dye-stuff produced annually [1, 2]. Reactive dyes represent by far the most important development in synthetic dyes after 1935. The ease of application and the brilliance of the shades are two outstanding properties of reactive dyes and which have been responsible for their success in use [3, 4]. Reactive dyes are characterized by a fiber-reactive component bonded to an appropriate azo, anthraquinone, phthalocyanine or metal complex dye [4]. These dyes represent an increasing market share, about 20-30% of the total market for dyes, because they are used to dye cotton which makes up about half of the world's fiber consumption [5, 6].

However, reactive dyes present low exhaustion [7] and high solubility what causes losses between 10 and 20% of dyes in their use [4] which approximately is 100-150 L of water per kg of product [8].

Textile wastewater is characterized by high color, BOD, COD (or TOC) and should be treated before discharging it into the environment [9]. Most of the residual color is due to the hydrolysis of the dye. Figure 1 shows the reactions of the dye with the fiber and the hydrolysis.

Due to the poor biodegradation of reactive dyes under aerobic conditions [10], especially those containing azo-groups, a conventional biological wastewater treatment process is not suitable [11, 12] to remove color from wastewater. Therefore other techniques or combination of them must be applied.


Chemical Reaction with Cellulose Structure

Competitive Hydrolyzes Reaction

Figure 1. Chemical reactions of the dye with the fiber and with water.

Nanofiltration experiments on dye bath wastewater treatment have been undertaken since 1990 [5]. Membrane technologies are being increasingly used in the treatment of textile wastewater for the recovery of valuable compounds from the wastewater as well as reuse of the water [13]. The use of membrane technology is widely reported in many studies. Nanofiltration can be used for color removal, water and salts recovery, and COD reduction [14-21].

In figure 2 are indicated the different filtration ranges and the general type of compounds they can filter.

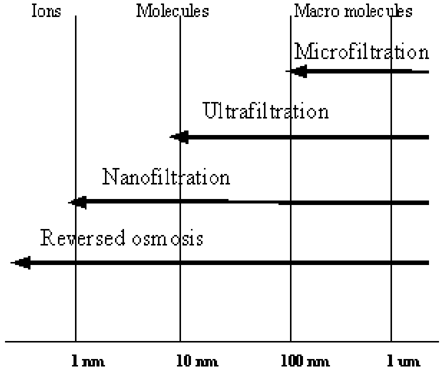


Figure 2. Filtration ranges and type of compounds filtered in microfiltration, ultrafiltration, nanofiltration and reversed osmosis.

However, the basic problem involved in any membrane-based process is the decline in the flux and the fouling of the membrane surface [13, 22]. To overcome this problem, a combination of various separation methods has been adopted in recent years to achieve a high quality of separation [13, 23-25].

One of the more usual techniques applied before filtration is adsorption onto power activated carbon [26]. However the high cost of the activated carbon [27] and the fact that is not a selective adsorber [28] makes the scientific to develop other solutions.

The combination of a coagulation-flocculation treatment before nanofiltration was studied in this work. Both techniques are able to remove color from wastewater. The use of coagulation-flocculation is widely reported for dyes removal [29-32]. Two main inorganic coagulants used in water treatment are salts of aluminium and ferric ions [33, 34]. The treatment can be carried out at room temperature as it is demonstrated that the temperature has no a significant effect what is in agreement with the theoretical prediction of the Poisson-Boltzman equation [35]. However, the most essential disadvantages of this technique are the large amount of sludge produced, which has to be buried and the low efficiency with respect to some dyes [36].

In this work, coagulation-flocculation and nanofiltration techniques were used alone and combined to remove five reactive dyes from wastewater. The goals of this study were to demonstrate that both techniques can remove color from the wastewater and that their combination improved the decolourization results by reducing sludge production and consumption of chemical products (coagulant and flocculant agents).

2. Material and methods

2.1 Dyes

Five reactive dyes, kindly provided by DyStar, were selected: Remazol Black 133 B (C. I. Reactive Black 5), reactive group sulfatoethylsulfone and chromophore diazo; Procion Crimson H-EXL, Procion Navy H-EXL, Procion Yellow H-EXL and Procion Blue H-EXL them all with monochlorotriazine reactive group and chromophore azo. From this section, these dyes will be referred in the text as: RB5, PC, PN, PY and PB respectively. Figure 3.a and 3.b shows the two available structures of the dyes. The formulas corresponding to PC, PN and PB have not been already published.

2.2 Reactive dyebath effluent preparation

Simulated dyebath effluents were prepared in distilled water. A solution of 0.1 g L $^{-1}$ of the commercial dyestuff was first hydrolyzed. The hydrolysis was carried out as follows: the pH of the solution was adjusted to 12 with NaOH (Flucka) and then heated at 80 ºC for two hours. After the hydrolysis, it was let cool down to room temperature and the pH was adjusted to 9 with sulphuric acid (Scharlau). Sodium sulphate (Scharlau), 40 g L^{-1}, was added to the solution to simulate the conductivity of industrial effluents corresponding to the dyeing process with reactive dyes.

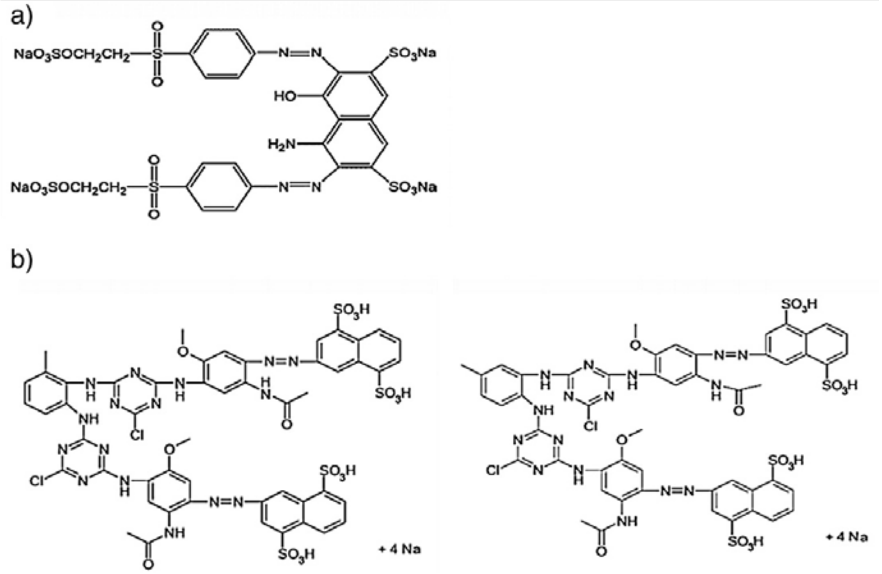


Figure 3. Chemical structure of a) C.I. Reactive Black and 5 b) Procion Yellow H-EXL.

2.3 Treatments

2.3.1 Nanofiltration treatments

For the filtration experiments, a nanofiltration ESNA (Energy Saving Nanofiltration) 1 Lf2 (Hydranautics) membrane was selected and used as such. The membrane was made of polyamide and designed for hardness, iron and color rejection as well as for the removal of organics, bacteria and viruses.

The experimental plant was a laboratory pilot specially constructed by (Polymem) whose vessel volume was 0.5 L. The pilot plant operated in batch mode. The pilot allows to work up to 40 bar and the pressure was maintained constant by operating two valves manually. Inside the cell a circular membrane was placed over a plastic porous support. The diameter of the membrane was 90 mm and the area was 644 mm^2.

Filtration experiments were performed with 0.4 L of the synthetic effluent at constant pressure of 10 bar in the pilot plant and conducted until 300 mL of filtrated were collected. Experiments time ranged from 30 min to 50 min what represent flow rates between 10 mL/min and 6 mL/min.

At the end of the treatment, absorbance measurements of the filtrate were made to establish the yield of color removal.

2.3.2 Coagulation– Floculation treatments

In the coagulation – flocculation treatments the following reagents were used: anionic polyelectrolyte HIMOLOC SS-120 (Derypol) as a flocculant agent, $FeCl_3$ (Merck) as a coagulant agent, and two resins, both commercialized by Ashland: Amerfloc 445 which was identified as melamine-urea-formaldehyd from the IR spectrum (figure 4) and Amerfloc 485, polyamine resin. Finally, NaOH and $Ca(OH)_2$ were used as alkalis.

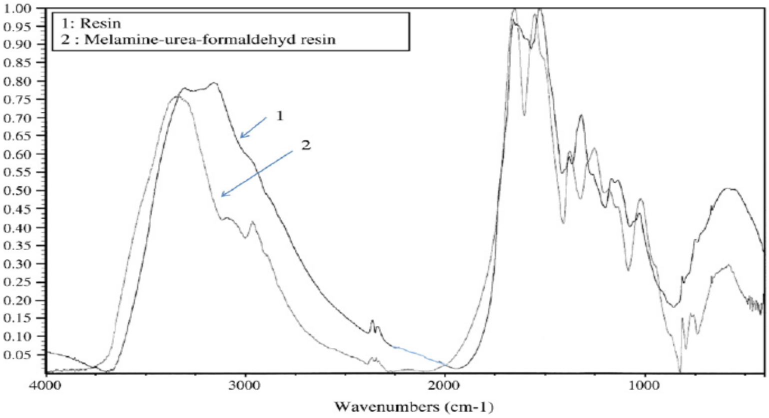


Figure 4. IR spectrum of Amerfloc 445 resin.

Precipitation, coagulation and flocculation experiments were performed in a jar-test apparatus (ISCO). Aliquots of 0.5 L of the synthetic dye effluents were treated as indicated in figure 5.

2.3.3 Combined treatment

The schematic design of the combined treatment is shown in figure 6.

As can be seen, in the combined treatment the coloured dye solution initially undergoes a coagulation-flocculation treatment which partially removes its color. The resulting partially decoloured dye solution is treated by nanofiltration to accomplish the complete remove of the dye.

2.4 Analytical measurements

Results presented in this work were the mean of three measurements. The minimum reproducibility of measurements was fixed over the 98%.

2.4.1 Dye removal measurements

The removal of the dyes was followed by absorbance measurements. The evolution of solutions color was calculated from the initial dye concentration and dye concentrations at time t (c_i and c_t respectively) by measuring the absorbance at the visible maximum dye absorption wavelength (545 nm for PC, 583 nm for RB5, 606 nm for PN, 418 nm for PY and 604 for PB).

Decolourization (D) was reported in %:

$$D\ (\%) = \frac{(c_i - c_t)}{(c_i)} \cdot 100$$

Absorbance measurements were carried out with a UV-visible spectrophotometer (Shimadzu UV-2401 PC).

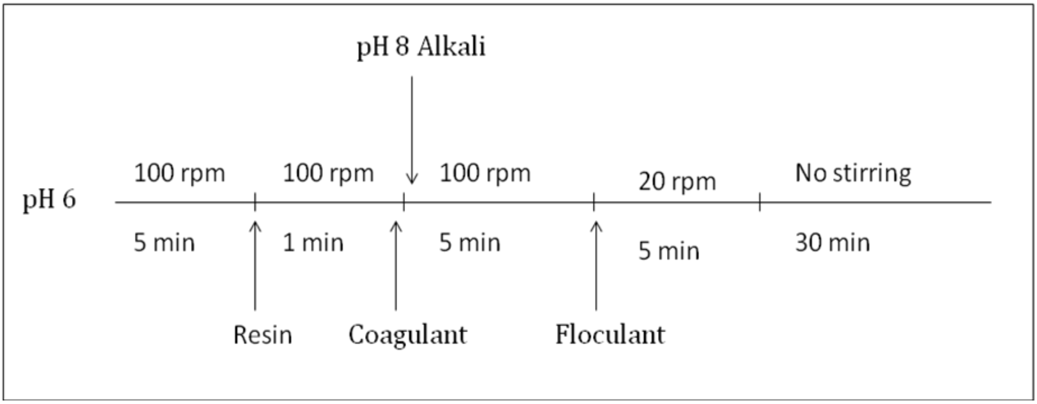


Figure 5. Schema of the coagulation – flocculation treatment conditions (rpm: revolutions per minute).

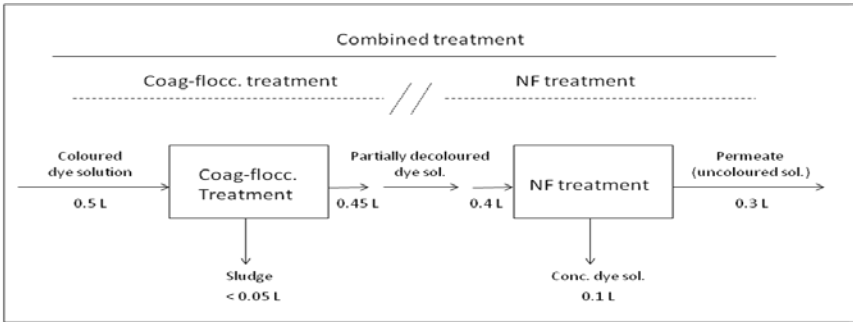


Figure 6. Schematic design of the combined treatment, coagulation-flocculation followed by nanofiltration. Coag-flocc.: Coagulation-flocculation treatment. NF: nanofiltration treatment.

Dye absorbance has a linear behavior versus the concentration in the range between 0.001 and 0.020 g L^{-1} according to the equation:

$Abs = 27.784 \cdot c - 2exp\text{-}5$ ($R^2 = 0.9999$) for PC
$Abs = 30.858 \cdot c - 0.002$ ($R^2 = 0.9999$) for RB5
$Abs = 26.149 \cdot c - 0.004$ ($R^2 = 0.9999$) for PN
$Abs = 14.315 \cdot c - 0.003$ ($R^2 = 0.9999$) for PY
$Abs = 16.816 \cdot c - 0.999$ ($R^2 = 0.9999$) for PB

where c is the dye concentration expressed in g L^{-1}.

2.4.2 COD removal

The organic matter removal of the effluents was evaluated from COD measurements [37] as follows:

$$COD\ removal\ (\%) = \frac{(COD_i - COD_t)}{(COD_i)} \cdot 100$$

where COD_i corresponds to the initial value and COD_t is the value at time t.

3. Results and discussion

3.1 Nanofiltration treatments

Nanofiltration experiments were performed for each dye. In figure 7, the % of dye removal can be seen.

From the figure, it can be seen that in the case of PB, an 82% dye removal was reached after the nanofiltration treatment and 71% was achieved for RB5. The other three dyes were removed 53% and 54% respectively in the cases of PC and PY and 39% for PN solutions which provided the poorest results for nanofiltration experiments.

In addition, it must be considered that when conducting nanofiltration treatments, a part of the initial solution remains in the pilot plant containing almost the whole dye. In other words, there is a filtrated cleaner solution (permeate) which is partially dye free and much lower volume of a dye concentrated solution which must be treated separately.

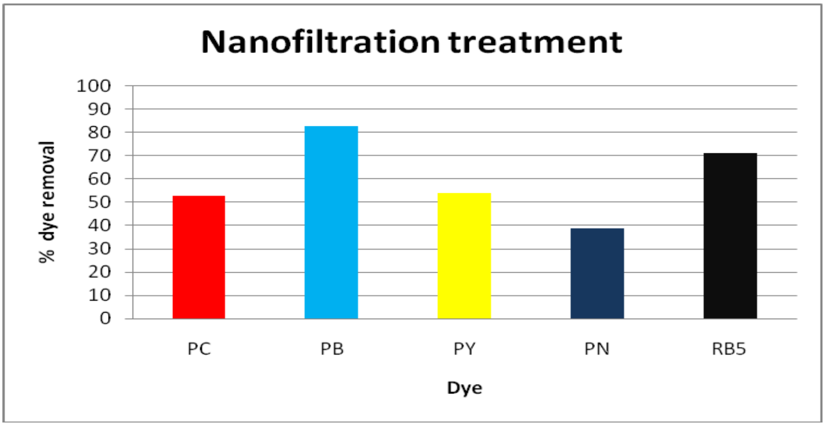


Figure 7. % of dye removal after nanofiltration with membrane ESNA 1 Lf2 at 10 bar pressure.

From the results, it can be concluded that the use of nanofiltration as unique treatment provided poor results of dye removal for most the studied dyes under the selected conditions.

3.2 Coagulation – Floculation treatments

In coagulation-floculation treatments different steps can be considered. Broadly speaking, colloids particles in solution must be destabilized due to the action of chemical species and then joined to form bigger particles called floccules. More detailed, water can contain suspended solids able to sediment under repose and dispersed particles that do not sediment easily, mainly colloids. Individual colloids are stabilized when they have the same charges on their surface, what causes repulsion between them. Due to this fact, colloids do not aggregate each other and therefore do not form bigger particles able to precipitate by themselves.

Coagluation-floculation treatments destabilize colloids and achieve their sedimentation. These actions are usually due to the action of chemical species and stirring. Defining each part, coagulation can be understood as the destabilization of the colloids due to the charges compensation on their surface what leads to the formation of the core. On the other hand, flocculation is the agglomeration of the destabilized particles to form microfloccules leading to the formation of bigger agglomerates called floccules able to sediment.

In the whole treatment, the use of resins enhances the initial grouping of the particles assisting the coagulant. In this case, the resin interacts with the dye and forms the pre-coagulum leading to a coagulum thanks to the action of the coagulant. Stirring the solution is needed to distribute the coagulant and to allow the particles interaction to form the coagulum. After coagulation, it is necessary to group the coagulum to form the floccules. This process is driven by the action of a flocculant, which group them under slow stirring.

The influence of each reagent involved in the coagulation-floculation treatment was evaluated in order to establish the best experimental conditions for the dye removal.

Methodology was the following: in the first step 1) the alkali influence was evaluated. In these experiments, resin, coagulant and floculant conditions were the same for each alkali. Results were compared to determine which alkali provided best dye removals. Once determined the most proper alkali, the second step 2) was to evaluate the resin influence. Two resins were tested as indicated in section 2.4 and best resin concentration was determined. For these two first steps, experiments were performed with PC. The alkali selected and the proper resin concentration were applied to the third step 3) where the influence of coagulant was studied for the five dyes. Finally, in the fourth step 4), the flocculant influence was studied at the previous conditions determined for each single dye.

To sum up, in the first two steps, the influence of alkali and resin concentration were evaluated for PC. In the third step, the obtained values were applied to the rest of dyes to determine the best proper coagulant concentration for each dye. At the end, in the fourth step, the optimum flocculant concentration for each dye was determined at the conditions established in the previous steps.

3.2.1 Alkali influence

In the coagulation-floculation treatment, the alkali is added immediately after the addition of the coagulant. In our studies $FeCl_3$ was used as a coagulant. When it is added, the pH of the solution decreases hindering the precipitation of ferrous, which optimum precipitation pH is above 6.5; therefore, the alkali is added to increase the pH about 8. Two different alkalis were selected, NaOH and $Ca(OH)_2$ and their influence in dye removal was evaluated measuring the color absorbance of the solution once the whole coagulation-flocculation process was finished. For that purpose, the dye PC was selected.

In these experiments, the alkali influence was evaluated. To be able to compare the results, concentrations of resin, coagulant and flocculant were the same for each alkali. Experiments performed with $Ca(OH)_2$ removed 85,4% of PC while experiments where NaOH was used removed 84,3% of PC for the same conditions. Therefore, the results showed slight difference between alkalis.

3.2.2 Resin influence

In order to evaluate the influence of both the concentration and the type of resin, a melamine-urea-formaldehyd resin and polyamine resin were compared. Concentrations from 100 to 600 ppm of both resins were tested for the dye PC.

The extent of dye removal was determined by measuring the absorbance of the solution at the end of the flocculation-coagulation treatment.

In figure 8 are shown the results of dye removal depending on the resin concentration in the experiment. In these experiments, $Ca(OH)_2$ was used as alkali and both coagulant and flocculant were fixed at 0.5 g L^{-1} and 0.5 ppm respectively.

As can be seen from the figure, the resin concentration exhibit a very strong influence in dye removal whereas both resins provided similar results, no significant differences are appreciated in % of dye removal.

When adding 100 ppm of resins only the 9% and 10% of dye was removed by Amerfloc 445 and Amerfloc 485 respectively.

The 14% and 15% of dye removals were obtained respectively for 200 ppm of resins. When resin concentration was 300 ppm, dye removals reached the 38% and 39% respectively and 61% and 60% respectively for 400 ppm of resin. Best dye removal results were obtained when resin concentration was 600 ppm. At this concentration, the 83% and 80% of dye was removed respectively for Amerfloc 445 and Amerfloc 485; hence 600 ppm of resin was the most appropriate concentration.

Although it is clear that when increasing resin concentration dye removal increases it must be taken into account that COD also does. In table 1 are listed the COD values for each resin (Amerfloc 485) concentration.

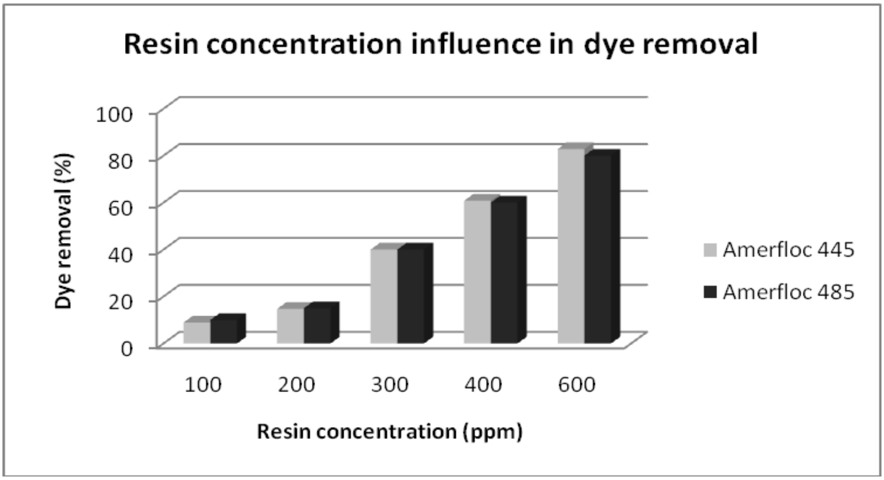


Figure 8. Influence of resin concentration in % of dye removal. Coagulant 0.5 g L^{-1} and floculant 0.5 ppm.

Table 1. COD values (mg O_2 L^{-1}) for different resin (Amerfloc 485) concentrations (ppm).

Resin concentration (ppm)	COD (mg O_2 L^{-1})
100	25
200	38
300	70
400	173
600	205

Comparing the figure 8 and the table 1 it can be appreciated that when resin concentration increased from 200 to 300 ppm, the dye removal increased almost three times while COD values only doubles (from 38 mg O_2 L^{-1} to 70 mg O_2 L^{-1} respectively). From this point, their tendencies change, and dye removal increases slower than COD. It would be interesting to find a solution that provided good dye removals at low resin concentration avoiding resin excess what increases COD. Further studies in this sense will be found in section 3.3.

3.2.3 Coagulant influence

In this section, the coagulant influence in the dye removal was studied. For this purpose, Amerfloc 445 was selected as resin. In the experiments, the coagulant concentration varied from 0.2 to 0.8 g L^{-1} maintaining the resin concentration at 600 ppm and the flocculant concentration fixed at 0.5 ppm.

The experiments were run for the five dyes. In table 2 are listed the dye removal values after the coagulation-flocculation treatment.

From the table 2, it is possible to see that the coagulant concentration influence in the dye removal is very poor. Its influence represent about the 2% for PC and PB and the 6% for PN of difference of dye removal, only in the case of PY, its influence is higher and represents up to 30% more of dye removal depending on the coagulant concentration, in the studied range.

Table 2. Values of % of dye removal versus coagulant concentration. Resin 600 ppm, and floculant 0.5 ppm (highligted: the optimal conditions).

Coagulant (g L^{-1})	PC	PB	PY	PN	RB5
0.2	86,5	92,7	86,4	88,8	73,9
0.4	85,1	98,2	86,9	89,3	67,6
0.6	83,1	97,3	76,5	84,3	69,9
0.8	84,9	94,6	56,6	82,5	71,3

The best results were bold. It is important to indicate that the best dye removals were obtained at low coagulant concentrations, contrary than increasing the resin concentration.

3.2.4 Flocculant influence

In order to determine the flocculant influence in dye removal, similar methodology than for coagulant was followed. In this case, the resin concentration was also constant at 600 ppm and the coagulant concentration used was the determined before for each single dye in table 2.

The flocculant dye removal results are listed in table 3.

From the results of this table, high differences are easily appreciated with respect to table 2 from the coagulant influence table.

As can be seen, the flocculant concentration strongly affects the % of dye removal of PB, PY and RB5 varying their removals the 8%, 9% and 18% respectively. For the case of PC and PN its influence was lower, the 1% and 5% respectively.

Another difference from the coagulant study is its concentration. Contrary than before, flocculant optimum concentrations range from the lowest to the highest and its general tendency is to increase the dye removal when increasing the flocculant concentration.

3.2.5 Comparison between resins

In section 3.2 the influence of four parameters in the dye removal was studied. With the optimal conditions established for each dye, the experiments were conducted using the resin Amerfloc 485 to verify the possible effect of the resin.

In figure 9 the dye removal results obtained for both resins can be compared.

Table 3. Values of % of dye removal versus polyelectrolyte concentration. The resin concentration was 600 ppm, being the coagulant concentration the value establish from the table 2 for each dye.

Floculant (ppm)	PC	PB	PY	PN	RB5
0.2	84,4	90,6	87,3	85,7	80,4
0.4	85,7	99,6	87,1	83,7	75,7
0.6	82,7	99,8	87,6	88,6	71,5
0.8	83,7	98,6	78,3	90,5	62,8

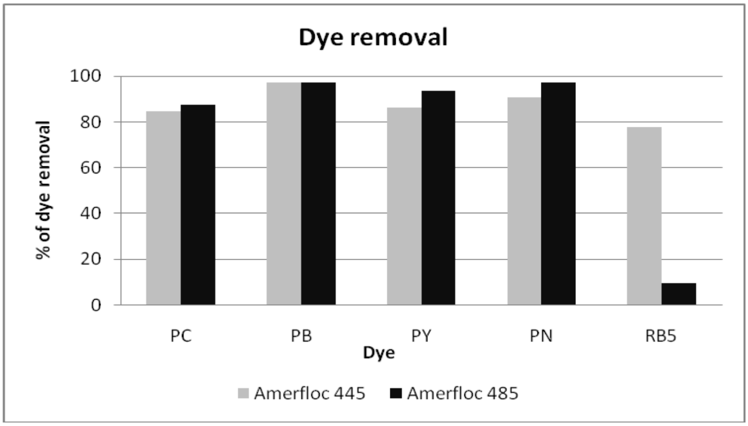


Figure 9. Comparison of dye removal results for the five reactive dyes with different resins.

From the figure, it is appreciated that both resins provided similar dye removal results for PC, PB, PY and PN. The different results between resins in the case of RB5 can be attributed to the different reactive group of this dye respect to the others.

The different reactive group played an important role in the resin affinity and therefore different behaviors were expected.

From this consideration, it can be stated that urea-formaldehyd resins can be satisfactorily applied to more reactive dyes than polyamine ones. In other words, urea-formaldehyd resins are more general than polyamine resins.

3.3 Combination of nanofiltration and coagulation-floculation treatments

In this section, the combination of coagulation-filtration treatment followed by nanofiltration treatment was evaluated. Two main goals were fixed: firstly to achive total dye removal in the wastewater and secondly to minimize the reagents consumption in the first step. In this sense, the objective was the reduction of the resin concentration in the coagulation-floculation treatment, as other reagents were found not to have a strong influence in dye removal as previously demonstrated and therefore the corresponding values used in this section were the same than previously established for each dye.

To determine the minimun resin concentration for the combined treatment, the dye PC and the resin Amerfloc 445 were selected. This resin provided the more satisfactory results for all dyes. Resin concentrations from 100 to 600 ppm were evaluated. Results of dye removal at the end of the combined treatment ranged from 99.9% when 600 ppm of resin were used and 98.5% for 100 ppm of resin. These results proves that the addition of only 100 ppm of resin is enough to obtain a total color removal of the PC dyebath wastewater when the coagulation-floculation treatment is completed by a nanofiltration treatment.

Following the same methodology than in the previous section, the optimum resin concentration obtained for PC were applied to the rest of dyes. In figure 10 are shown the dye removals for all the dyes after the combined treatment for 100 ppm of resin (other reagents conditions for each dye were the same that established in section 3.2).

From the figure, it can be appreciated that the combined treatment provided almost 100% of dye removal for four of the five reactive dyes. Only in the case of RB5 removal was lower but in the order of 90%.

To sum up, it is possible to conclude that coagulation-floculation treatment followed by nanofiltration provided the best results in dye removal. Besides this, the combination of them, allowed to treat the wastewater reducing the use of resin from 600 to 100 ppm for all dyes what implies the less formation of sludge in the process.

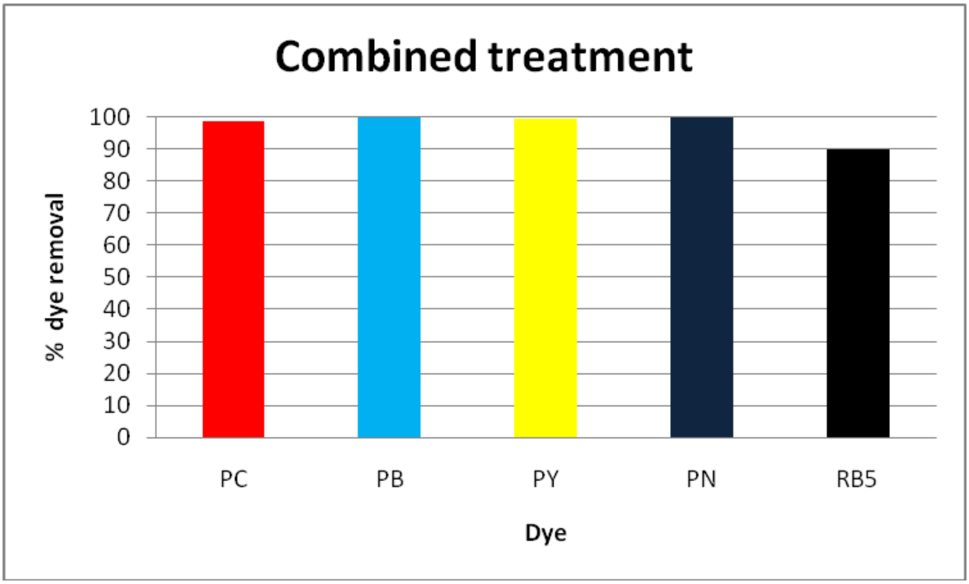


Figure 10. Dye removals results for the combined treatment. Resin concentration 100 ppm.

4. Conclusions

The main conclusion of this work stated that the combination of the two treatments, membrane filtration and coagulation-floculation process, provided almost 100% of dye removal for four of the studied dyes and 90% for RB5, providing better results than each technique separately. Moreover, this combination permit to reduce the concentration of resins needed in the process.

In the coagulation-floculation process, it was found that the resin was the most influential reagent in dye removal. The choice of the proper resin was also critical to obtain satisfactory dye removal results as can be seen in the case of RB5. Other reagents as cogualant, floculant and alkali agent did not substantially affect the results. Once determined the best conditions for each dye, removals up to 90% were obtained for most of the dyes and up to 97% for PB. Therefore, the coagulation-floculation treatment option to remove dyes form wastewater.

Finally, in the case of PB acceptable dye removals in the range of 80% were obtained when nanofiltration treatment was used. For the rest of dyes, removals were insufficient, in the order of 50%.

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Chapter 7

Article on reuse:

Influence of electrochemical pre-treatment in dyeing wastewater reuse for five reactive dyes

INFLUENCE OF ELECTROCHEMICAL PRE-TREATMENT IN DYEING WASTEWATER REUSE FOR FIVE REACTIVE DYES

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Abstract

In this study the influence of an electrochemical pre-treatment was evaluated in dyeing wastewater reuse for five reactive dyes for cotton fabrics. The most proper dyeing method was established and the alkali influence was also studied. Wastewater was treated in an electrochemical cell at 20 L h^{-1} and 40 mA/cm^2 for times of 3 to 15 minutes before being reused. Along the electrochemical treatment the evolution of the dye degradation was evaluated by COD measurements. From the results, it can be concluded that 70% of the water and salts can be satisfactorily reused by DBR in most of the reactive dyes obtaining DE (CMC (2:1)) values below 1 with respect to the reference. Results can be improved up to 75% by applying an electrochemical pre-treatment. In DE (CMC (2:1)) values, DL was found to be the most influential parameter. Finally, the influence of the level of dye degradation in the wastewater was observed as a no relevant parameter in DBR for the most studied dyes.

Keywords: Direct Bath Reuse (DBR), reactive dyes, textile dyeing, organic matter removal, electrochemical pre-treatment.

1. Introduction

Textile industry uses and rejects high amounts of water, being wastewaters the main way by which dyes are discharged into the environment. Textile effluents have high concentrations of organic and inorganic compounds and strong color, caused by residual dyes that were not fixed to the fibers during the dyeing process, and show as main characteristics high variations of flow and composition, the presence of non-biodegradable compounds and toxic substances, high temperature and high pH value [1]. In the last few years, the use of double reactive group dyes in cotton dyeing process has increased quickly. These dyes present higher exhaustion which implies less residual hydrolyzed dye in solution after the dyeing process.

Environmental pressures on textile industry and the consumption of water and energy in this sector, lead to the adoption of measures that directly influence to the industrial processes. In order to reduce the environmental impact, optimizing process to improve exhaustion level and/or the reuse of final baths with or without intermediate treatment, are some of the measures that have been applied [2]. Two fundamental methods of control are wastewater treatment and source reduction. The latter is very attractive in many cases since it avoids cost and liability involved in waste disposal.

In one hand, the most common wastewater treatments to remove colour consist in *oxidation techniques* such as electrochemical treatments alone or assisted by UV [3-6], ozone treatments [7, 8], Fenton processes [9, 10]; *Physicochemical techniques* such as the use of adsorbents like alumina, silica gel and activated carbon [11-13] and coagulation-floculation treatments [14], and *membranes*; mainly nanofiltration membranes [15, 16]. These treatments usually focus on color removal of textile dyeing wastewaters.

On the other hand, in the last years, textile industry has increased the efforts to optimize the processes and also to reuse water.

Most of the studies that improve or optimize textile effluents are focused on the current dyeing processes [17] mainly for cotton dyeing [18-20], wool [21], cotton-wool mixtures [22] and acrylics [23].

The studies on water reuse are based in nanofiltration, ultrafiltration, reverse osmosis and their combinations [24 – 33]. These techniques usually allow the reuse of salts [34, 35]. Other techniques used for the wastewater reuse are ozonation [36, 37], physico-chemical treatments [38 – 40] and electrochemical treatments [41, 42].

Other important source reduction treatment is the Direct Bath Reuse (DBR). DBR was studied by Cook and Tincher for disperse-dye mixtures in polyester [43]. Their experiments demonstrated that multicolor sequences that are not in a color line can be dyed satisfactorily if at least one of the dyes overlaps and if the shade series are chosen judiciously. Further investigations held by Cook et al. [44] concluded that DBR can be feasible in multishade sequences (light-medium-dark) with an acceptable color correlation to their standards [45]. When performing DBR, it must be taken into account that some water and auxiliaries must be added to the dyeing to obtain a specific volume because there are some losses when the dyed material is taken out of the exhausted dye bath as some liquor is physically retained in the fabric [46]. Besides this, certain substances can accumulate in the dye bath [47].

Despite the numerous studies of wastewater treatment, only a few propose specific uses for the reused water. Wastewater is proposed to be reused as process and cleaning water [48, 49] or in new dyeing processes [50] although no dyeing results are given.

In this work, bath reuse was studied for five reactive dyes as well as the influence of an electrochemical pre-treatment of the reused wastewater for new dyeing. The electrochemical process permit to treat the wastewater at the original pH contrary to Fenton process, there is no loss of salts like with some filtration processes, does not generate sludge as in the case of coagulation-floculation processes and uses a “clean reactive”, electron transfer, contrary for instance to the activated sludge. Moreover, electrochemical treatment allows fast and high organic matter degradation of the effluents.

DBR was performed for each dye in the study. Electrochemical treatments were conducted to determine the influence of the presence of organic matter removal in new dyeing. For that purpose, the effluents to be reused were treated in the electrochemical cell at different time expositions. The extent of dye degradation was determined by COD measurements and its influence was evaluated in dyed fabrics, as mentioned before, by color measurements comparison with a standard. All experiments were performed reusing the 70% of wastewater, the other 30% is assumed to be lost during the dyeing process.

The goal of this study is to minimize in a 70% the water and salt consumption in dyeing process by DBR and to establish whether color removal, dye degradation or both are required to reuse dyeing wastewater

2. Material and methods

2.1 Dyes and fiber

Five reactive dyes, kindly provided by DyStar, were selected: Remazol Black 133 B (C. I. Reactive Black 5), reactive group bissulfatoethylsulfone and chromophore diazo; Procion Crimson H-EXL, Procion Navy H-EXL, Procion Yellow H-EXL and Procion Blue H-EXL, all of them with bismonochlorotriazine reactive group and chromophore azo. From this section, these five dyes will be referred in the text as: RB5, PC, PN, PY and PB respectively.

Figure 1 shows the available structures of the dyes [51-54]. PN and PY are a blend of two monomers. The formula corresponding to PB has not been already published.

Dyeings were performed in 100% cotton fabrics kindly provided by TIPSA.

2.2 Reactive dye bath effluent preparation

Simulated dye bath effluents were prepared in the laboratory in soft water at 0.1 g L $^{-1}$ of the commercial dyes, previously hydrolyzed to simulate an industrial effluent.

The hydrolysis was carried out as follows: pH was adjusted to 12 with NaOH (Flucka) and then the solution was heated at 80 ºC for two hours. After the hydrolysis, it was let cool down to room temperature and the pH was adjusted to 9 with sulphuric acid (Scharlau).

Sodium sulphate (Scharlau), 40 g L^{-1}, was added to the solution to simulate the conductivity of industrial effluents after dyeing process with reactive dyes.

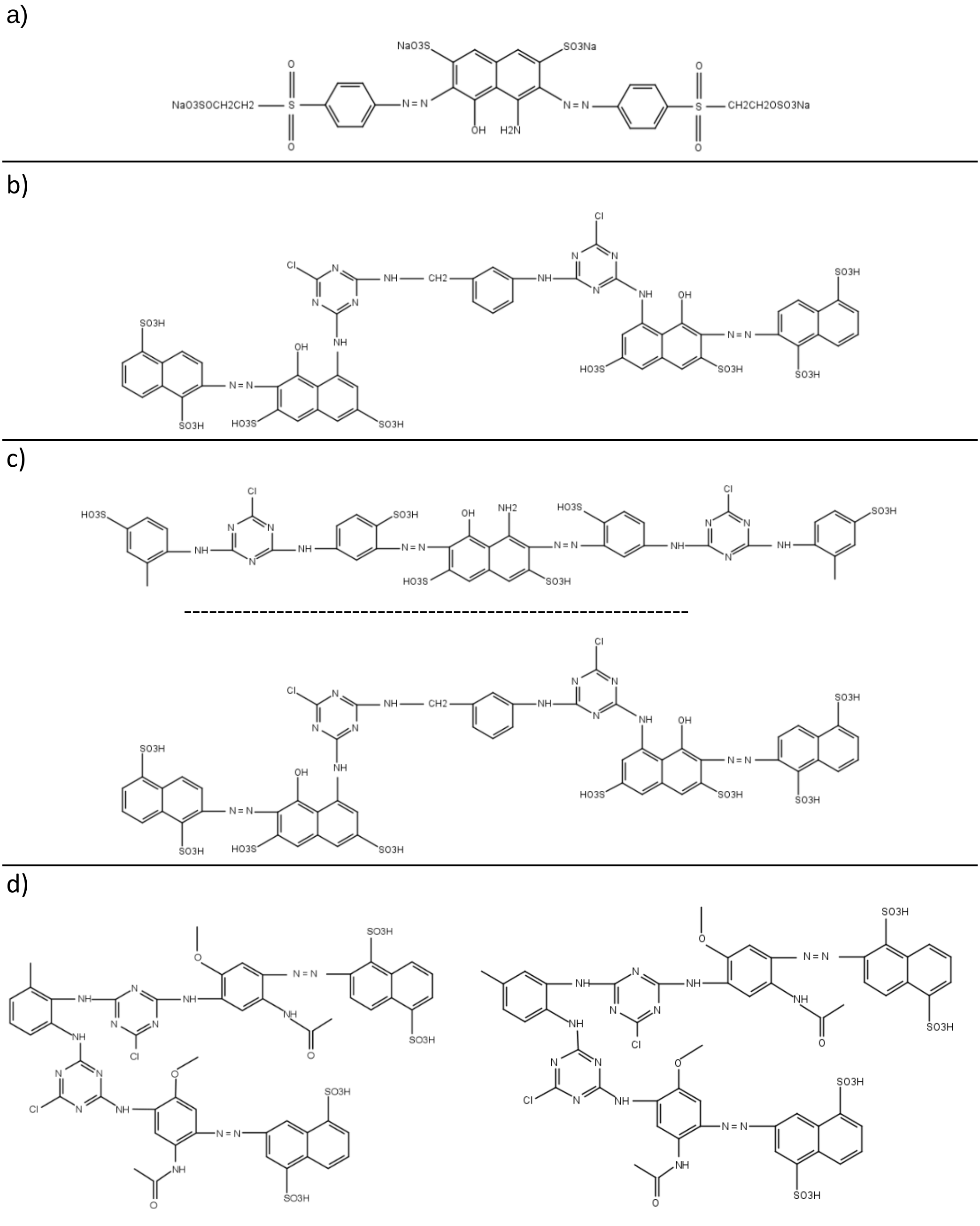

Figure 1. Chemical structure of: a) C. I. Reactive Black 5, b) Procion Crimson H-EXL, c) Procion Navy H-EXL and d) Procion Yellow H-EXL.

2.3 Dye degradation in the effluent

Effluents to be reused underwent an electrochemical treatment in order to degrade the organic matter present in them. These treatments were conducted in an undivided electrolytic cell, ECO 75 (ELCHEM, Germany). In figure 2 it can be seen the outline system associated with the electrolytic cell ECO 75 and the cell itself. Cathodes were constituted by titanium and anodes were made of titanium covered by platinum oxides.

The total surface of each electrode was 486 cm^2. The volume of the vessel was 1 L. The plant operated continuously at 20 L h^{-1} and 40 mA/cm^2. Each effluent underwent five times to the electrochemical treatment. The retention time in the reactor was calculated in 3 minutes.

Taking into account that dyes are the only organic compounds in the wastewater, the evolution of the dye degradation was followed by COD measurements [55] as follows:

$$COD\ removal\ (\%) = \frac{(COD_i - COD_t)}{(COD_i)} \cdot 100$$

where COD_i corresponds to the initial value and COD_t is the value at time t.

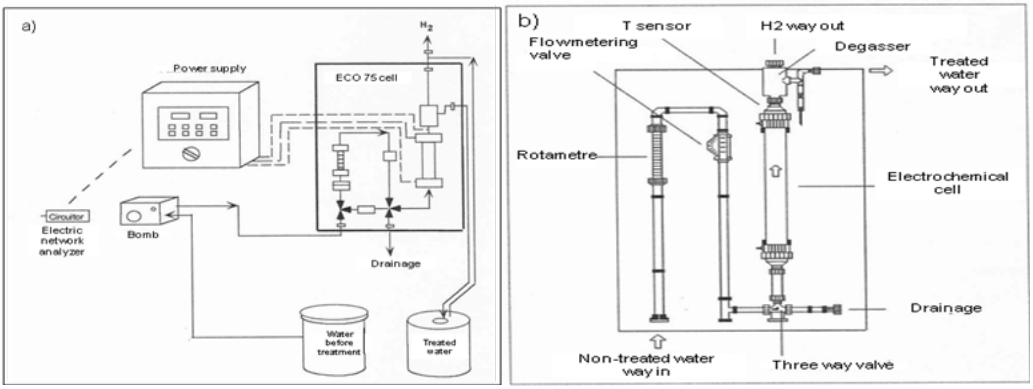

Figure 2. a) Outline system associated with the electrolytic cell ECO 75. b) Schema of the ECO 75 cell.

2.4 Dyeing method and chlorine removal

Dyeing experiments were performed in a Linitest apparatus (Original Hanaut Heraeus) under the following conditions: 10 g of cotton fabric; 3% o.w.f. of dyestuff; liquor ratio 1/10 and 40 g L^{-1} of Na_2SO_4 in the effluent.

Two different dyeing methods were studied as well as the influence of the alkali, used to adjust the dyeing pH. Table 1 summarizes the evaluated conditions. All experiments were run in triplicate.

Table1. Dyeing methods, alkali used and replicates.

Replicate	Method	Alkali
1, 2, 3	Isothermic	$NaOH + Na_2CO_3$
4, 5, 6	Isothermic	NaOH
7, 8, 9	All in	$NaOH + Na_2CO_3$
10,11,12	All in	NaOH

In figure 3 are schematized the dyeing methods conditions.

After electrochemical treatment, free chloride present in the effluents was measured by Chlorine Kit (Chemetrics) and removed by the stoichiometric addition of $NaHSO_3$. Chlorine detection limit of the method was 0.1 ppm.

Cleaning process of the fabrics was divided in ten steps as indicated in figure 4. All steps (rinsing and soaping) were performed at liquor ratio 1:10. Steps four and seven correspond to soaping with 2 g L^{-1} of Cotemoll T-LTR kindly provided by Color Center.

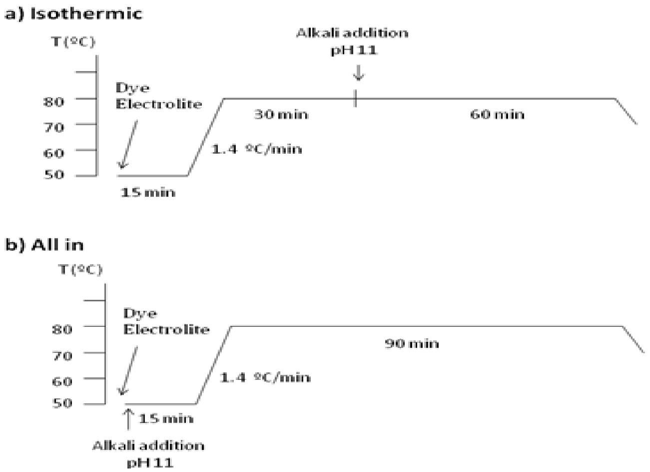

Figure 3. Dyeing methods a) Isothermic b) All in

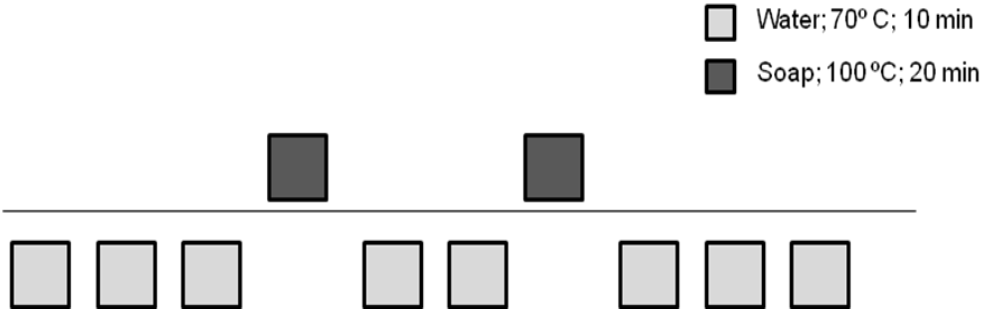

Figure 4. Cleaning process of fabrics after dyeing process

2.5 Color evaluation

Fabric color was measured using a Minolta Colorimeter, with the following measuring conditions: illuminant D65 and 10º standard observer.

The CMC (l:c) color difference formula was used as a tolerance system, which allows tolerance ellipsoids to be calculated around the target where the dimensions of the ellipsoid are functions of the position in color space of the target. The standard corresponds to the fabric dyed in the original dye bath without reuse.

The color differences between the standard and another fabric are

$$\Delta E_{CMC\,(l:c)} = \left[\left(\frac{\Delta L^*}{lS_L}\right)^2 + \left(\frac{\Delta C^*_{ab}}{cS_C}\right)^2 + \left(\frac{\Delta H^*_{ab}}{S_H}\right)^2\right]^{1/2}$$

where

$S_L = 0.04097L^*/(1 + 0.01765L^*)$

unless $L^* < 16$, in which case

$S_L = 0.511$

$S_C = \{0.0638\Delta C^*_{ab}/(1 + 0.0131\Delta C^*_{ab})\} + 0.638$

$S_H = S_C(TF + 1 - F)$

$F = \{(\Delta C^*_{ab})^4/[(\Delta C^*_{ab})^4 + 1900]\}^{½}$

$T = 0.38 + |0.4\cos(h_{ab} + 35)|$

unless $164^o < h_{ab} < 345^o$, in which case

$T = 0.38 + |\cos(h_{ab} + 35)|$

$$\Delta E^*_{ab} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

$\Delta C^*_{ab} = C^*_{ab,b} - C^*_{ab,s}$

$$\Delta H^*_{ab} = \left[(\Delta E^*_{ab})^2 + (\Delta L^*)^2 - (\Delta C^*ab)^2\right]^{1/2}$$

The values l and c used in the CMC (l:c) color difference formula are l = 2, c = 1 according to the recommendation for acceptability color differences [56].

3. Results and discussion

3.1 Dyeing method and alkali selection. Determination of reference fabrics.

In this section, the dyestuff PC was selected to determine the best way to reuse dyeing waste water. For that purpose, two different dyeing methods, Isothermic and All-in and two different alkalis systems, NaOH and mixture of NaOH + Na_2CO_3 (5 g L^{-1} both) were studied. All experiments were run in triplicate and numbered as indicated in table 1 (section 2.4). Prior to establish the final proper dyeing conditions the standard replicate for each condition must be determined. For this purpose, color coordinates (L, C, h) were measured and color differences (DE, DL, DC and DH) were calculated and compared between replicates. DE, DL, DH and DC were respectively compared between reused dyeing and the standard. As an example, table 2 shows the values of these parameters for the isothermic method when a mixture of NaOH + Na_2CO_3 was used as alkali.

From this table, it can be concluded that color differences between replicates are very low and due to experimental system limitations in the measurements. Besides this, DE variations are mainly due to the influence of DL. Taking all this into account, replicates number 1 and 3 are the most alike, being selected the number 1 as the standard for these dyeing conditions. The same criterion was used to select the other references for each dyeing process and alkali system. Replicates 1, 5, 8 and 11 were finally selected. Figure 5 shows a photography of the standards selected.

Table 2. Comparison of DE, DL, DC and DH values between the three replicates for the isothermic method and NaOH + Na_2CO_3 alkali.

DE	replicate				DL	replicate		
replicate	1	2	3		replicate	1	2	3
1		0,57	0,18		1		-0,52	-0,08
2	0,58		0,46		2	0,53		0,44
3	0,18	0,46			3	0,09	-0,44	
DC	replicate				DH	replicate		
replicate	1	2	3		replicate	1	2	3
1		0,11	0,01		1		0,2	0,16
2	-0,11		-0,11		2	-0,21		-0,05
3	-0,01	0,11			3	-0,16	0,05	

From the photography, the influence of the alkali on the final result is appreciated. Standards 1 and 8 were obtained when mixture of NaOH + Na_2CO_3 was used while standards 5 and 11 were obtained when only NaOH was used as alkali. These last two standards show higher intensity of color.

At this point, the comparison between methods and alkalis was done. Table 3 compares the results of these four samples.

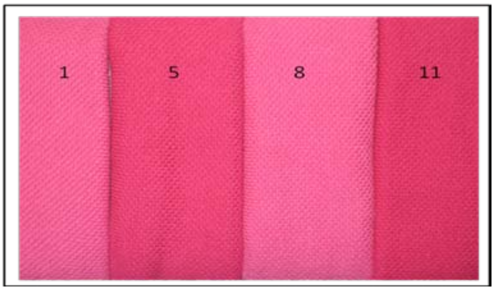

Figure 5. Standard replicates selected for Crimson.

Following the same methodology stated before, from the comparison of these results it can be concluded that different results are obtained depending on dyeing method and alkali. Again, DL is the most influential parameter in DE. Apart from this, it is possible to state that the dyeing method (Isothermic or All-in) has a greater influence in the results than the alkali system (NaOH or NaOH + Na_2CO_3).

To sum up, the best results in terms of color intensity were obtained when All-in method and NaOH alkali were used, which correspond to sample 11.

Once selected the proper dyeing method and alkali system, the standards of the other four dyes were also determined using the same methodology indicated at the beginning of this section (comparison of three replicates).

3.2 Dye degradation

Degradation of the hydrolyzed residual dye was evaluated by COD measurements for all the dyes. In table 4 are listed COD values and their % removal with respect to the initial values.

Table 3. Comparison of DE, DL, CD and DH values between standards for each method.

DE	Isothermic		All-in	
	1	5	8	11
1		5,25	2,33	6,04
5	5,7		3,22	0,89
8	2,41	3,07		3,9
11	6,67	0,91	4,16	

DL	Isothermic		All-in	
	1	5	8	11
1		-3,94	-1,82	-4,61
5	4,37		2,34	-0,75
8	1,91	-2,21		-2,91
11	5,23	0,76	3,16	

DC	Isothermic		All-in	
	1	5	8	11
1		1,83	0,99	1,93
5	-1,76		-0,81	0,1
8	-0,97	0,82		0,92
11	-1,85	-0,1	-0,9	

DH	Isothermic		All-in	
	1	5	8	11
1		2,96	1,06	3,4
5	-3,2		-2,05	0,48
8	-1,1	1,97		2,43
11	-3,71	-0,48	-2,55	

Table 4. COD values and % of dye removal for PY, PN, PC, RB5 and PB.

Electr.	Yellow		Navy		Crimson		Black		Blue	
Time (min)	COD	% COD removal	COD	% COD removal	COD	% COD removal	COD	% COD removal	COD	% COD removal
0	83.2	-	59.1	-	159.1	-	154,6	-	173.0	-
3	73.3	12	49.2	17	138.7	13	94,5	39	60.8	65
6	55.5	33	46.5	21	106.0	33	74.1	52	46.9	73
9	39.6	52	44.7	24	73.4	54	56.3	64	38.28	78
12	29.7	64	43.2	27	57.1	64	43.6	72	29.58	83
15	25.8	69	29.5	50	40.8	74	34.5	78	26.1	85

As can be seen, over 70% of organic matter removal was achieved after 15 minutes of electrochemical treatment for almost all dyes. Short electrochemical treatments remove residual color of the wastewater and longer treatments imply the gradual mineralization of the dye into CO_2 and water. In this study it will be also important to establish whether color removal, dye mineralization or both are required to reuse dyeing wastewater.

From the results it is important to note that different behavior was appreciated for the dyes. PY, PN and PC were initially difficult to degrade, between the 12 and 17% of dye removal were reached in three minutes, while 39% and 65% were achieved in the case of RB5 and PB, respectively. This could be understood as PY, PN and PC structures are very stable contrary to RB5 and PB that are easily degraded.

Another factor in dye degradation could be the size of the dyes. From figure 1 (section 2.1) it is possible to see that PY, PN and PC are large dyes while RB5 is a small one. In this sense, larger dyes are probably more difficult to degrade than small ones.

In the electrochemical treatments, the degradation of the dyes is due to the direct and indirect oxidation. Direct oxidation takes place on the anode surface while indirect oxidation is due to the action of radical species formed in the anode [57]. Indirect oxidation is usually more effective than direct oxidation [58]. The main radical species involved in the indirect oxidation are hydroxyl radical ($E^o = 2.8$ V), chlorine species such as hypochlorite ($E^o = 1.49$ V), chlorine ($E^o = 1.36$ V) and chloride dioxide ($E^o = 1.27$ V) and hydrogen peroxide ($E^o = 1.87$ V). Although the hydroxyl is the most oxidizing radical, the chlorine radicals play a very important role in the electrochemical treatment as their presence is needed for the electrochemical treatment to be efficient [57, 6]. Therefore, the degradation mechanism of the dye is mainly due to the action of hydroxyl radicals and chlorine radicals.

The influence of dye degradation in the reuse of wastewater will be discussed in the following section.

3.3 Behavior of reused dyeing baths with the five dyestuffs.

In this section the possibility of reusing dyeing wastewater was studied. For that purpose, the influence of an electrochemical pre-treatment was evaluated.

In all experiments, the 70% of water and salts were reused and in the remaining 30% of clean water the dye and needed salts were added. The dyeing conditions were the same for the standards and the later replicates. References were dyed in 100% soft water.

In figure 6a and 6b can be seen the evolution of DE (CMC (2:1)) for every dye at different electrochemical pre-treatment times with respect to the reference. In the figure, the tolerance DE limit value 1 is dotted. Values differences between the reference and the sample below 1 are considered acceptable, over 1 are not acceptable.

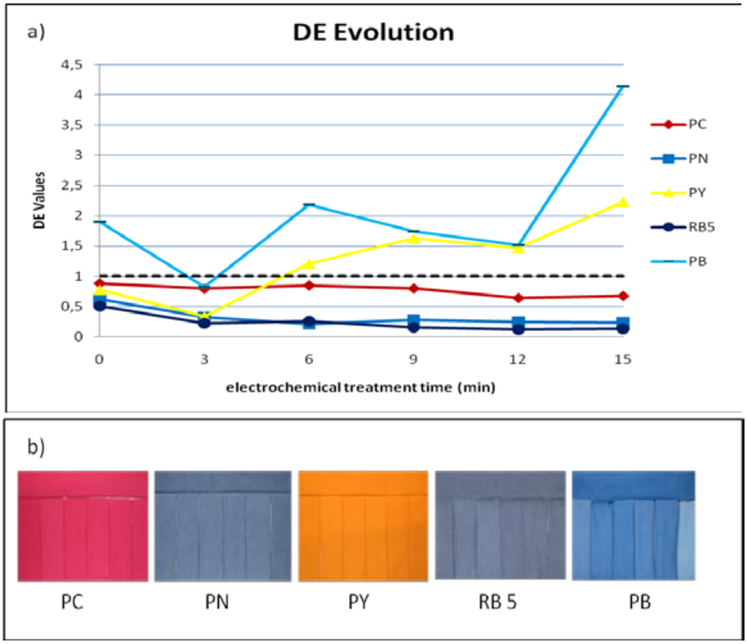

Figure 6. a) Evolution of DE (CMC (2:1)) with respect to the reference for every dye at different electrochemical pre-treatment times and b) visual comparison between replicates and the standard. Each standard is horizontally placed. Samples are vertically placed and sequentially from 0 minutes to 15 minutes.

From figure 6 a), it can be seen that in the majority of dyes: PC, PN and RB5 the DBR and all electrochemical pre-treatments times are below DE (CMC(2:1)) 1 and therefore, all samples are acceptable and not different from the standards.

An important fact of the evolution of DE versus electrochemical treatment residence times in the cases of PC, RB5 and PN is their tendency versus time. For these dyes, after 3 minutes of electrochemical pre-treatment DE values tends to remain constant and lower than when no electrochemical pre-treatment was applied to the reused wastewater.

In the case of PY, the figure 6a shows that DBR without electrochemical pre-treatment provides DE values with respect to the reference below 1, this means, acceptable. In this case, the application of only three minutes of electrochemical pre-treatment to the wastewater to be reused reduces DE values up to 56%. Longer electrochemical pre-treatments are not advisable as DE values rise over 1 and their tendency is to increase.

For PB dye, similar results than for PY were obtained. The best DE value was also achieved after 3 minutes of electrochemical pre-treatment. Either DBR without electrochemical pre-treatment and longer electrochemical pre-treatments did not provide acceptable DE values and results did not exhibit clear tendency.

The different behavior of PY and PB respect to PC, RB5 and PN can be attributed to their high sensibility to chlorinated water in their dyeing processes [59]. It must be considered that chlorine was removed from the wastewater by the use of a kit based on a visual comparison and therefore, this can imply an experimental error. The influence of small amounts of residual chlorine in the dyeing liquor is much greater for PY and PB rather than PC, RB5, and PN, as expected taking into account the chlorinated water sensibility.

Another possibility is that the residual organic products coming from dye breaking interfere in new dyeing as they can physically fix to the fiber what may hinder their chemically fixation. It is also thought that the new species and/or radicals, product of dye degradation, could react with dyes added in the new process. A further study is required to evaluate the type of interference.

However, with respect to the dye degradation extent, it was observed that in general this is not an influential factor in DE values, therefore the removal of color from the wastewater is enough. However, the formation of species and/or radicals during the electrochemical pre-treatment that can react with the dye modifying its characteristics and properties could be further studied specially in the case of PY and PB.

As mentioned in section 3.1, DL has a greater influence in DE than DC and DH. As an example, figure 7 shows the contribution of DL, DC and DH values in DE for RB5.

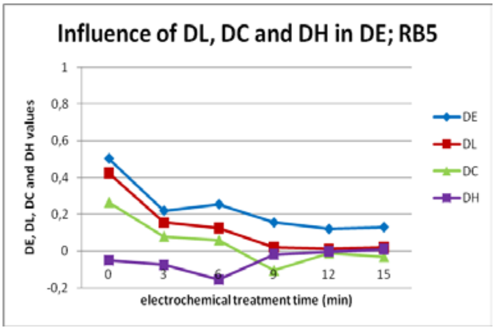

Figure 7. DE, DL, DC and DH values evolution versus electrochemical treatment duration for RB5.

From this figure, it is possible to state that DE and DL parameters present very similar and almost parallel tendency. The rest of parameters that influence in DE, DC and DH, have lower values and for instance in the case of DH also different tendency than DE. When electrochemical pre-treatment is short, DH has a very low influence in DE but increases its influence for longer treatments.

4. Conclusions

Form the obtained results, it can be concluded that 70% of water and salts can be reused by DBR in most reactive dyes studied in this work providing acceptable DE values.

In general, the application of an electrochemical pre-treatment before the reuse of the wastewater, improved the results of dyeing, as it reduces DE values of fabrics dyed with reused water with respect to the references.

In the case of PC, RB5 and PN, the DBR can be applied directly without electrochemical pre-treatment as DE values are below 1 respect to the standard. However, electrochemical pre-treatment reduces DE values around 50% after only 3 minutes and up to 75% after 15 minutes.

For PY dye, results show that DBR can also be applied without electrochemical pre-treatment but contrary than before, only 3 minutes of electrochemical treatment improves DE results and longer electrochemical treatments leads to non-acceptable DE values respect to the reference. It also can be observed that DE tendency is to increase with time, and this phenomenon can be attributed either to the great influence of chlorinated water in the dyeing process and/or to the formation of new radical species as previously discussed.

Finally, bath reuse can only be applied to PB after short electrochemical pre-treatment, 3 minutes, for the rest of times DE values are greater than 1. In this case, there is no a clear tendency of values so further investigations should be done.

In all cases, DL is the most influent parameter in DE values.

With respect to the influence of a further dye degradation in the wastewater, it was observed that it is not an important parameter in DBR for the most studied dyes.

Acknowlegdements

The authors thank Ariadna Sáez for her help in the experimental work of this study and the Spanish Ministry of Science and Innovation (MICINN) for its financial support (projects CTM2004-05774-CO2-01/TECNO and CTM2007-66570-C02-01/TECNO).

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Chapter 8

Patent: NaClO encapsulation

Chapter 8. NaClO encapsulation

The work presented in this chapter was performed during a staying (March 2008 – August 2008) at the Max Planck Institute of Colloids and Interfaces, Golm, (Berlin) under the supervision of Dr. Tauer, responsible of the heterophase polymerization research group of the Colloid Chemistry Department.

No detailed conditions for the preparation of NaClO core capsules can be given in this thesis as this work is currently under patent process by the Universitat Politècnica de Catalunya. Spanish patent register number: P201000011.

8.1 Introduction and aims

Several technologies are applied nowadays to remove colour of wastewater. Some of them are very efficient, but they all have any inconvenient. For this reason, researchers are searching alternatives in new technologies.

Among the used technologies, oxidation techniques such as electrochemical treatments are one of the most important [8.1 - 8.4]. Oxidation processes can take place either on the electrode surface, known as direct oxidation, or due to the action of oxidizing molecules formed in the anode, known as indirect oxidation. Indirect oxidation is more effective than direct oxidation [8.5]. One of the most common specie used in indirect oxidation is hypochlorite [8.6] due to its high oxidation potential, $E^o = 1{,}48$ V.

When chloride oxidation products are used for the treatment of wastewater, they can react with the organic matter leading to the possible formation of halogenated organic compounds [8.7]. In order to minimize the possible formation of these compounds, in this thesis (chapter 4) the application of indirect oxidation and later UV exposure is studied. Other authors propose the simultaneous use of both techniques [8.8 – 8.11]. This combination also reaches higher colour removal than indirect oxidation treatment alone [8.12].

This work proposes a new approach to overcome this problem through the use of NaClO microcapsules. The microencapsulation of NaClO water solutions and the application of these microcapsules to the coloured wastewater are studied.

NaClO is stable in aqueous solutions but its decomposition into chlorine and other byproducts is speeded up by heat (above 40ºC) and under light influence. The objectives of this study are the encapsulation of NaClO aqueous solution as well as to study their use to remove colour of dyes solutions by controlling the chlorine release from NaClO core capsules by using UV light irradiation.

The NaClO decomposition into chlorine increases the internal pressure of the capsule leading to its breakage and allowing the release of its content. To accomplish this purpose, NaClO must be encapsulated in capsules that meet the following conditions: controlled release of its content, stable on storage under normal conditions, UV transparent and non permeable to gases.

Industries such as pharmacy and food have been using microencapsulation for the last years in many applications [8.13 – 8.17]. In this regard, textile industry has already started to incorporate the use of microencapsulated materials both in fabrics [8.18 – 8.20] and in wastewater treatment [8.21, 8.22]. This last application is still very scarce.

8.2 Material and methods

8.2.1 Materials

NaClO 5% chlorine solution (Acros Organics), diethylenetriamine and terephthaoyl dichloride monomers (Acros Organics) were used as such. Methylcyanoacrylate, 1-buthylcyanoacrylate, β-methoxyethylcyanoacrylate and ethylcyanocrylate were kindly supplied by Henkel. Span 80 (Acros Organics) was used as surfactant. Solvents were analytical grade: benzene (Sigma-Aldrich), xylene (Acros Organics), n-hexane (Sigma-Aldrich), miglyol (Sasol), n-hexadecane (Acros Organics), acetone (Roth), ethanol (J.T.Baker) and methanol (Merck).

8.2.2 Preparation of capsules

Two methods were tested to achieve the encapsulation of NaClO aqueous solution. The first method, condensation method, relays on the basis of the polymer formed by the reaction between diethylenetriamine and terephthaoyl dichloride monomers. The second method, interfacial polymerization, is based on the rapid polymerization catalyzed by reaction between cyanoacrylate and traces of OH^- from water.

Condensation method

In this method, an aqueous phase (distilled water) containing NaClO 5% chlorine solution and diethylenetriamine was emulsified in an oil phase (benzene/xylene 2:1) containing span 80. Once the emulsion was stabilized, terephthaloyl dichloride dissolved in oil phase was added. The solution was maintained under slow stirring while the reaction between monomers proceeded. The capsules were separated by decantation and repeatedly washed with distilled water.

The following parameters were studied:

- Surfactant concentration in oil phase: between 0% and 10%.
- Diethylenetriamine concentration in oil phase: between 5% and 50%.
- Ratio between monomers: dietilenetriamine / terephthaloyl dichloride between 10 and 30.
- Ratio between water phase and oil phase: between 1/10 and 1/30.
- Speed of stirring: 600 rpm and 1200 rpm.

Interfacial polymerization method

Preparation of empty capsules (water core capsules)

Water phase (distilled water) was emulsified in an oil phase containing span 80 under vigorous stirring using an ultraturrax followed by the addition of cyanoacrylate under slow stirring. Resuspension of capsules in aqueous medium was achieved by centrifugation to separate capsules from the oil phase and re-dispersion of the capsules in water under sonication.

Parameters studied:

- Cyanoacrylate: methylcyanoacrylate, 1-buthylcyanoacrylate, ethylcyanocrylate and β-methoxyethylcyanoacrylate.
- Surfactant concentration in oil phase: between 0% and 10%.

- Oil phase solvent: miglyol, n-hexadecane and paraffin.
- Ratio between water phase and oil phase: between 1/10 and 1/20.
- Presence of ethanol in the water phase.
- Speed of the cyanoacrylate addition.
- Speed of stirring: 600 rpm and 1200 rpm.

Preparation of NaClO core capsules

Capsules containing NaClO aqueous solution core were prepared following the same methodology than water core capsules but in this case, the water phase was NaClO 5% chlorine solution.

8.2.3 Equipment and methods

Digital, TEM and SEM images

Digital microscope images were taken at the Max Planck Institute using a Keyence VHX-100K equipment. SEM (Scanning Electron Microscope) and TEM (Transmission Electron Microscopy) images were kindly provided by the Max Planck Institute.

SEM/EDS measurements

The SEM/EDS (Scanning Electron Microscope with X-ray microanalysis) were performed at the Departament de Ciència dels Materials of the UPC using a JEOL JSM 6400 equipment. Results were the mean of three replicates.

Samples were prepared as follows: a dried non-conducting sample was mounted on a cupper layer and introduced into a vacuum chamber. Sample must be less than 2 cm in diameter.

Particle diameter and Zeta Potential Measurements

Capsule diameter and the zeta potential were determined after dilution in bidistilled water (Millipore) using a Zetasizer Nano Series (Malvern) equipment at the Institut d'Investigació Tèxtil i Cooperació Industrial de Terrassa, INTEXTER. Results were the mean of three replicates.

Sodium content analyses

Sodium content analyses were performed by the Serveis Cientificotècnics Unit of the Universitat de Barcelona.

Decolourization experiments

25 mL of 0,1 g L^{-1} of C.I. Reactive Black 5 (DyStar) dye solution were treated with NaClO core capsules under UV light irradiation.

The dye solution, which contained the capsules formed from 0,2 mL of NaClO 5% chlorine solution, was irradiated with an UV light fluorescent 6W UV (Vilber Lourmat) with a maximum emission spectra centred at 254 nm. The experiments were performed under stirring.

Decolourization of the solution was calculated from the initial dye concentration and dye concentration at time t (c_i and c_t respectively) by measuring the absorbance at the visible maximum dye absorption wavelength (583 nm). Measurements were carried out every 60 min.

Decolourization (D) was reported in %:

$$D\ (\%) = \frac{(c_i - c_t)}{c_i}\ x\ 100 \qquad (1)$$

Absorbance measurements were carried out with an UV-vis spectrophotometer (Shimadzu UV-2401 PC). Dye absorbance has a linear behaviour versus the concentration in the range between 0,001 and 0,02 g L^{-1} according to the equation 2:

$$\text{Abs} = 30{,}858c - 0{,}002 \quad (R^2 = 0{,}9999). \qquad (2)$$

8.3 Results

8.3.1 Condensation method

The digital images obtained for the experiments carried out following this method showed no capsules formation under any tried condition.

The conditions selected in this method for the polymerization reaction between the two monomers were obtained from the bibliography [8.23] and therefore were assumed to be effective.

These conditions were used for the encapsulation of the NaClO solution, but no satisfactory results were obtained. One possible explanation to this fact is the presence of NaClO in the reaction medium. NaClO is a strong oxidizing agent able to oxidize one or both monomers involved in the polymerization reaction preventing it to take place.

At this point, the polymerization reaction conditions were verified but no capsules were formed even in the absence of NaClO. Because of this, another capsule preparation method was tried.

8.3.2 Interfacial polymerization method

This method relies on the basis of the rapid polymerization reaction of cyanoacrylate (generally acrylic resin) initiated by hydroxide ions from water.

From the results and considerations of the condensation method, the work conditions to obtain empty capsules (water core capsules) using this method were initially determined. The obtained conditions were then applied and adjusted to encapsulate a NaClO 5% chlorine aqueous solution.

This section is structured in two parts: a) determination of the conditions for the formation of capsules and b) characterization of the capsules.

a) Determination of the conditions for the formation of capsules

The methodology used to determine the most proper conditions for the formation of capsules was the following:

- Selection of the cyanoacrylate

Four cyanoacrylates were tested under other fixed conditions for the formation of capsules. These experiments were conducted using toluene as an oil phase and distilled water as a water phase. Figure 8.1 shows the results of the experiments.

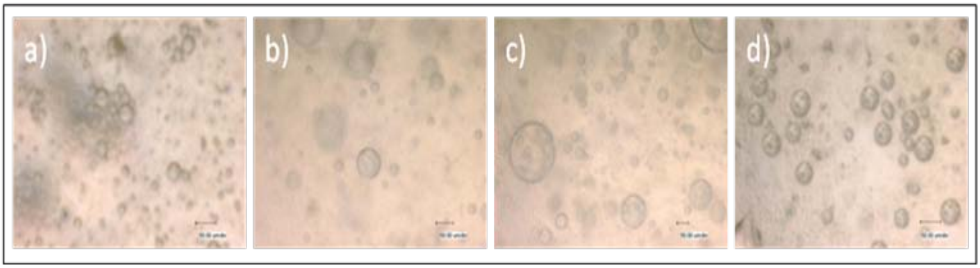


Figure 8.1 Influence of the cyanoacrylate used in the formation of water core capsules using toluene as an oil phase and distilled water as a water phase. Span 80 was used as surfactant. Cyanoacrylates: a) Methylcyanoacrylate; b) 1-buthylcyanoacrylate; c) Ethylcyanoacrylate and d) β-methoxyethylcyanoacrylate.

The four cyanoacrylates provided good results for the formation of capsules as can be seen in Figure 8.1. However, the β-methoxyethylcyanoacrylate leads to less formation of undesired polymer, what is useful for the later separation of capsules from the reaction medium.

- Surfactant concentration

Once determined the proper cyanoacrylate, the influence of the surfactant concentration in the oil phase was evaluated. For this purpose, several concentrations of surfactant were tested. The rest of conditions were the same for all experiments.

In figure 8.2 can be seen the results for 0% and 1% of surfactant concentration in the oil phase.

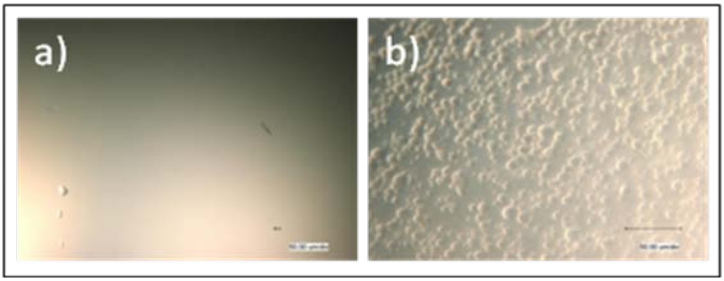


Figure 8.2 Influence of the surfactant concentration in the formation of water core capsules. Images: a) surfactant concentration in oil phase 0%; b) surfactant concentration in oil phase 1%.

From the figure, it can be concluded that the addition of surfactant is necessary for the formation of capsules.

- Selection of the oil phase solvent

Three organic solvents were tested under the same other conditions to determine the most appropriate solvent for the formation of capsules. In figure 8.3 are shown the results.

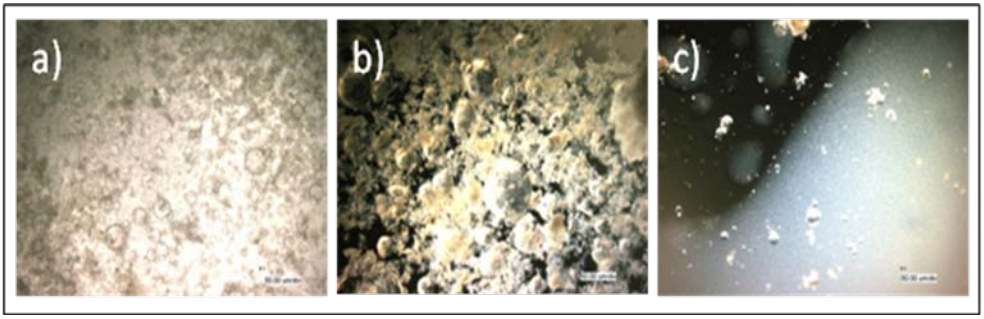


Figure 8.3 Influence of the organic solvent of the oil phase in the formation of water core capsules. Solvents: a) miglyol, b) n-hexadecane and c) paraffin.

From the images, it can be concluded that best results for the formation of capsules were obtained for miglyol and n-hexadecane. A part from this, it must be considered that when n-hexadecane was used, samples were clearer than the obtained for miglyol, which facilities the extraction of the capsules from the reaction medium. Scarce capsules were formed when using paraffin.

- Rest of parameters

Besides these three parameters, four other parameters were also tested. The presence of ethanol in the water phase was the only one that showed significant differences against the absence of it in the water phase. The rest of parameters: ratio between water phase and oil phase, speed of the addition of the cyanoacrylate and the speed of stirring after emulsification did not affect significantly the formation of capsules.

To sum up, the best results for the formation of capsules by interfacial polymerization method were obtained when a water phase containing ethanol was emulsified in n-hexadecane oil phase, using span 80 as a surfactant and β-methoxyethylcyanoacrylate as cyanoacrylate.

b) Characterization of the capsules

In order to characterize the capsules, SEM and TEM images were taken as well as determined their diameter and zeta potential. Besides this, it also should be verified that NaClO is contained inside the capsules.

In figures 8.4 and 8.5 it can be seen the SEM and TEM images of the NaClO core capsules.

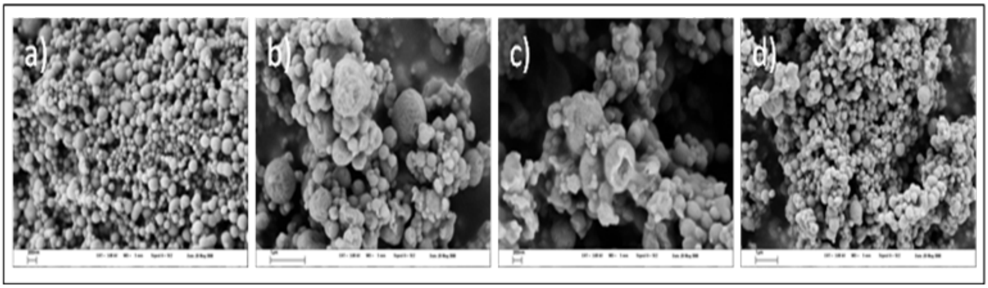


Figure 8.4 SEM images of the NaClO core capsules obtained by the interfacial polymerization method.

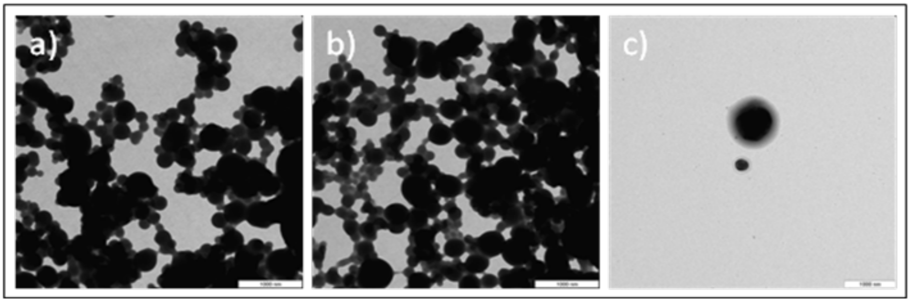


Figure 8.5 TEM images of the NaClO capsules obtained by the interfacial polymerization method.

From the SEM images it can be seen that capsules were satisfactorily formed under the selected conditions. In TEM images, differences in the black intensity can be appreciated. The contrast is due to the absortion of electrons in the material, and can be attributed to different thickness and/or composition of the analyzed material. Therefore, in this case, it could be an indication of the presence of NaClO in the capsule.

8.3.3 SEM/EDS measurements

EDS provide quantitative analyzes of the elemental composition with a sampling depth of 1-2 microns. However, the X-ray detection limit is aprox. 0.1% in weight depending on the element.

The determination of chlorine was performed. Three different samples were analyzed: water core capsules, NaClO core capsules and crushed NaClO core capsules. The obtained X-ray spectra are shown in figure 8.6.

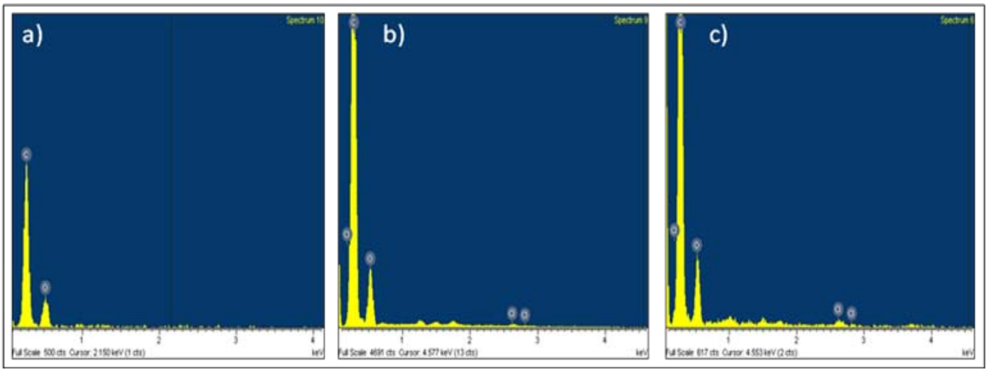


Figure 8.6 X-ray spectra of: a) water core capsules, b) NaClO core capsules and c) crushed NaClO core capsules.

The results showed that chlorine was not detected in the water core capsules while the two NaClO core capsules samples had chlorine presence. This can indicate the possible encapsulation of NaClO.

The analyzes of the NaClO core capsules and the crushed NaClO core capsules showed more superficial chlorine content in the crushed NaClO core capsules. The 0.5% of chlorine weight content for the crushed NaClO core capsules and the 0.14% chlorine weight content for the NaClO core capsules were obtained. Although the chlorine weight percentages results were near of the detection limit of the technique, these results can be understood as a promising indication that NaClO was inside the capsule and not in the shell.

8.3.4 Particle diameter and Zeta Potential Measurements

The size of the capsule plays a crucial role in drug release. It was found that a linear relationship between the degradation rate of the polymer and particle size existed, with the larger particles degrading fastest. In smaller particles degradation products formed within the particle can diffuse easily to the surface while in larger particles degradation products have a longer path to the surface of the particle during which autocatalytic degradation of the remaining polymer material can occur [8.24].

The significance of zeta potential is that its value can be related to the stability of colloidal dispersions.

These parameters were determined both for empty capsules (water core capsules) and NaClO core capsules after one month of their preparation. The evolution in time of these parameters could not be determined. Values obtained are indicated in table 8.1.

Table 8.1 Diameter (nm) and Zeta potential (mV) values of the capsules prepared by the interfacial polymerization method.

Sample	**Parameter**	
	Diameter (nm)	**Zeta potential (mV)**
Water core capsules	272	- 3,06
NaClO core capsules	249	- 26,0

From the capsule diameter results, it can be concluded that capsules were in the range of microcapsules and that after one month from their preparation the NaClO core capsules were more stable than the water core capsules. Moreover, NaClO core capsules were still near of the moderate stability limit (± 30 mV).

8.3.5 Sodium content determination

The sodium content of the water core capsules and the NaClO core capsules was determined. The first sample was used as a reference for the sodium content. The second sample was 5 mL of water containing the capsules formed with 0,2 mL of NaClO 5% chlorine solution. Results are shown in table 8.2.

Table 8.2 Sodium content (ppm) in water core capsules and NaClO core capsules.

Sample	Na concentration (ppm)
Water core capsules (reference)	19,2
NaClO core capsules	95,7

It can be observed that the sodium content in NaClO core capsules was five times higher than in the water core capsules. From these results, it can be said that there are promising indications of the NaClO encapsulation.

8.3.6 Decolourization experiments

Azo dyes contain one or more azo bonds (-N=N-), combined with aromatic carbons, which are the main responsible of the dye colour. These bonds can be oxidized by the action of an oxidant agent such as NaClO.

In these experiments, the NaClO core capsules formed from 0,2 mL of NaClO 5% chlorine solution were added to a dye solution. Experiments were run under UV light exposure, which increases the action of the NaClO but do not degrade reactive dyes, as they are UV light resistant [8.25].

In figure 8.7 are shown the absorbance spectra of the dye solution. Two different data are plotted: the dye solution before the treatment and after NaClO core capsules addition followed by 5 hours of UV light exposure.

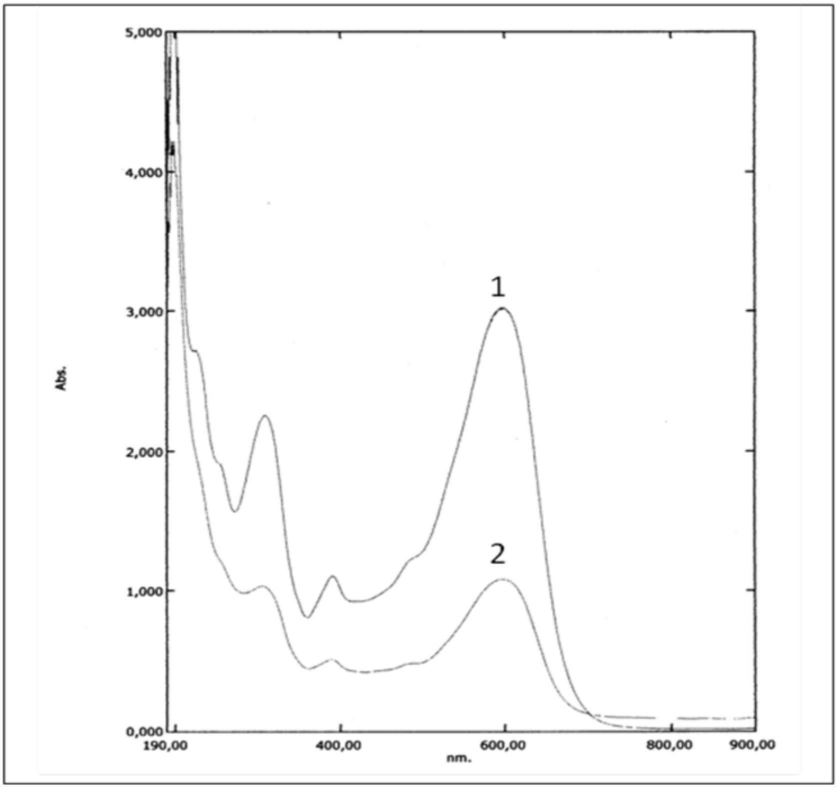
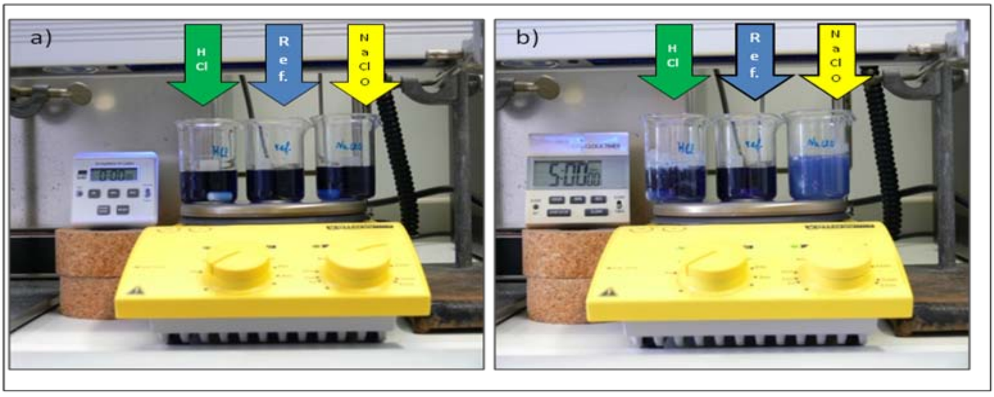


Figure 8.7 Evolution of the decolourization of C. I. Reactive Black 5 (0,1 g/L) after NaClO capsules addition and UV light irradiation (254 nm, 6 W). Curves: (1): before NaClO capsules addition, (2) 5 hours of UV exposition after the NaClO capsules addition.

From the spectra, it can be clearly observed that after the NaClO core capsules addition and 5 hours of UV light exposure, the absorbance decreased dramatically, both in the maximum of absorbance of the dye (583 nm) and in the region of 300 nm. The decrease in the maximum at 583 nm indicates that the azo bond of the dye was broken. The decrease in the region of 300 nm, which corresponds to the aromatic rings of the dye, indicates that the dye structure was partially degraded.

The decolourization at the end of the experiment (5h) reached the 61,5 %.

The following figure (figure 8.8) shows two photos taken during the decolourization experiment. In the images it can be seen the reference, a dye solution, and the NaClO core capsules decolourization experiment; both at t = 0 h of UV light irradiation and at t = 5 h of UV light irradiation respectively. It also can be seen a third glass, named HCl, which corresponds to an experiment not included in the thesis as it did not provided satisfactory results.



Where Ref. indicates de reference, NaClO indicates the NaClO experiment and HCl indicates an HCl experiment.

Figure 8.8 Evolution of the decolourization of C. I. Reactive Black 5 solution (0,1 g/L) after NaClO core capsules addition and later UV light irradiation (254 nm, 6 W). Images: a) before NaClO core capsules addition, b) 5 hours of UV after the NaClO core capsules addition and c) HCl experiment (no included in the thesis).

These images show the high decolourization degree (more than 60%) of the dye solution obtained after the addition of the NaClO core capsules and subsequent UV light irradiation.

Despite the previous results, it must be considered that further investigations have to be performed particularly for the capsules formation method, their characterization and also for the resulting effluents after been treated with NaClO core capsules.

Regarding the capsules formation and characterization, it should be optimized the obtaining method and calculated its yield of encapsulation as well as determined the capsules stability in time. The rate and conditions of their content release should be also explored in more detail.

Regarding the treated effluents, some parameters must be determined mainly to establish the increase of the organic matter in the effluent due to the shell of capsules. Among them, the most important are: Chemical Oxygen Demand (C. O. D.), Biological Oxygen Demand (B. O. D.) and turbidity.

Another important consideration is to perform a decolourization experiment of the C.I. Reactive Black 5 dye solution with water core capsules to evaluate the influence of the polymer in the decolourization experiments. This is necessary as a reference value.

Most of these experiments and determinations could not be performed, as the establishment of the conditions for the obtaining of capsules represented the main part of this chapter, for this reason they are proposed for future investigations. From the results obtained in these investigations, it could be determined the feasibility of this method to treat specific wastewater, for instance those which have to be treated under controlled reagent delivery.

8.4 Patent abstract

As mentioned at the beginning of the chapter, this work is part of a Spanish patent. In this thesis only the abstract of the patent is included and its translation to English.

Resumen: Procedimiento para la obtención de nanocápsulas de hipoclorito mediante polimerización interfacial entre un monómero que contiene un éster de metilo o de etilo y grupos hidróxido presentes en el medio de reacción. Se parte de una fase acuosa que contiene hipoclorito emulsionada en una fase lipídica constituida por un compuesto alquílico lineal y estabilizada por un tensioactivo con valor de HLB entre 4-8.

Nanocápsulas obtenidas por dicho procedimiento con paredes poliméricas que comprenden un núcleo que contiene una solución acuosa de hipoclorito.

Abstract: Process for the obtention of hypochlorite nanocapsules by interfacial polymerization between monomer containing methyl esther or methyl ethyl and hydroxide present in the reaction medium. A water phase containing hypochlorite is emulsified in an oil phase constituted by compuesto alquilico lineal stabilized by a HLB 4-8 surfactant.

Nanocapsules obtained by the above method having polymeric walls with a water phase core containing hypochlorite.

8.5 Conclusions

The main conclusions of this chapter are:

- Results show promising indications that the encapsulation of NaClO aqueous solutions was achieved by the polymerization method.
- Due to the novelty and difficulty of the obtaining NaClO core capsules, the method conditions are now under patent process.
- The condensation method was discarded for the obtaining of NaClO core capsules. The trials carried out did not show evidences of their formation.
- The best results for the formation of capsules by the interfacial polymerization method were obtained when a water phase containing ethanol was emulsified in n-hexadecane oil phase using span 80 as a surfactant and β-methoxyethylcyanoacrylate as cyanoacrylate.
- The colour of C.I. Reactive Black 5 dye solutions was removed in a 61,5% after the application of NaClO core capsules followed by 5h of UV light exposure under the studied conditions.
- The possibility of controlling the dosage of reagents, as microencapsulation does, is expected to provide new ways for the treatment of particular wastewater.
- Further studies must be done to optimize the preparation method of the NaClO core capsules. Capsules must be also further characterized as well as determined their stability and release rate in time.

- To evaluate the effectiveness of this method for the treatment of wastewater, analytical parameters of the treated effluent must be considered. Among them: biodegradability of the capsules shell, Chemical Oxygen Demand (C. O. D.), Biological Oxygen Demand (B. O. D.), turbidity, etc.

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Chapter 9

General discussion

Chapter 9. General discussion

In this thesis various techniques to decolourize and to reuse reactive dye effluents in new dyeing processes are studied. These dyes are widely used nowadays in the industry due to their good dyeing properties. However, their effluents are characterized by strong colour and difficulty to be biodegraded.

To carry out the study, six reactive dyes, most of them with azo chromophore group were selected: C.I. Reactive Orange 4, C.I. Reactive Black 5, Procion Crimson H-EXL, Procion Navy H-EXL, Procion Yellow H-EXL and Procion Blue H-EXL. These dyes are characterized by a double monochlorotriazine reactive group except C.I. Reactive Black 5, which has two sulfatoethylsulfone reactive groups and C.I. Reactive Orange 4 which has only one dichlorotriazine reactive group. Synthetic effluents of these dyes in their hydrolyzed form were prepared in order to simulate industrial effluents.

To remove colour, the following techniques were evaluated: electrochemical, UV irradiation, coagulation-flocculation, nanofiltration and ozonation.

Electrochemical treatments were performed in an electrochemical cell constituted by Ti/Pt oxide electrodes. UV irradiation treatments were carried out after conducting an electrochemical treatment of effluents. The tested UV lamps allowed two different UV irradiation positions, over the dye solution and submerged into it.

It was found that the application of UV irradiation to the effluents previously submitted to electrochemical treatment is more advantageous, in terms of decolourization and degradation, than the electrochemical treatment alone. The combination of these two techniques allows to perform the electrochemical treatment at a lower current density. It was also observed that the best decolourization results were obtained when 254 nm maximum emission spectra UV lamps were submerged into the solution.

The chloride effluent concentration was studied to evaluate its influence in the effectiveness in the combined treatment. It was concluded that a chloride concentration in the order of 200 ppm, similar to the net water chloride concentration, provided about the 90% of decolourization for the treated effluents. These decolourizations values are enough when the treated effluents are mixed with the rest of industrial effluents prior to a biological treatment. The low chloride concentration needed to reach good decolourization results also minimizes the possible formation of organic halogenated compounds during the electrochemical treatment.

Only four organic halogenated compounds were detected after the electrochemical treatment (among the 25 organic halogenated compounds analyzed following the gas chromatography-mass spectrometry method established in this thesis). The concentrations of the halogenated compounds formed were in the range of ppb except the chloroform whose concentration ranged ppm, been always lower than 2 ppm. In all cases, the UV irradiation assisted the removal of these compounds. Chloroform removal reached the 75% due to the UV action.

The possible formation of aromatic amines was also studied. These compounds can be formed due to the reduction of the azo bond (-N=N-) of the dyes during the electrochemical treatment. A gas chromatography-mass spectrometry method was also established to determine their concentration. This method allows the identification and quantification of the 24 aromatic amines listed in the EN 14362 standard. It was shown that some dyes contained very low concentrations of aromatic amines in their commercial form. It was also found that these amines concentration decreased due to the electrochemical treatment and also due to the UV irradiation. In all cases, the total amine concentration was much lower than the stated by the EN 14362 standard.

Besides the combination of electrochemical treatment-UV irradiation, other decolourization techniques were studied in this thesis, among them: nanofiltration, coagulation-flocculation and their combination.

On one side, the nanofiltration treatments reached only the 40-80% of decolourization for the studied dyes under the selected conditions. On the other side, the influence of the parameters involved in the coagulation-flocculation treatments was studied. The resin concentration was found to be the most influential parameter for this combination of techniques. The decolourization achieved by this technique ranged the 85% and 95% for the majority of dyes using a polyamine resin.

In order to improve the results obtained for each separate technique, the application of coagulation-flocculation treatment prior to nanofiltration was proposed. Over 98% of decolourization was achieved by the combined treatment for the majority of studied dyes. In addition, to improve the decolourization of the effluents, the combined treatment permits to use lower resin concentration in the coagulation-flocculation step, what implies minor sludge formation.

The effluents decolourization by means of ozonation was also studied. After five hours of exposure, Procion Blue H-EXL and C. I. Reactive Black 5 reached over 95% of decolourization but lower values were achieved for the rest of dyes. Although the ozone treatment applied was not as intense as electrochemical, it is useful to compare their respective decolourization kinetics constants: dyes had similar decolourization tendencies for both techniques.

Among all the studied techniques, the most common to decolourize textile effluents in industry is the coagulation-flocculation because its simplicity and low cost. Other common treatments are the adsorption of dyes with powdered activated carbon.

Also membrane filtration is becoming more popular. All these techniques provide good decolourization results but produce high amounts of sludge. In addition, membrane techniques have the inconvenient of fouling. The use of ozonation is also a good alternative but its use is not very extended, mainly due to its high cost.

In this thesis, the electrochemical treatments have been proved to be one of the best options to decolourize textile effluents since they do not produce sludge and the addition of chemicals is not necessary to obtain high colour removals. However, the intensity of the treatment must be carefully controlled to avoid the production of halogenated compounds. For this reason, the best option is the combination of the electrochemical technique with UV irradiation, which improves the decolourization degree and also minimizes the organic halogenated compounds generation.

Although the electrochemical treatment alone or combined with UV could be used to obtain complete organic matter degradation, this implies a very high energy consumption. For this reason, the electrochemical treatments are proposed as a previous step to biological degradation of reactive dye effluents and as a prior step to dyebath reuse.

Regarding the effluent reuse, the influence of an electrochemical pre-treatment before reuse was studied. The results show that the electrochemical pre-treatment prior to the effluents reuse minimizes the colour differences DE (CMC(2:1)) between the reused water dyed fabrics and the reference fabrics. It was concluded that it is possible to reuse, for new dyeing processes, the total residual dyebath which corresponds to the 70% of water and electrolyte of the initial dye bath electrolyte.

Finally, in this thesis the encapsulataion of NaClO aqueous solutions was studied. The application of the obtained capsules to the previous effluents was proposed as an alternative new decolourization method. A 60% of decolourization for C. I. Reactive Black 5 was achieved after applying NaClO capsules under UV irradiation. These results show promising indication of the effectiveness of the method.

Chapter 10

Conclusions

Chapter 10. Conclusions

From the consecution of the objectives and the results obtained in this thesis, the main conclusions are:

- ✓ The application of UV light irradiation after an electrochemical treatment improves the yield of colour removal and COD removal of the reactive dye effluents. The optimum conditions to apply UV irradiation to the dye solutions are with a UV lamp, with maximum emission spectra centred at 254 nm, submerged into the solution. The use of UV irradiation after the electrochemical treatment allows to perform it at lower current densities with respect the electrochemical treatment alone to obtain the same decolourization.

- ✓ The application of UV irradiation after an electrochemical treatment at only 6 mA/cm^2 provide satisfactory results of colour removal for all the studied dyes (C.I. Reactive Black 5 and Navy, Yellow and Blue Procion H-EXL) except for Procion Crimson H-EXL. For this dye, higher current densities improve significantly the final colour removal.

- ✓ A small amount of Cl$^-$ ion is recommended in order to obtain an effective combination of electrochemical treatment and UV exposure. The optimum was found to be between 0,25 and 0,5 g L^{-1} of NaCl. In this range, aproximately the order of the net water Cl$^-$ content, decolourization kinetic constants values (k_d) are much greater than expected and a 95% of colour removal can be reached in short times of exposure.

- ✓ Radical hydroxyl mechanism is assumed for the decolourization and degradation of dye solutions for the UV irradiation after electrochemical treatment. However, other species as free chlorine and radical species such as $Cl^{\bullet}$, $Cl_2^{\bullet -}$, $HClO^-$ play also a very important and necessary role to the process to proceed efficiently.

✓ No aromatic amines are found to be generated during the treatment. Some of these compounds were detected in the untreated dyes solutions. They were removed during the electrochemical. The extent of their removal depends on the current density applied in the electrochemical treatment. A further UV irradiation of the treated dye effluents is also effective to decrease the aromatic amines concentration.

✓ During the electrochemical treatment some halogenated compounds can be formed due to the chloride reactions. At low current densities, mainly ppb levels of four halogenated compounds: dichloromethane, chloroform, trichloroethylene and bromodichloromethane were detected after the electrochemical treatment. Their formation extent was found to be dependent on the Cl^- concentration and their concentrations were dramatically reduced when the Cl^- concentration decreased. The UV irradiation showed a chloroform destruction up to a 75%.

✓ The best COD removals of the dye solutions were obtained after an electrochemical treatment at 40 mA/cm^2. However, lower current densities are sufficient in order to remove colour and to obtain biodegradable compounds able to undergo a biological treatment.

✓ The combination of nanofiltration and coagulation-floculation techniques provide almost 100% of dye removal for Crimson, Navy, Yellow and Blue Procion H-EXL, and 90% for C. I. Reactive Black 5. These results improve the obtained for each technique separately. Moreover, this combination of techniques permit to reduce the resin concentration used in the coagulation-flocculation step what implies less sludge formation.

- ✓ In the coagulation-floculation treatment, the resin is the most influential reagent in dye removal. The choice of the proper resin is critical to obtain satisfactory dye removal results, as in the case of C. I. Reactive Black 5. Other reagents such as cogualant, floculant and alkali agent do not substantially affect the results. At the proper experimental conditions for each dye, removals up to 97% and 95% are obtained for Blue and Crimson Procion H-EXL respectively, 88% for Procion Navy H-EXL and 80% for C. I. Reactive Black 5 and Procion Yellow H-EXL.

- ✓ The nanofiltration treatment provides 83% of colour removal for Procion Blue H-EXL, the 71% for C. I. Reactive Black 5, the 54% and 52% for Yellow and Crimson Procion respectively and the 39% for Procion Navy H-EXL at the studied conditions.

- ✓ The ozone treatment reaches over 95% of decolourization for Procion Blue H-EXL and for C.I. Reactive Black 5 under the studied conditions. Similar tendencies of dye decolourization are obtained for ozonation and for the electrochemical UV combined treatment as show form the calculation and comparison of their respective decolouization kinetic constants.

- ✓ An electrochemical pre-treatment of the dyebath effluents prior to their reuse for new dyeing processes, improves the dyeing results respect to direct reuse. The reuse of dyebath effluents also implies the reuse of salts.

- ✓ The application of an electrochemical pre-treatment reduces the colour difference DE (CMC (2:1)) from 50% after 3 min of electrochemical treatment to 75% after 15 min of electrochemical treatment for C. I. Reactive Black 5, Procion Crimson H-EXL and Procion Navy H-EXL between the reference dyeing and the reused water dyeing respect to direct bath reuse.

- ✓ Direct bath reuse is possible for Procion Yellow H-EXL but the application of only 3 min of electrochemical pre-treatment significantly reduces DE (CMC (2:1)) between the reference dyeing and the reused water dyeing; longer electrochemical pre-treatments increase DE (CMC (2:1)) values over 1. Procion Blue H-EXL dye bath effluents can only be reused after an electrochemical pre-treatment of 3 min.

- ✓ Most of the studied dyes show clear tendencies in time with respect to the electrochemical treatment. Three of them: C. I. Reactive Black 5, Procion Crimson H-EXL and Procion Navy H-EXL tend to reduce colour differences of the reused water dyeing respect to the reference dyeing for longer electrochemical treatments. Procion and Yellow H-EXL, presents the minimum colour difference after 3 min of electrochemical treatment and tends to increase its colour difference with electrochemical treatment exposure. Procion Blue H-EXL does not show a clear tendency in time with respect to the electrochemical treatment.

- ✓ Colour coordinates (L, h, C) and colour differences (DE, DL, DH, DC) were determined for the five studied dyes. These differences were compared between replicates and between the obtained after each electrochemical treatment and the references. It was concluded that DL is the most influential parameter in DE.

- ✓ The All-in dyeing method provide better results than the isothermic method for the dye bath reuse process in terms of colour intensity of the dyed fabrics. In this sense, NaOH is also a better dyeing alkali than the mixture of NaOH and Na_2CO_3.

- ✓ The degradation degree of the organic matter present in the dye bath effluents is not an influential parameter in DBR for most of the studied dyes.

- ✓ Results show promising indications of the encapsulation of NaClO aqueous solutions by the polymerization method. The best results for the formation of capsules by the interfacial polymerization method were obtained when a water phase containing ethanol was emulsified in n-hexadecane oil phase using span 80 as a surfactant and β-methoxyethylcyanoacrylate as cyanoacrilate.

- ✓ The condensation method was discarded for the obtaining of NaClO core capsules as the trials carried out did not show evidences of capsules formation.

- ✓ The colour of C.I. Reactive Black 5 dye solutions was removed in a 61,5% after the application of NaClO core capsules followed by 5h of UV light exposure under the studied conditions.

- ✓ The method conditions to obtain NaClO core capsules are under patent process by the Universitat Politècnica de Catalunya.

- ✓ Further studies must be done to optimize the preparation method of the NaClO core capsules. Capsules must be also further characterized as well as determined their stability and drug release rate in time.

- ✓ The effectiveness of the application of capsules for the treatment of wastewater must be evaluated. In this sense, some analytical parameters of the treated effluent must be considered. Among them: biodegradability of the capsules shell, Chemical Oxygen Demand (C. O. D.), Biological Oxygen Demand (B. O. D.), turbidity, etc.

- ✓ Chromatographic methods for the separation, identification and quantification of aromatic amines and halogenated organic compounds were satisfactorily established.

✓ A gas chromatography mass spectrometry analytic method was established to separate, identify and quantify 25 organic halogenated compounds. The method conditions are:

- GC: - Column program T: initial 40ºC (10 min), increasing gradient rate 5ºC min^{-1}, final 225ºC (10 min)
  - Column: TRB-5MS
  - Injection T: 230 ºC
  - Carrier gas: He
  - Injection mode: Split 1/20

- MS: - Ion source T: 200ºC
  - Interface T: 250ºC
  - Mass range acquired: 40 m/z 350 /z

Identification of the compounds was performed using Nist 147, Nist 27 and Wiley 229 as reference libraries. p-bromofluorobenzene was selected as internal standard for the quantification of organic halogenated compounds.

✓ A gas chromatography mass spectrometry analytic method was established to separate, identify and quantify 24 aromatic amines (EN 14362). The method conditions are:

- GC: - Column program T: initial 120ºC (2 min), increasing gradient rate 5ºC min^{-1}, final 300ºC (2 min),
  - Column: DB-35 MS
  - Injection T: 260ºC
  - Carrier gas: He
  - Injection mode: Splitless

- MS: - Ion source T: 200ºC
  - Interface T: 260ºC
  - Mass range acquired: 40 m/z 350 /z

Identification of the compounds was performed using Nist 147, Nist 27 and Wiley 229 as reference libraries. 2,4,5-tricloroanilina was selected as internal standard for the quantification of the aromatic amines.

✓ The liquid-liquid extraction method for the aromatic amines provided similar or better results than the diatomaceous earth column proposed by the EN 14362 standard. The liquid-liquid extraction method is also faster and easier to use.

Chapter 11

Recommendations

Chapter 11. Recommendations

A thesis work is finite; therefore, besides the presentation of results, it is also necessary to propose new research areas.

In this sense, the main proposals of this thesis are:

- To extend the current reuse study of dye mixtures, mainly dichromies and trichromies.
- To search for new electrodic materials in order to improve the current processes and to obtain further decolourization and degradation of the treated effluents.
- To study the simultaneous application of the electrochemical and UV treatments; photoelectrochemistry.
- To extend the current study to other chemical constitution dyes, such as anthraquinone or phthalocyanine.
- To extend the current study to different dye groups, such as sulfur, vat, disperse, etc.
- To evaluate new applications of the electrochemical treatments: industrial wastewaters from the pharmaceutical, food, paint or other sectors.
- Application of the electrochemical techniques to industrial effluents. These effluents are more complex than synthetic ones as they contain, among others, traces of surfactants and fibres.

- Combination of nanofiltration and electrochemical treatments. Study of the electrochemical treatment applied to concentrated effluents resulting from the nanofiltration.

- To assess the influence of UV irradiation in ozone treatments.

- To optimize the NaClO microcapsules obtaining method.

- To extend the characterization of the NaClO microcapsules.

- To evaluate the application of NaClO microcapsules for the treatment of textile effluents.

- New applications of NaClO microcapsules.

- To study of the dye degradation mechanism in the electrochemical treatment by means of GCMS and HPLC.

Annex I

Thesis references

Annex I. Thesis references

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