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TRATAMIENTO Y REUTILIZACIÓN DE EFLUENTES DE LA INDUSTRIA TEXTIL MEDIANTE TÉCNICAS DE MEMBRANAS

Memoria presentada por

Valentina Buscio Olivera

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“Mucha gente pequeña,

en lugares pequeños,

haciendo cosas pequeñas,

pueden cambiar el mundo”.

Eduardo Galeano

RESUMEN

La industria textil consume grandes cantidades de agua en sus procesos, principalmente en las operaciones de tintura y acabado. En general, durante el proceso de tintura, hasta un 30% del colorante utilizado puede ser vertido en las aguas residuales. Por esta razón, las aguas residuales generadas por esta industria se caracterizan por presentar una fuerte coloración.

Diferentes tratamientos, como procesos biológicos o físico-químicos, han sido usados para tratar este tipo de aguas residuales. Sin embargo, ninguno de estos tratamientos permite la degradación del colorante, siendo necesario un post-tratamiento. Por ello, en los últimos años, se ha incrementado el interés por la tecnología de membranas en la eliminación de los colorantes.

En este trabajo, se ha estudiado la viabilidad de los procesos de membranas para el tratamiento de efluentes textiles que contenían colorantes residuales. Además, también se evaluó la posibilidad de reutilizar los colorantes recuperados y/o el efluente tratado en nuevos procesos de tintura. Para llevar a cabo este objetivo, se seleccionaron dos clases de colorantes: tina, representados por el colorante índigo, y los dispersos.

Los colorantes tina son uno de los más utilizados en la industria textil, especialmente el colorante índigo el cual se usa en la industria del denim. Una de las principales ventajas de este colorante es su baja solubilidad en agua cuando se encuentra en su forma oxidada, lo que facilita su separación mediante membranas. Antes del estudio de recuperación del colorante índigo, fue necesario desarrollar y validar métodos analíticos para su determinación en los baños residuales. Aunque los tres métodos estudiados permitieron su cuantificación, el método basado en la valoración redox fue seleccionado como el más adecuado para la determinación de índigo en baños de tintura. Con respecto al tratamiento con membranas, efluentes industriales que contenían colorante índigo fueron tratados mediante membranas de ultrafiltración de PVDF a escala de laboratorio y semi-industrial. El tratamiento permitió recuperar el índigo y concentrarlo hasta 20 g·L^{-1}, pudiendo ser reutilizado en nuevos procesos de

tintura. Las tinturas llevadas a cabo con el 100% del colorante recuperado mostraron similares características que las tinturas con colorante comercial.

Los colorantes dispersos fueron seleccionados debido a que se utilizan en la tintura de fibras de poliéster, la cual es la más consumida a nivel mundial. En primer lugar, los efluentes que contenían colorantes dispersos fueron tratados con membranas de ultrafiltración de PVDF, consiguiéndose hasta un 90% de DQO y un 96% de disminución en la concentración del colorante. El 100% del permeado obtenido se reutilizó en nuevas tinturas sin observarse diferencias de color significativas con respecto a las tinturas de referencia llevadas a cabo con agua descalcificada. Posteriormente, efluentes suministrados por una empresa especializada en la tintura de fibras de poliéster, fueron tratados mediante la combinación de un proceso de homogenización-decantación y dos membranas de ultrafiltración de PVDF, a escala de laboratorio y semi-industrial. Al final de ambos tratamientos, se obtuvo una eliminación de DQO del 66% y una reducción del color del 30%. El 100% del permeado obtenido pudo ser reutilizado en el caso de monocromías, mientras que el 50% fue reutilizado en tinturas con tricromías. Finalmente, se evaluó la degradación de los colorantes dispersos con un sistema hibrido formado por un procesos fotocatalítico y una membrana de microfiltración de polisulfona. El tratamiento fotocatalítico se optimizó obteniéndose una eliminación del colorante entre el 60% y el 90%, y una eliminación de DQO entre el 70% el 98%. La membrana permitió separar las partículas de TiO_2, consiguiéndose un permeado de alta calidad.

ABSTRACT

Textile industry consumes large amount of water in their processes, mainly in dyeing and finishing operations. In general, during the dyeing process, up to 30% of dyes used can be discharged into wastewater. For this reason, the wastewater generated by this industry is characterized by high colouration.

Different treatments such as biological or physico-chemical processes have been used to treat this kind of wastewater. Nonetheless, these treatments do not degrade dyes and, in general, a post-treatment is required. In recent years, the interest for the application of membranes technologies to the removal of dyes has increased significantly.

In this work, the feasibility to treat textile effluents containing residual dyes by means of membrane processes has been studied. In addition, the reuse of recovered dyes and/or treated water in new dyeing processes has been also tested. With this propose, two classes of dyes were selected: vat, represented by indigo, and disperse dyes.

Vat dyes are one of the most popular dyes in the textile industry, especially indigo dye which is used in the denim industry. Its main advantage is the low solubility in water when is into its oxidized form, being easily separated by means of membranes. Before the membrane study, it was necessary to develop and validate analytical methods for indigo dye determination in dye baths. Although the three studied methods were able to quantify the indigo dye, the redox titration was selected as the most suitable for the measurement of indigo dye concentration in dye baths. Regarding the membrane treatment, industrial effluents that contained indigo dye were treated by means of different PVDF ultrafiltration membranes at laboratory and semi-industrial scale. The membrane treatment enabled to remove and recover indigo dye from wastewater. Moreover, the concentrates containing 20 $g \cdot L^{-1}$ of indigo dye were able to be reused in new dyeing processes. Fabrics dyed with 100% of recovered indigo exhibited similar characteristics than the ones obtained with the commercial dye.

Disperse dyes were selected because they are used for dyeing of polyester which is the most consumed fibre in the world. First of all, synthetic effluents containing disperse dyes were treated by a PVDF ultrafiltration membrane. About 90% and 96%

COD decrease and dye removal were achieved, respectively. The 100% of the obtained permeate was reused in new dyeings and no significant colour differences were observed between reference fabrics and the ones dyed with the permeate. Subsequently, textile effluents supplied by a polyester mill were treated by coupling a homogenization-decantation treatment with two PVDF ultrafiltration membranes at both laboratory and semi-industrial scale. At the end of treatments, the COD removal was 66% and colour reduction was 30%. Regarding the permate study, 100% permeate could be reused in the case of monochromies whereas 50% permeate was reused for trichromies. Finally, a hybrid treatment based on the combination of polysulphone membrane microfiltration and heterogeneous photocatalytic process was evaluated to degrade disperse dyes. The photocatalytic treatment was optimized and provided 60-90% dye degradation and COD removal from 70% to 98%. The membrane treatment enabled to separate the TiO_2 particles and provided very high quality permeates.

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Nomenclatura

ΔP: Presión transmembrana

A: Área de la membrana

AOP: Procesos de oxidación avanzada

C_0: Concentración inicial de contaminante

Cf: Concentración de contaminante en el alimento

Cp: Concentración de contaminante en el permeado

C: Concentración de contaminante

CA: Acetato de celulosa

COV_s: Compuestos orgánicos volátiles

CN: Nitrato de celulosa

CTA: Triacetato de celulosa

DBO/BOD: Demanda biológica de oxígeno

$DE_{cmc(l:c)}$: Diferencias de color

DQO/COD: Demanda química de oxígeno

J: Flujo volumétrico

k: constante de reacción

Lp: Permeabilidad

λ: Longitud de onda

LoD: Límite de detección

LoQ: Límite de cuantificación

MF: Microfiltración

NF: Nanofiltración

NMP: 1-Metil-2-pirrolidona

OI/RO: Osmosis Inversa

PA: Poliamida

PAN: Poliacrilonitirlo

PC: Policarbonato

PE: Polietileno

PEA: Polieteramida

PES: Poliestersulfona

PP: Polipropileno

PPO: Óxido de polifenileno

PS: Polisulfona

PTFE: Politetrafluoroetileno

PVA: Polialcoholvinilico

PVC: Cloruro de polivinilo

PVDF: Fluoruro de polivinilideno

pzc: Punto isoeléctrico

RFM: Reactores fotocatalíticos de membrana

RSD$_r$: Repetitividad

RSD$_R$: Reproducibilidad

SS: Sólidos en suspensión

UF: Ultrafiltración

UV: Ultravioleta

CAPÍTULO 1:

Introducción

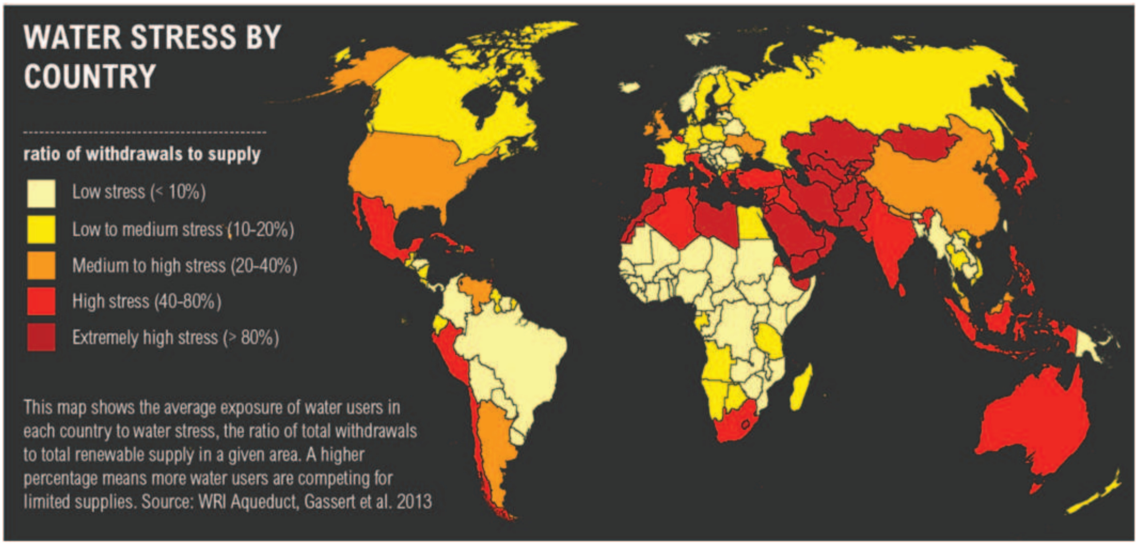
INTRODUCCIÓN

1.1- Situación global del agua

Uno de los mayores problemas del siglo XXI es la calidad y la gestión del agua. Aunque el agua es el elemento más abundante en la Tierra, el agua dulce, y por lo tanto apta para el consumo humano, sólo representa el 3% del total. Aproximadamente el 68,9% del agua dulce se encuentra en los glaciares o en los casquetes polares y el 29,9% es agua subterránea. Por lo que el ser humano solo tiene acceso al 0,3% del agua dulce presente en la Tierra [1.1].

Según el tercer informe sobre el desarrollo de los recursos hídricos en el mundo (WWDR3) presentado por las Naciones Unidas en 2009 [1.2], la población mundial está creciendo a un ritmo de 80 millones de personas al año, lo que implica un aumento de la demanda de agua dulce de aproximadamente 64 mil millones de m^3 anuales. Además, se prevé que en 2030 el 47% de la población mundial viva en zonas con estrés hídrico.

La escasez de agua se mide a través de la relación agua/población. Se considera que una zona presenta estrés hídrico cuando su suministro anual de agua cae por debajo de los 1700 m^3 por persona. Por debajo de los 1000 m^3 se habla de escasez de agua, y de escasez absoluta cuando el suministro menor a 500 m^3 [1.3]. La Figura 1.1 muestra las zonas con mayor estrés hídrico [1.4].



This map shows the average exposure of water users in each country to water stress, the ratio of total withdrawals to total renewable supply in a given area. A higher percentage means more water users are competing for limited supplies. Source: WRI Aqueduct, Gassert et al. 2013

Figura 1.1- Indicador de estrés hídrico global, 2013. (Fuente: World Resource Institute)

Los niveles de estrés hídrico más altos se encuentran en la zona del Mediterráneo, el este China, India y en la zona suroeste de Estados Unidos. Sin embargo, es necesario destacar que el bajo estrés hídrico no implica tener acceso al agua. El estrés hídrico se calcula en función de la disponibilidad de agua, mientras que el índice de escasez de agua tiene en cuenta también la posibilidad de acceder a la misma. Por ejemplo, existen regiones en África Central o el suroeste de Asia que presentan medio o bajo estrés hídrico, pero experimentan escasez de agua debido a limitaciones económicas o, en muchos casos, institucionales [1.3].

1.1.1- Usos del agua

El sector agrícola es el mayor consumidor de agua a nivel mundial con un 69%, seguido por la industria (19%) y el uso doméstico con un 12% [1.5] (Figura 1.2).

Sin embargo, la distribución del consumo de agua entre los diferentes sectores suele variar en función del nivel de desarrollo de cada región. Así, los países en vías de desarrollo presentan un consumo más elevado en el sector agrícola mientras que en los países desarrollados aumenta el consumo en el sector industrial [1.3]. Esto se puede observar en la Figura 1.2, donde África y Asia tienen un consumo superior al 80% en el sector agrícola mientras que Europa muestra un mayor consumo de agua en el sector industrial (57%).

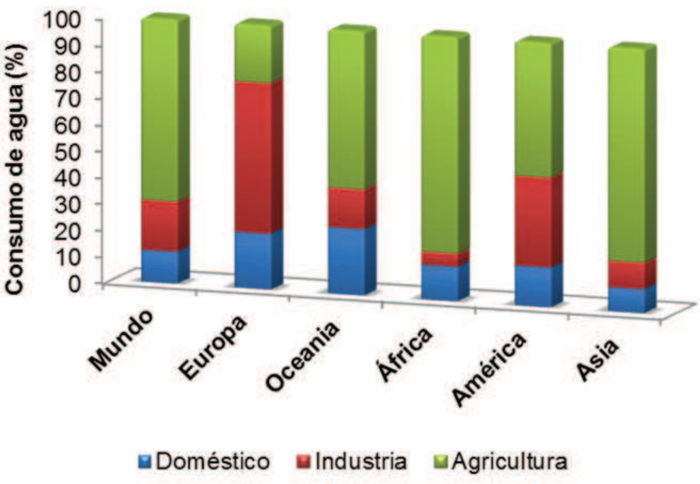


Figura 1.2- Consumo de agua mundial por sectores, 2007. (Fuente: Aquastat)

En cuanto a España y Cataluña, los datos se muestran en la Figura 1.3 [1.6, 1.7]. Se puede observar como no se sigue la tendencia de Europa, siendo la actividad agrícola la que más agua consume (superior al 70%), seguida por el doméstico (20%) y finalmente el industrial (10%).

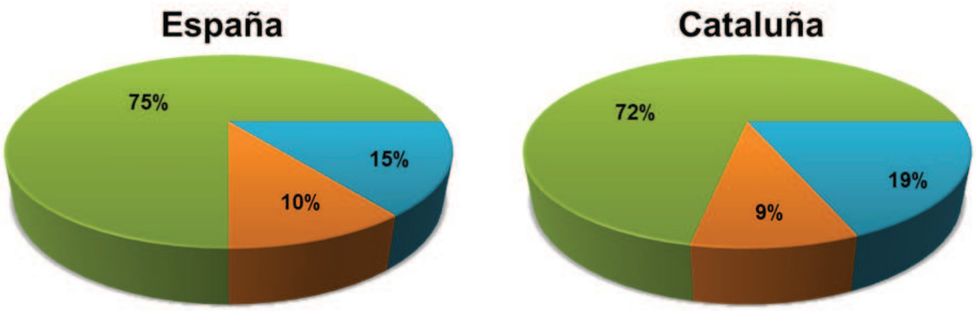


Figura 1.3- Consumo de agua por sectores, España 2005. (Fuente: INE), Cataluña 2008 (Fuente ACA)

El agua en la industria se utiliza principalmente para enfriar, generar vapor, como materia prima o como parte del producto final (especialmente en la industria alimentaria).

El consumo de agua varía en función del tipo de industria. En relación a España, los últimos datos encontrados sobre la distribución del consumo de agua en los diferentes sectores industriales son del 2004 [1.6] y se representan en la Figura 1.4.

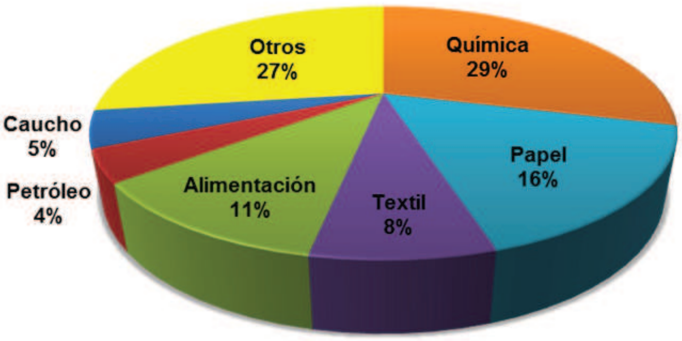


Figura 1.4- Distribución del consumo de agua en España por sectores industriales, 2004. (Fuente: INE)

Se observa que el textil es el cuarto sector en consumo de agua, sólo superado por la industria química, papelera y alimentaria. En la industria textil, el 73% del agua es utilizada en el proceso (preparación, tintura y acabados) y el 27% restante se utiliza en las operaciones de refrigeración, calderas, limpieza, etc. [1.8].

1.2- Problemática de la industria textil

La caracterización de la contaminación producida por la industria textil es compleja debido a la gran variedad de fibras y métodos de producción utilizados [1.9]. Los diferentes procesos llevados a cabo en la industria textil generan una gran cantidad de residuos, que se pueden clasificar en gaseosos, líquidos y sólidos. Algunos de los contaminantes más comunes se presentan en la Tabla 1.1 [1.10].

Tabla 1.1- Contaminación de la industria textil. (Fuente: Ghaly et al., 2014)

Proceso	Emisión	Aguas residuales	Residuos
Desencolado	COV_s procedentes de esteres de glicol	DBO elevada, biocidas	Envases, fibras, residuos de hilos, material de mantenimiento
Desengrasado	COV_s procedentes de esteres de glicol y disolventes	Desinfectantes, insecticidas, NaOH, detergentes, lubricantes y disolventes	-
Blanqueo	-	H_2O_2, estabilizantes, pH alto	-
Mercerizado	-	pH alto, NaOH	-
Tintura	COV_s	Metales, sales, tensioactivos, productos auxiliares, colorantes, DBO, DQO, disolventes, ácidos/álcalis	-
Acabado	COV_s, vapores de formaldehído, gases de combustión	DQO, sólidos en suspensión, disolventes	-

La industria textil presenta dos grandes problemas: su elevado consumo de agua y la complejidad y variabilidad de sus aguas residuales [1.11-1.13].

1.2.1- Principales características de los efluentes textiles

Las principales características de los efluentes textiles dependen principalmente del proceso y la maquinaria utilizada por la empresa [1.14]. Los efluentes contienen subproductos, colorantes residuales, sales, ácidos/álcali, productos auxiliares y disolventes [1.15]. En la Tabla 1.2 se muestran los valores medios de los parámetros correspondientes al agua residual generada en cada etapa del proceso textil [1.16].

Tabla 1.2- Carga contaminante en los diferentes procesos textiles. (Fuente: Dasgupta et al., 2015)

Parámetro	Lavado	Blanqueo	Mercerizado	Tintura
pH	9-14	8.5-11	8-10	1.5-10
Sólidos disueltos (mg/L)	12000-30000	2500-11000	2000-2600	1500-4000
Sólidos en suspensión (mg/L)	1000-2000	200-400	600-1900	50-350
Color	-	-	Fuerte coloración	Fuerte coloración
DBO (mg/L)	2500-3500	100-500	50-120	100-400
DQO (mg/L)	10000-20000	1200-1600	250-400	400-1400
Cloruros (mg/L)	-	-	350-700	-
Sulfatos (mg/L)	-	-	100-350	-

En general, las aguas residuales procedentes de la etapa de tintura se caracterizan por su alta coloración, DBO, DQO, pH y salinidad [1.17-1.25].

1.2.2. Problemática de los colorantes en los efluentes textiles

Los colorantes son sustancias que al aplicarse a un sustrato (materiales textiles, papel, pelo, piel etc.) le proporcionan color. Se caracterizan por su capacidad de absorber la luz visible (400-700 nm), propiedad que les confiere su coloración.

Desde las tinturas con colorantes naturales (vegetales, animales o minerales) hasta las tinturas con colorantes sintéticos utilizados en la actualidad, siempre se han buscado sistemas más eficientes para dar color a las prendas. Por ello, industrialmente se utilizan más de $1 \cdot 10^5$ colorantes diferentes con una producción anual de $7 \cdot 10^5$ toneladas [1.26].

Los colorantes se pueden clasificar según su estructura química. Toda molécula de colorante tiene un grupo cromóforo, el cual es el portador del color, y grupos auxiliares conocidos como auxocromos los cuales, además de acentuar el color del grupo cromóforo, también a veces permiten la fijación del colorante al sustrato gracias a su carácter ácido o básico. Los grupos cromóforos más importantes son los azo, antraquinona, nitro, metino y arilmetano. Dentro de los auxocromos podemos encontrar el grupo amino, carboxilo, sulfónico e hidroxilo [1.27]. Los colorantes azo son los más utilizados, representando el 60% del total de colorantes producidos [1.28].

Los colorantes también se pueden clasificar según su forma de aplicación, dividiéndose principalmente en directos, dispersos, ácidos, premetalizados, básicos, catiónicos, reactivos, tina y sulfurosos.

Los colorantes directos reciben este nombre porque tiñen la fibra sin necesidad de mordiente. Son solubles en agua y su solubilidad aumenta al aumentar el número de grupos sulfónicos y también con la temperatura, y disminuye al aumentar su peso molecular. Los colorantes ácidos se utilizan para teñir sustratos que tienen grupos con carga positiva, como por ejemplo la lana la cual presenta grupos catiónicos amonio ($-NH_3^+$). Los colorantes básicos y catiónicos se usan para teñir sustratos con carga negativa, como es el caso de la seda que presenta grupos aniónicos carboxilato ($-COO^-$-). Los colorantes reactivos son los más utilizados en la tintura de las fibras de celulosa. Son aquellos que tienen de uno a tres grupos capaces de formar enlaces covalentes con la fibra, lo que los hace muy resistentes al lavado. Se utilizan principalmente para la tintura de algodón y otras fibras celulósicas, aunque también tienen aplicación en la tintura de lana, seda y poliamida. La tintura con colorantes reactivos presenta como principal inconveniente que el grupos reactivo del colorante puede reaccionar con el agua dando lugar a la forma hidrolizada del colorante, la cual no puede formar enlaces covalentes con la fibra.

Los colorantes dispersos se utilizan principalmente para la tintura del poliéster, la fibra de mayor consumo a nivel mundial. Son insolubles en agua y se aplican utilizando dispersiones coloidales de colorante. Debido a su importancia en la industria textil, han sido seleccionados para su estudio en esta tesis por lo que se describirán en detalle más adelante. Finalmente, los colorantes tina y sulfurosos son insolubles en agua por lo que deben ser utilizados en su forma leuco, es decir en su forma reducida. Uno de los colorantes tina más importantes es el colorante índigo, el cual ha sido seleccionado para su recuperación en este trabajo.

En la industria textil, entre el 1 y el 15% de los colorantes utilizados en el proceso de tintura se pierden en las aguas residuales [1.29] debido a la ineficiencia del proceso o a la baja afinidad del colorante con la fibra. Es necesario destacar el carácter tóxico y mutagénico de algunos colorantes. Además, la presencia de colorantes en el agua, aunque sea en concentraciones muy pequeñas, provoca la disminución de la penetración de luz lo que afecta gravemente a la flora y la fauna [1.27].

Debido a la importancia comercial del índigo y de los colorantes dispersos en la actual industria textil, en este trabajo se centrará en el tratamiento de estos colorantes.

En general, el tratamiento de los colorantes reactivos residuales ha sido ampliamente estudiado. Sin embargo, los estudios publicados sobre el tratamiento de colorantes dispersos y colorantes tina, especialmente el índigo, son escasos.

El **colorante índigo** es uno de los colorantes naturales más antiguos que se conoce (Figura 1.5) y a pesar de ello, es uno de los más importantes en la actualidad, aunque la mayor parte del que se utiliza hoy en día es sintético.

Figura 1.5- Antigua representación de la obtención de colorante índigo natural a partir de la indigofera tinctórea (Jean Baptiste Du Teatre, 1667).

El colorante índigo es ampliamente utilizado en la tintura de prendas tejanas o vaqueras, los cuales representan el 14% del consumo de algodón mundial. En la coloración de fibras de celulosa, el índigo representa el 7% de los colorantes utilizados a nivel mundial (Figura 1.6) [1.30].

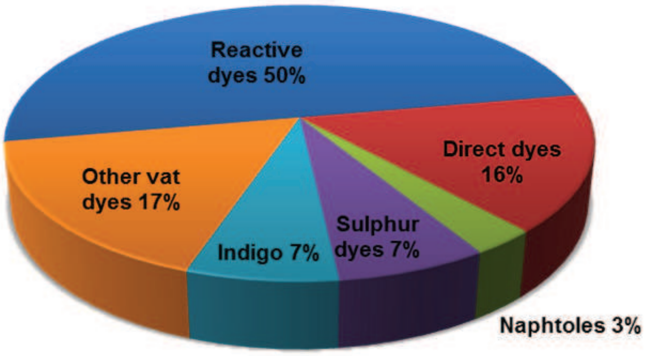


Figura 1.6- Consumo mundial de colorantes en la coloración de fibras de celulosa. (Fuente: Bozic et al., 2008)

Para proceder a la tintura con índigo, el colorante es reducido previamente a su forma leuco mediante agentes reductores, como el ditionito sódico, en medio alcalino. El tejido pasa por un baño que contiene el índigo reducido y luego es expuesto al aire. En contacto con el aire, el índigo se oxida obteniéndose el color azul. Después de la tintura es necesario un proceso de lavado para eliminar el colorante que no ha quedado fijado sobre la fibra, por lo tanto este tipo de tintura genera una gran cantidad de aguas residuales con una alta coloración. Además, las aguas residuales producidas a lo largo del proceso de tintura presenten un alto contenido de sulfatos, sulfitos, tiosulfatos y sulfuros, que son tóxicos, lo que incrementa el impacto medioambiental del proceso de tintura y en consecuencia, el coste del tratamiento de estas aguas. Por ello, en los últimos años se está investigando también la posibilidad de reducir el colorante índigo mediante técnicas electroquímicas [1.30-1.38].

Los **colorantes dispersos** son compuestos no iónicos que se utilizan para la tintura de fibras hidrofóbicas como el poliéster. El poliéster es la fibra más importante a nivel mundial, con un consumo de $38,7 \cdot 10^6$ toneladas al año [1.39].

Como se ha comentado anteriormente, los colorantes dispersos son poco solubles en agua, por lo que la tintura se lleva a cabo mediante la adición de agentes dispersantes, los cuales permiten mantener una dispersión estable de las partículas de colorante.

El proceso de tintura de la fibra de poliéster con colorantes dispersos se realiza en tres etapas [1.40]:

- Difusión de la solución o dispersión del colorante hacia la superficie de la fibra.
- Adsorción del colorante por la superficie de la fibra.
- Difusión del colorante desde la superficie hacia el interior de la fibra.

Se pueden distinguir dos métodos de tintura: tintura en presencia de un agente acelerador o transportador, o tintura a alta temperatura [1.40].

En el primer método, el transportador permite que el colorante sea adsorbido de forma más rápida por la fibra. Un proceso de tintura tipico implica calentar el baño de tintura hasta los 60ºC y añadir el agente dispersante, el carrier emulsionado y por último el colorante. El baño de tintura se lleva a ebullición y finalmente, el carrier debe ser eliminado de la fibra mediante un proceso de secado a 150-180ºC. Debido al carácter tóxico y/o carcinógeno de algunos carriers, el proceso de tintura con carriers está siendo cada vez más desplazado por la tintura a alta temperatura.

1.2.3- Tratamientos para eliminación de color de los efluentes textiles

En los últimos años se han investigado diferentes técnicas para el tratamiento de los efluentes textiles [1.41]. La mayoría de los estudios publicados se centran en la eliminación de los colorantes ya que es el proceso que conlleva mayor dificultad (Figura 1.7).

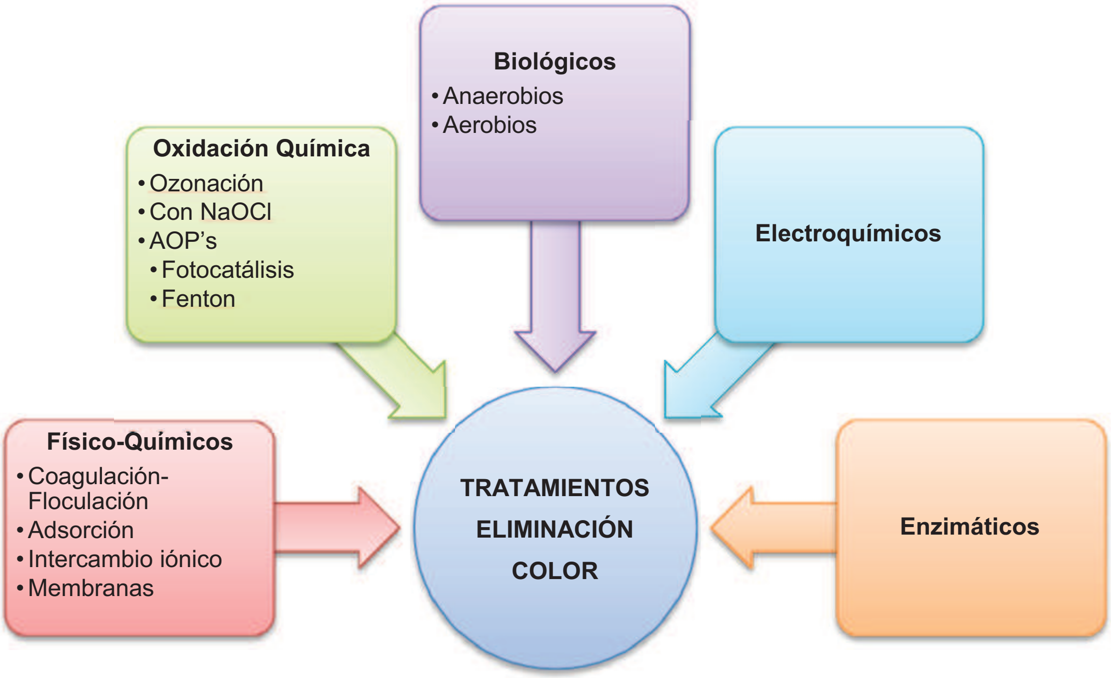


Figura 1.7- Tratamiento para la eliminación de color en las aguas residuales textiles. (Fuente: Robinson, 2001)

Los **procesos biológicos** son ampliamente aplicados en el tratamiento de las aguas residuales de las tintorerías. Son tratamientos simples y con bajo coste de operación. Muestran alta eliminación de DQO y turbidez, pero baja eficiencia en la eliminación de color debido a la estabilidad química y resistencia a los ataques microbiológicos que presentan los colorantes [1.42]. En general, en los procesos aerobios, la eliminación de color se debe principalmente a la adsorción de los colorantes en la biomasa y no a su degradación [1.43, 1.44]. Con el fin de mejorar el rendimiento de los tratamientos biológicos, los procesos anaerobios y aerobios pueden combinarse en una o más etapas [1.45-1.54].

El tratamiento de efluentes textiles mediante **técnicas electroquímicas** ha sido estudiado por diversos autores con resultados satisfactorios en cuanto a la eliminación de color [1.18, 1.55-1.62]. Sin embargo, esta técnica suele tener un coste operacional elevado [1.41].

Uno de los tratamientos emergentes para la decoloración de aguas residuales textiles son los **métodos enzimáticos**. Su principal inconveniente es que las variables del proceso deben estar muy controladas (temperatura, pH, salinidad, etc.). Además, la separación y purificación de la enzima es un proceso muy delicado [1.63].

Entre los **tratamientos físico-químicos**, la coagulación-floculación es el más utilizado ya que es muy efectivo en la eliminación de color. Esta técnica, sin embargo, genera un residuo concentrado que requiere un tratamiento adicional [1.14, 1.63]. La decoloración por adsorción (generalmente con carbón activo) está influenciada por diversos parámetros como interacciones entre el colorante y el adsorbente, área superficial del adsorbente, tamaño de partícula, etc. [1.64]. Presenta alta eficacia para una gran variedad de colorantes, pero es una técnica con un elevado coste ya que el material adsorbente debe ser regenerado después de varios tratamientos. Los tratamientos de intercambio iónico presentan también el problema de la regeneración de la resina y además no son efectivos para todos los colorantes.

En cuanto a los tratamientos físicos, los más conocidos son las técnicas de filtración que se explicarán más detalladamente en la sección 1.3.

Los **tratamientos de oxidación química** requieren de la adicción de compuestos oxidantes como ozono (O_3), peróxido de hidrógeno (H_2O_2) y permanganato (MnO_4^-). El ozono es el más utilizado debido a su alto rendimiento en la eliminación de colorantes, pero no resulta eficaz al tratar colorantes insolubles como los tina o los dispersos [1.14].

1.3- Tecnología de membrana

La tecnología de membrana es uno de los procesos de separación más importantes y más utilizados en los últimos años. A pesar de que los primeros estudios con membranas comenzaron el siglo XVIII, no fue hasta el siglo XX cuando esta técnica comenzó a despertar el interés de los investigadores [1.65]. El avance que ha experimentado la tecnología de membranas en estas últimas décadas se centra en el desarrollo de nuevos materiales para la fabricación de membranas, la modelización de sus procesos y el efecto de las diferentes variables que intervienen en el mismo.

En un proceso de membranas, la corriente de alimento queda dividida en dos: un permeado o filtrado que contiene toda aquella fracción que ha conseguido pasar por la membrana y un concentrado o rechazo que contiene las especies que no la atraviesan.

Según la dirección del flujo respecto a la membrana se pueden distinguir dos tipos de filtración: convencional y *cross-flow*. En la filtración convencional, el efluente a tratar se hace pasar perpendicularmente a la superficie de la membrana, lo que provoca un elevado ensuciamiento de la misma. Sin embargo, en la filtración de *cross-flow*, el flujo circula de forma tangencial a la superficie de la membrana. Así, al tiempo que se efectúa la filtración, se limpia la membrana (Figura 1.8).

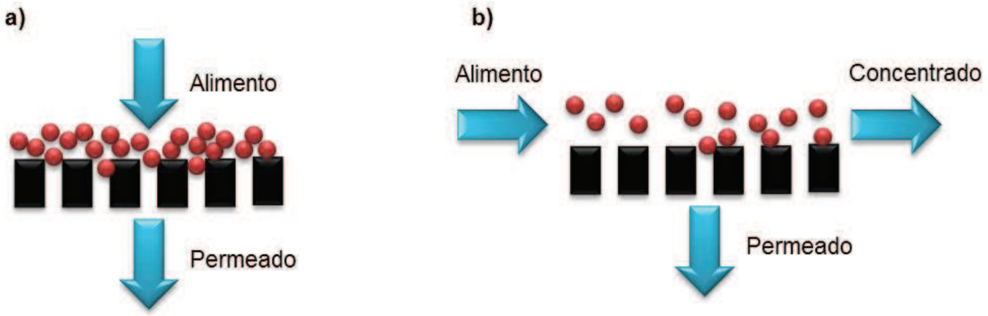


Figura 1.8- Esquema de a) filtración convencional, b) filtración cross-flow

1.3.1- Clasificación de los procesos de membrana

Los procesos de membrana se pueden clasificar según la fuerza impulsora, el mecanismo de separación, la estructura de la membrana o el tamaño de partículas que retienen (Tabla 1.3) [1.66].

Tabla 1.3- Clasificación de los procesos de membrana según la fuerza impulsora y su rango de separación (Fuente: Pandolfi, 2008)

Proceso	Fuerza impulsora	Rango de separación
Microfiltración (MF)	Gradiente de presión	10 – 0,1 µm
Ultrafiltración (UF)	Gradiente de presión	0,1 – 0,04 µm
Nanofiltración (NF)	Gradiente de presión	0,001 µm
Osmosis Inversa (OI)	Gradiente de presión	0,0001 µm
Electrodiálisis	Gradiente de potencial eléctrico	< 0,005 µm
Diálisis	Gradiente de concentración	< 0,005 µm

Hasta el momento, las membranas más estudiadas y aplicadas a nivel industrial son aquellas en la que la fuerza impulsora es el gradiente de presión (Figura 1.9).

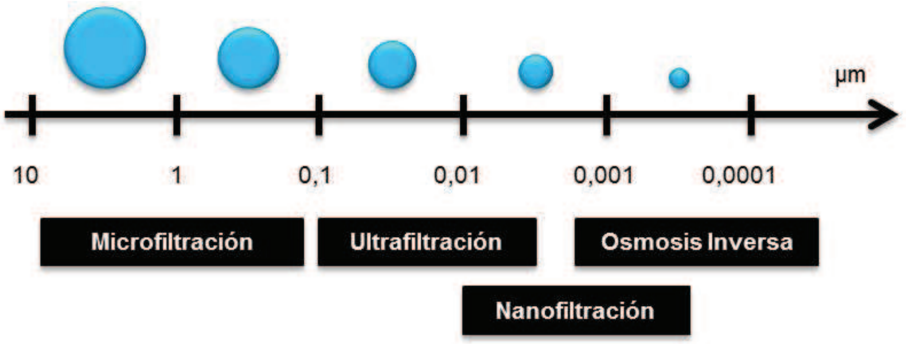


Figura 1.9- Membranas que utilizan el gradiente de presión como fuerza impulsora

1.3.2- Materiales empleados en la fabricación de membranas

Como se ha comentado anteriormente, la evolución de la tecnología de membrana se centra principalmente en el uso de diferentes materiales para su fabricación. Los materiales utilizados pueden ser de naturaleza orgánica o inorgánica.

Las **membranas orgánicas** se fabrican a base de polímeros. La Tabla 1.4 muestra los más utilizados en membranas comerciales y su rango de aplicación [1.67].

Tabla 1.4- Polímeros utilizados en la fabricación de membranas y su aplicación (Fuente: Macanás, 2006)

Polímero	Siglas	MF	UF	NF/OI
Acetato de celulosa	CA	*	*	*
Cloruro de polivinilo	PVC	*		
Fluoruro de polivinilideno	PVDF	*	*	
Nitrato de celulosa	CN		*	
Óxido de polifenileno	PPO		*	
Poliacrilonitirlo	PAN		*	
Polialcoholvinilico	PVA		*	
Poliamida	PA		*	*
Policarbonato	PC	*		
Polieteramida	PEA			*
Poliéstersulfona	PES		*	
Polietileno	PE	*		
Polipropileno	PP	*		
Polisulfona	PS		*	
Politetrafluoroetileno	PTFE	*		
Triacetato de celulosa	CTA		*	*

Las membranas de celulosa y sus derivados fueron las primeras membranas orgánicas utilizadas. A pesar de que este tipo de membranas siguen siendo fabricadas en la actualidad, su baja resistencia a los agentes químicos y a la temperatura, ha provocado su sustitución por otros polímeros con mejores prestaciones.

Las **membranas inorgánicas** son más resistentes mecánicamente, térmicamente y químicamente que las membranas orgánicas, sin embargo su aplicación a nivel industrial actualmente es limitada. Dentro de las membranas inorgánicas, las cerámicas son las más utilizadas. También se pueden encontrar membranas fabricadas a partir de vidrio, carbón o metal.

1.3.3- Configuración de los módulos de membrana

Las membranas, para su funcionamiento, se acoplan a una unidad denominada módulo. En general se pueden distinguir cuatro módulos:

El **módulo plano** es la configuración más antigua y sencilla. Se trata de una hoja o lámina semipermeable en la que el agua a tratar incide sobre un solo lado de la membrana. Su principal desventaja es su baja superficie activa, por lo que generalmente se disponen varias membranas en forma de pila o columna.

En el **enrollamiento en espiral**, varias láminas de membrana plana se enrollan separándose mediante un espaciador. Su principal ventaja es su bajo coste de operación.

En el **módulo tubular**, la membrana se dispone en forma de tubo con su capa activa en la parte interior. El permeado fluye radialmente desde el interior al exterior y el concentrado se recoge en uno de los extremos del tubo.

Finalmente, en el módulo de **fibra hueca** la capa activa de la membrana se encuentra en el exterior, por lo que el permeado fluye desde el exterior al interior y se recoge en el extremo de la fibra. Este tipo de configuración presenta ciertas ventajas respecto al resto: ocupa menor volumen, presenta más superficie activa y es más resistente.

1.3.4- Ensuciamiento de las membranas

El ensuciamiento o *fouling* es el principal inconveniente de la tecnología de membranas. Se produce cuando las partículas presentes en el efluente a tratar se depositan sobre o dentro de los poros de la membrana. La consecuencia principal del ensuciamiento es una disminución del caudal del permeado, lo que implica aumentar la frecuencia de lavados de la membrana y, en algunos casos, la sustitución de la misma.

Se pueden distinguir dos tipos de ensuciamiento. El ensuciamiento interno o irreversible es aquel en el que las partículas se depositan dentro de los poros de la membrana, y el ensuciamiento externo o reversible en el que las partículas se sitúan únicamente sobre la membrana.

Actualmente existen métodos, tanto físicos como químicos, que permiten disminuir el ensuciamiento. Dentro de los métodos físicos es necesario destacar la creación de turbulencias o el lavado a contracorriente que se efectúa con el permeado obtenido. Este método sólo puede ser utilizado en el caso de ensuciamiento externo. Los métodos químicos se basan en el lavado de la membrana con agentes químicos, lo que permite eliminar completamente el ensuciamiento, tanto interno como externo, pero puede dañar la membrana.

1.3.5- Aplicación de los procesos de membranas en el tratamiento de efluentes textiles

En los últimos años, diferentes autores han estudiado la posibilidad de aplicar esta técnica para el tratamiento de aguas residuales textiles [1.68-1.77].

El tratamiento con membranas permite obtener un permeado libre de colorantes y un concentrado que los contiene. Ambos pueden ser reutilizados en el proceso de tintura. A pesar de que la mayoría de los estudios realizados hasta el momento se centran en la reutilización del permeado, principalmente mediante membranas de nanofiltración y osmosis inversa [1.78-1.84], algunas clases de colorantes como los sulfurosos y tina, especialmente el índigo, son idóneos para ser tratados mediante esta técnica debido a que son insolubles en agua y pueden ser separados del efluente con cierta facilidad.

El tratamiento con membranas de efluentes textiles que contenían colorante índigo comenzó a estudiarse en la década de los 80. La empresa T.I.A. de Bélgica encargó un estudio sobre la recuperación de índigo mediante procesos de filtración con membranas, consiguiéndose una eficiencia de separación superior al 98% [1.85]. El principal inconveniente observado en este estudio fue la rápida colmatación de las membranas y la disminución del flujo durante la fase de concentración. En 1987, nuestro grupo de investigación realizó pruebas de recuperación de índigo. Se trabajó con membranas cerámicas, obteniéndose buenos resultados de decoloración pero sólo el 10% del colorante recuperado pudo ser reutilizado para nuevas tinturas. Sin embargo, recientemente han aparecido nuevos tipos de membranas que han permitido replantear la recuperación de este colorante.

Por otra parte, en 2008 Unlu *et al.* [1.86] estudiaron diferentes tratamientos para la eliminación de color en aguas residuales textiles que contenían índigo, llegando a la conclusión que la técnica de coagulación-floculación no resulta eficaz debido a la necesidad de añadir altas dosis de coagulante. En cambio, la microfiltración proporciona una reducción del color del 64%. Con la combinación de la microfiltración y la ultrafiltración se obtenía una reducción del color adicional del 62%. Finalmente, estudiaron la combinación de la microfiltración y la nanofiltración consiguiendo reducir el color en un 99%, lo que lleva a la conclusión que la tecnología de membranas es una técnica prometedora para el tratamiento de este tipo de aguas residuales.

Como se ha comentado anteriormente, uno de los principales problemas que presentan las membranas es su ensuciamiento ya que provoca un aumento en su coste de mantenimiento [1.87]. Con el fin de disminuir este fenómeno y de aumentar la eficiencia del tratamiento, los procesos de membrana suelen combinarse con procesos convencionales de depuración como tratamientos biológicos [1.21, 1.88-1.91] o procesos de coagulación-floculación [1.20, 1-92-1.96].

1.4- Procesos fotocatalíticos

La fotocatálisis es un proceso de oxidación avanzada (AOP's) basado en la generación de especies reactivas oxidantes, como los radicales hidroxilo ($OH^{\cdot}$), los cuales son capaces de degradar la materia orgánica en especies de menor peso molecular sin la adición de ningún reactivo químico [1.97, 1.98]. La mineralización total de la materia orgánica daría lugar a CO_2 y H_2O.

El proceso fotocatalítico comienza cuando un fotocatalizador adsorbe fotones cuya energía es igual o superior a su salto de banda. Los electrones (e^-) en la banda de valencia son promovidos a la banda de conducción, generándose un hueco (h^+). Los h^+ producidos en la superficie del fotocatalizador pueden oxidar tanto el agua como los OH^-, generando $OH^{\cdot}$ que finalmente degradarán la materia orgánica [1.97-1.103].

En la Figura 1.10 se representan los pasos principales en un proceso fotocatalítico.

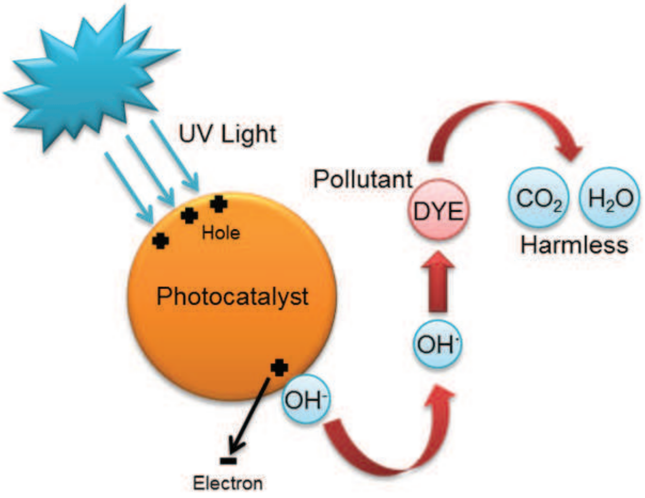


Figura 1.10- Esquema del proceso fotocatalítico

Un fotocatalizador debe tener alta actividad, resistencia térmica y mecánica, y debe ser física y químicamente estable bajo las diferentes condiciones de trabajo [1.97, 1.104]. Se han estudiado diferentes óxidos (ZnO, WO_3, V_2O_5, Fe_2O_3, etc.) y sulfuros (CdS, ZnS, etc.) como fotocatalizadores [1.105-1.107], siendo el dióxido de titanio (TiO_2) el más utilizado en los últimos años.

1.4.1- Principales factores en un proceso fotocatalítico

La velocidad de los procesos fotocatalíticos no resulta afectada por la **temperatura**, por lo que suelen llevarse a cabo a temperatura ambiente. Sin embargo, hay muchos otros factores que influyen en un proceso fotocatalítico, los cuales han sido estudiados por diversos autores. Algunos de los más importantes son: el pH, la fuente e intensidad de radiación, la concentración de fotocatalizador, la naturaleza del contaminante, la presencia de aditivos y el diseño del reactor. A continuación se describe la influencia de estos factores de forma general.

El **pH** puede afectar tanto a la superficie del fotocatalizador como a las características del contaminante a degradar. El efecto del pH sobre el fotocatalizador dependerá de su punto isoeléctrico (pzc). Por ejemplo, el pzc del TiO_2 P25 (fabricado por Degussa) es 6,5 [1.108, 1.109] comportándose de acuerdo con las reacciones 1.1 y 1.2:

- ♣ pH < pzc: $TiOH + H^+ \rightarrow TiOH_2^+$ (1.1)
- ♣ pH > pzc: $TiOH + OH^- \rightarrow TiO^- + H_2O$ (1.2)

En cuanto a la **fuente e intensidad de radiación**, se puede utilizar luz artificial o natural, pero solo el 5% del total de la luz natural irradiada tiene suficiente energía como para producir el proceso, por lo que suelen utilizarse lámparas UV [1.110, 1.111]. En la Figura 1.11 se muestra la relación entre la intensidad de radiación y la velocidad de reacción [1.111].

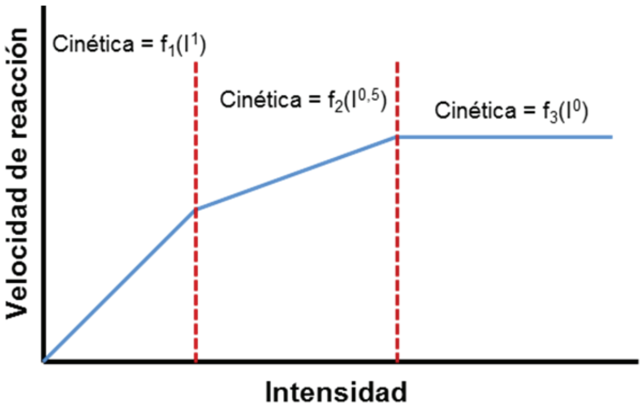


Figura 1.11- Relación entre intensidad de radiación y velocidad de reacción (Fuente: Romero et al, 1999)

Se pueden observar dos cambios de orden: el primero (de 1 a 0,5) es debido a la recombinación de e^- y h^+ lo que limita el proceso, el segundo (cambio a un orden 0) indica que el fotocatalizador no puede generar más pares aunque se aumente la intensidad [1.112].

En general, cuanto mayor sea la **concentración del fotocatalizador**, mayor será la eficiencia del proceso. Sin embargo, a concentraciones elevadas el efecto de la turbidez ocasionada por sus partículas y la aglomeración de las mismas dificultan la difusión de la luz [1.107, 1.113].

Existe también una relación entre la velocidad de reacción y la **naturaleza del contaminante**. Los subproductos generados durante su degradación pueden favorecer o perjudicar el proceso. Generalmente, la cinética de degradación de compuestos sigue la ecuación de Langmuir-Hinshelwood (ecuación 1.3) [1.107, 1.108, 1.114].

$$-\frac{dc}{dt} = \frac{k_1 K c}{1 + Kc} \qquad (1.3)$$

Después de integrar se obtiene la ecuación 1.4:

$$\ln\left(\frac{c_0}{c}\right) + K(c_0 - c) = k_1 K t \qquad (1.4)$$

Donde c_0 es la concentración inicial de contaminante, c es la concentración de contaminante a tiempo t, K es la constante de adsorción en el equilibrio y k es la constante de reacción [1.108].

Cuando la solución se encuentra muy diluida ($c<10^{-3}$ mol/cm^3), el termino Kc será <<1 y la reacción es de pseudo-primer orden (ecuación 1.5).

$$-\frac{dc}{dt} = k_1 K c = kc \qquad (1.5)$$

Después de integrar la ecuación 1.3 obtenemos las ecuaciones 1.6 y 1.7:

$$\ln c - \ln c_0 = -kt \tag{1.6}$$

$$\ln c = -kt + \ln c_0 \tag{1.7}$$

La representación gráfica de t vs $\ln c$ forma una línea recta, cuya pendiente permite conocer el valor de k.

La **presencia de aditivos** es un factor importante en el proceso fotocatalítico. Los compuestos con capacidad de aceptar electrones (O_2, H_2O_2 o S_2O_8) favorecen el proceso, ya que reducen la recombinación e^--h^+. En cambio, la presencia de otros aditivos o impurezas (Cl^-, SO_4^{2-}, PO_4^{3-}, Ca^{2+}, Mn^{2+}y Ni^{2+}) pueden competir con el sustrato por los sitios de adsorción del fotocatalizador disminuyendo su eficiencia [1.115, 1.116].

Finalmente, el **diseño del reactor** debe asegurar el contacto entre las dos fases (sólido-líquido) y debe permitir la iluminación uniforme de todas las partículas del fotocatalizador [1.107].

Los reactores fotocatalíticos se dividen en dos grupos [1.117]:

- Reactores con el fotocatalizador en suspensión
- Reactores con el fotocatalizador fijo sobre un material

En el caso de reactores con el fotocatalizador fijo sobre un material se produce una disminución en la superficie activa y por lo tanto la eficiencia del proceso es menor [1.108]. El fotocatalizador puede fijarse sobre diferentes materiales como vidrio, carbón activo o materiales poliméricos [1.104]. Cuando se utilizan reactores con el fotocatalizador en suspensión se observa un aumento en la eficiencia del proceso, pero el fotocatalizador debe ser separado del agua tratada, por lo que se requiere de una operación adicional [1.108].

1.4.2- Reactores fotocatalíticos de membrana (RFM)

El principal objetivo de combinar un proceso fotocatalítico con membranas es la separación y recuperación del fotocatalizador [1.117].

Al igual que los reactores utilizados para llevar a cabo procesos fotocatalíticos, los RFM pueden dividirse en dos grupos: reactores con el fotocatalizador en suspensión y reactores con el fotocatalizador sobre/en la membrana (membrana fotocatalítica) [1.118]. En el estudio llevado a cabo por Grzechulska *et al.* [1.119] se realizó una comparación entre los dos RFM para el tratamiento de aguas contaminadas con colorantes. Los autores observaron que la eficiencia del tratamiento era mayor al trabajar con el fotocatalizador en suspensión.

En los **RFM con membrana fotocatalítica**, la membrana actúa como soporte para el fotocatalizador y como barrera para los contaminantes presentes en la solución a tratar y los subproductos generados. En esta configuración, la reacción puede llevarse a cabo sobre la superficie de la membrana o dentro de los poros de la misma [1.120]. En la Tabla 1.5 se muestran las ventajas y desventajas de los RFM con membrana fotocatalítica [1.108].

Tabla 1.5- Ventajas y desventajas de las membrana fotocatalíticas. (Fuente: Mozia 2010)

Ventajas	Desventajas
No es necesario separar y reciclar el fotocatalizador	La eficiencia de degradación es menor que en el caso de trabajar con fotocatalizador en suspensión
No hay ensuciamiento de la membrana debido a las partículas de fotocatalizador	No se puede ajustar la dosis de fotocatalizador en función del efluente
Posibilidad de disminuir el ensuciamiento al modificar las propiedades de la membrana.	Riesgo de dañar la membrana por la acción de la luz UV o los radicales hidroxilo
	Necesidad de cambiar la membrana cuando el fotocatalizador pierde su actividad

Como se puede observar en la Tabla 1.5, uno de los principales problemas de esta técnica es el riesgo de dañar la membrana durante el tratamiento. La resistencia que presentan las membranas cerámicas hace que sean las más recomendadas para este tipo de tratamiento. Sin embargo, las membranas cerámicas son más caras que las membranas poliméricas, por lo que es importante encontrar una membrana polimérica estable bajo las condiciones de trabajo (exposición a luz UV y medio oxidante). Con esta finalidad, diferentes materiales poliméricos se han estudiado para la inmovilización del TiO_2. Por un lado Chin *et al.* [1.121] estudió el comportamiento de diez membranas bajo diferentes procesos fotocatalíticos. Los resultados mostraron que las membranas de politetrafluoroetileno (PTFE), polifluoruro de vinilideno (PVDF) y poliacritlonitrilo (PAN) presentaban mayor estabilidad. Por otro lado, Molinari *et al.* [1.101] observaron que las membranas hechas de fluoruro y polipropileno presentaban mayor estabilidad bajo luz UV.

En la **configuración con el fotocatalizador en suspensión**, la membrana permite recuperar el fotocatalizador, pero se observa una disminución del flujo del permeado debido al ensuciamiento de la membrana. Este fenómeno es especialmente importante cuando se utilizan membrana de MF, UF y NF [1.117, 1.122]. La Tabla 1.6 muestra las principales ventajas y desventajas de este proceso [1.108].

Tabla 1.6- Ventajas y desventajas de RFM con fotocatalizador en suspensión. (Fuente: Mozia 2010)

Ventajas	Desventajas
Separación y recuperación del catalizador	Ensuciamiento de la membrana debido a la presencia de fotocatalizador
Sustitución del fotocatalizador sin cambiar la membrana	Baja calidad del permeado al combinarse con membranas de MF o UF
Ajuste de la dosis de fotocatalizador en función de los efluentes a tratar	
Superior eficiencia de degradación	
Posibilidad de separar subproductos o de aplicar de altas temperaturas	
No existe el riesgo de dañar la membrana	

Se han llevado a cabo diversos estudios para la degradación de diferentes contaminantes con el fotocatalizador en suspensión, especialmente con membranas de MF [1.123-1.126] y UF [1.127-1.132]. Choo *et al*. [1.133] reportaron en sus estudios la formación de la segunda capa dinámica sobre la membrana debida a las partículas de TiO_2. Esta barrera permitía retener las partículas más pequeñas de TiO_2, aumentando de esta manera la eficiencia del proceso.

1.4.3- Aplicación de procesos fotocatalíticos en el tratamiento de efluentes textiles

Los procesos fotocatalíticos han sido estudiados para la degradación de diversos colorantes [1.115, 1.134-1.139], especialmente colorantes reactivos [1.106, 1.140-1.143], y el tratamiento de efluentes reales de tintura [1.144-1.146]. En la mayoría de los casos el tratamiento se lleva a cabo utilizando luz UV, aunque se pueden encontrar estudios en los que se emplea la luz solar [1.123, 1.147-1.149]. En este último caso no sólo se consiguen buenos resultados en cuanto a eliminación de color, sino también se obtiene un tratamiento simple y económico.

En cuanto a los reactores fotocatalíticos de membrana, también se han utilizado para la degradación de colorantes y tratamiento de efluentes textiles [1.118, 1.150-1.156]. En los últimos años las investigaciones se están centrando en la combinación de las técnicas fotocatalíticas con procesos de destilación por membrana [1.117, 1.122, 1.157-1.159]. La principal ventaja de este tipo de membranas es que durante el tratamiento, la adición de fotocatalizador no afecta el proceso y por lo tanto el flujo de permeado permanece constante. Los compuestos volátiles, los cuales pueden atravesar la membrana, se encuentran en el permeado en concentraciones muy bajas por lo que se considera que el permeado obtenido mediante este proceso tiene una calidad elevada.

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CAPÍTULO 2:

Objetivos

OBJETIVOS

Los objetivos generales de esta tesis se pueden desglosar en dos grupos bien diferenciados. En primer lugar, se ha planteado la aplicación de membranas a la depuración de aguas residuales textiles que contienen distintos tipos de colorantes, y se evalúa la eficiencia del tratamiento. Por otra parte, se estudia también la posible recuperación y reutilización del agua y/o de los colorantes en nuevos procesos de tintura.

Con el fin de desarrollar estos dos grupos de objetivos generales, se han planteado diversos objetivos específicos, los cuales varían en función del colorante presente en los efluentes estudiados. Por este motivo, se ha considerado más conveniente clasificar los objetivos específicos en base al tipo de colorante seleccionado, según se detalla a continuación:

1) Colorante índigo

    - ♣ Desarrollo y validación de métodos analíticos que permitan determinar adecuadamente la concentración de colorante índigo presente en los efluentes. Se realizará una comparación entre los distintos métodos estudiados y se seleccionará el más adecuado teniendo en cuenta los ensayos de validación, su facilidad, rapidez, coste y, sobre todo, su capacidad de adaptarse al proceso de recuperación estudiado.

    - ♣ Tratamiento de efluentes industriales que contienen colorante índigo mediante membranas de ultrafiltración, tanto con plantas piloto de laboratorio como con un sistema semi-industrial. Para este estudio se han seleccionado los efluentes procedentes del proceso de lavado posterior a la tintura.

    - ♣ Seguimiento de la evolución del tratamiento hasta obtener un baño con una concentración de colorante adecuada para su reutilización en un nuevo proceso de tintura industrial.

- ♣ Reutilización del colorante índigo en nuevas tinturas.

2) Colorantes dispersos

- ♣ Tratamiento de efluentes sintéticos que contienen colorantes dispersos mediante técnicas de membrana (ultrafiltración)
- ♣ Tratamiento de efluentes industriales (previamente sometidos a un tratamiento de homogenización-decantación) con membranas de ultrafiltración con plantas piloto de laboratorio.
- ♣ Tratamiento de los mismos efluentes industriales con un sistema semi-industrial.
- ♣ Estudio de reutilización del permeado en nuevas tinturas (monocromías y tricromías).
- ♣ Combinación de técnicas de membrana y procesos fotocatalíticos para el tratamiento de efluentes que contienen colorantes dispersos.

En base a los objetivos planteados, los resultados se han estructurado en 5 capítulos que corresponden al mismo número de artículos publicados. En primer lugar, los capítulos 4 y 5 comprenden el estudio relativo al colorante índigo. Finalmente, los resultados obtenidos en el tratamiento de efluentes con colorantes dispersos se presentan en los capítulos 6, 7 y 8.

CAPÍTULO 3:

Materiales y métodos

MATERIALES Y MÉTODOS

3.1- Colorantes y reactivos químicos

Para la realización de esta tesis se han seleccionados dos clases de colorantes: tina y dispersos. Los colorantes tina son uno las clases más populares en la industria textil, especialmente el colorante índigo. Los colorantes dispersos se utilizan principalmente en la tintura de fibras de poliéster, la más consumida a nivel mundial.

La Tabla 3.1 se muestra la descripción de los colorantes seleccionados para este estudio. En la Figura 3.1 se representa la estructura química de los colorantes registrados en el Colour Index.

Tabla 3.1- Colorantes utilizados en este estudio

Nombre comercial	**Nombre Colour Index**	**Peso molecular (g/mol)**
Brilliant Red S-RGL 200	Disperse Red 202	472,88
Índigo	Vat Blue 1	262,27
Marine Blue S-2GRL 200	Disperse Blue 79:1	625,38
Rubine RD-GFL 200	Disperse Red 73	348,36
Yellow-Brown S-2RFL 150	Disperse Orange 30	450,27
Blue E-BL 150	Disperse Blue 56	304,69
Blue RD-S	No registrado	-
Brilliant Yellow RD-E 0.5	No registrado	-
Scarlet RD-S 0.5	No registrado	-
Black BLN 200	No registrado	-

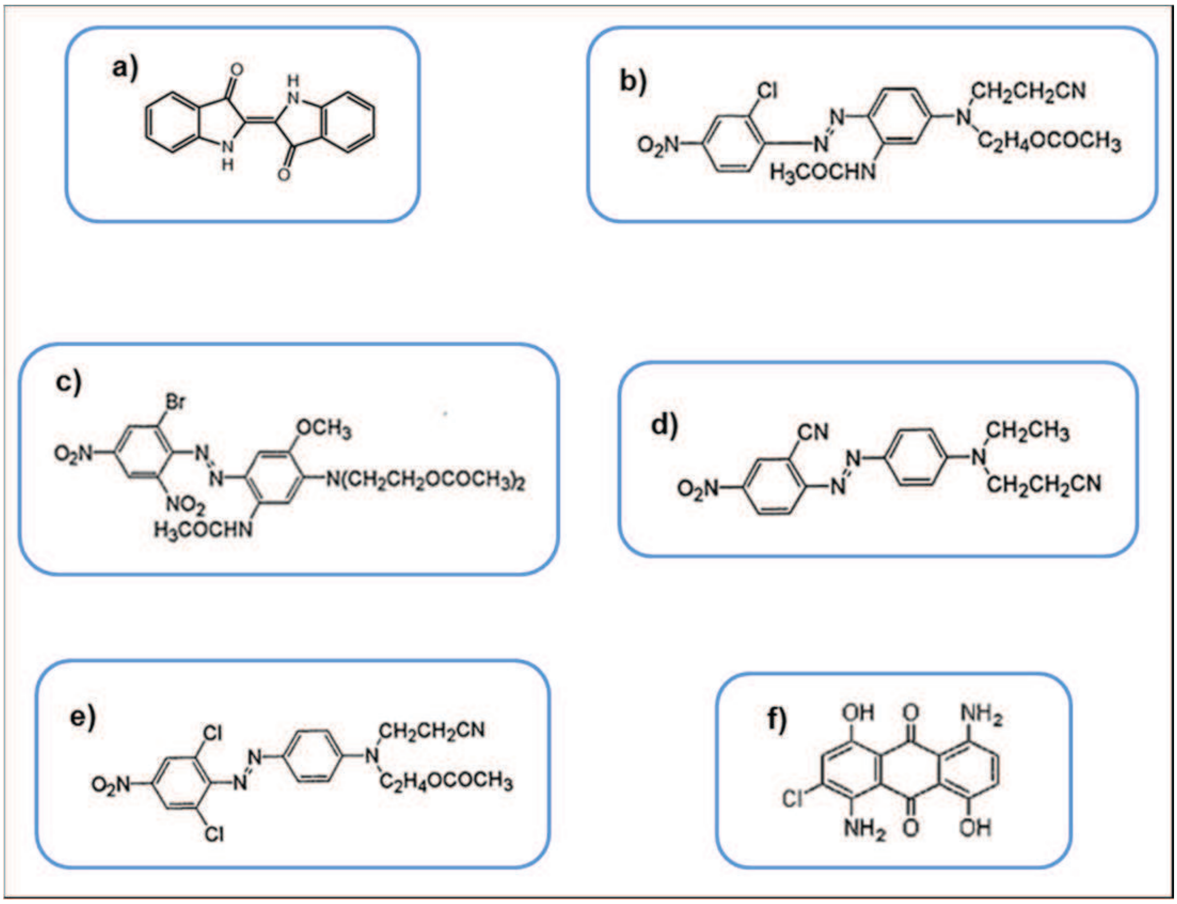

Figura 3.1- Estructura química de los colorantes: a) Indigo, b) Brilliant Red S-RGL 200, c) Marine Blue S-2GRL 200, d) Rubine RD-GFL 200, e) Yellow-Brown S-2RFL 150 y f) Blue E-BL 150

Por otra parte, en la Tabla 3.2 se detallan los reactivos químicos utilizados en el en la preparación de los efluentes sintéticos y también en el análisis de los efluentes industriales.

Tabla 3.2- Reactivos químicos utilizados en este estudio

Producto	Proveedor	Calidad	Uso
1-metil-2-pirrolidona	Scharlau	99%	Determinación de índigo
Ácido clorhídrico	Scharlau	37%	Ajuste pH
Ácido sulfúrico	Scharlau	97%	Limpieza membrana
Agua descalcificada	-	< 5,4ºf	Preparación de efluentes sintéticos y tinturas con colorantes dispersos
Agua destilada	Transpark	8,55 µS/cm	Preparación de disoluciones
Agua MILI-Q	Millipore	0,98 µS/cm	Preparación de disoluciones
Cloroformo	Scharlau	99%	Determinación de índigo
Dióxido de titanio	Sigma-Aldrich	99%	Fotocatalizador
Ditionito sódico	ACROS	85%	Reducción colorante índigo
EDTA	Panreac	99%	Determinación dureza
Fenolftaleina	Panreac	99%	Determinación alcalinidad
Ferroina	Scharlau	Análisis	Determinación DQO
Hexacianoferrato potásico	Panreac	99%	Determinación de índigo
Hidróxido sódico	Scharlau	98,5%	Ajuste pH y reducción índigo
Hipoclorito sódico	Sigma-Aldrich	6-14% cloro activo	Limpieza y conservación membranas
Kits spectroquant®	Merck	-	Determinación DQO
N-N,Dimetilformamida	Scharlau y Merck	99%	Determinación colorantes dispersos
Negro de eriocromo T	Panreac	Análisis	Determinación dureza
Patrón aniones	Fluka	Cromatografía	Determinación cloruros y sulfatos
Nitrógeno	Air Liquide	-	Determinación de índigo
Sal de Mohr	Scharlau	Análisis	Determinación DQO
Solución A	Scharlau	Análisis	Determinación DQO
Solución B	Scharlau	Análisis	Determinación DQO

3.2- Plantas piloto

Para el tratamiento y recuperación de efluentes textiles se seleccionaron cuatro membranas de ultrafiltración de PVDF: ZeeWeed-1 (GE Power & Water, Canada), UOF-1b (Motimo Membrane Technology, China), UOF-4 (Motimo Membrane Technology, China) and FP-T0008 (Motimo Membrane Technology, China), referenciadas como ZW-1, U-1b, U-4 y FP-T, respectivamente. Se construyeron tres plantas piloto de acuerdo a la geometría y las especificaciones de cada membrana.

Para el tratamiento fotocatalíticos de los baños sintéticos con colorantes dispersos se seleccionó una membrana de microfiltración de polisulfona, fabricada por la empresa Polymem (Toulouse-Francia).

Las principales características de las membranas y de las plantas piloto utilizadas en este estudio se presentan en el los capítulo 5-9, correspondientes a los resultados obtenidos en el tratamiento de cada uno de los efluentes.

3.3- Efluentes industriales y baño sintéticos

Los efluentes que contenían colorante índigo fueron suministrados por la empresa Tejidos Royo (Alcudia de Crespins-Valencia). Fueron recogidos del primer depósito de la etapa de lavado, después del proceso de tintura, y correspondían a diferentes condiciones de tintura (tipo de fibra, concentración de colorante, etc.).

Para el estudio de recuperación de efluentes provenientes de empresas que utilizan colorantes dispersos, se utilizaron las aguas residuales generadas en Vincolor S.A. (Terrassa-Barcelona).

Finalmente, para simular los efluentes industriales después de la tintura con colorantes dispersos se tuvieron en cuenta las siguientes consideraciones prácticas: relación de baño 1/20, intensidad 3% sobre peso de fibra y agotamiento del 95%.

3.4- Parámetros estudiados

A continuación se presentan los parámetros estudiados tanto para evaluar las tinturas como para caracterizar los efluentes.

3.4.1- Evaluación de las tinturas

Las **diferencias de color** ($DE_{CMC(l:c)}$) se llevaron a cabo siguiendo la norma UNE-EN ISO 105-J03 [3.1]. Para su determinación se utilizó el iluminante D65 y observador 10º.

La ecuación de DE_{CMC} describe un entorno elipsoidal en cuyo centro se sitúa la referencia (Figura 3.2) [3.2]

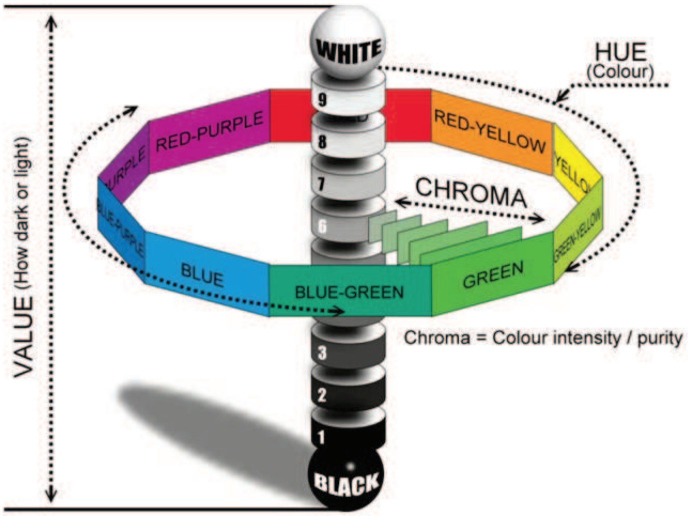

Figura 3.2- Coordenadas cromáticas

La diferencia de color se descompone en tres componentes:

- ♣ Claridad (L): puede tener valores entre 0 (negro) y 10 (blanco).
- ♣ Croma (C): permite diferenciar las intensidades de un mismo color.
- ♣ Matiz (H): puede tener valores entre 0 y 360º. Representa el recorrido que hace un tono hacia uno u otro lado del círculo cromático.

A partir de los diferentes valores de L, C y H se calculan los valores de DL, DC y DH que indican las diferencias cromáticas entre dos muestras y que permiten calcular las diferencias de color entre ellas (ecuación 3.1):

$$DE_{CMC\,(2:1)} = [(DL/2S_L)^2+(DC_{ab}/S_c)^2+(DH_{ab}/S_H)_2]^{1/2} \qquad (3.1)$$

Para la evaluación de las tinturas con colorante índigo también se llevaron a cabo ensayos de solidez al frote y al lavado. La solidez al frote se determinó siguiendo la norma UNE-EN ISO 105-X12 [3.3] y la solidez al lavado según norma UNE-EN ISO 105-C10 [3.4].

3.4.2- Caracterización de los efluentes

Los efluentes fueron caracterizados tanto a la entrada como a la salida de los diversos tratamientos con el fin de determinar su eficiencia. Los parámetros fueron determinados siguiendo el Standard Methods 22nd edition [3.5]:

- Para la determinación de DQO se han utilizado las normas 5220 C (valoración con sal de Mohr) y 5220 D (colorimetría).
- El color de una muestra se determina siguiendo la norma 2120 B. La determinación se lleva a cabo mediante comparación visual de la muestra con soluciones de concentraciones conocidas de color.
- La dureza del agua se determinó mediante valoración complejométrica con una solución estándar de ácido etilendiamintetraacético (EDTA) según método 2340 C.
- El pH y la conductividad se determinaron según métodos 2510 B y 4500 H^+B, respectivamente.
- La determinación de aniones se llevó a cabo con un cromatógrafo iónico siguiendo la norma 4110 A.
- Los sólidos en suspensión y la alcalinidad se determinaron a partir de los métodos 2540 D y 2320 B, respectivamente

3.5- Equipos utilizados

Para la determinación de la concentración de colorantes se utilizó un espectrofotómetro de UV-visible Shimadzu UV-2401 (Figura 3.3).

Figura 3.3- UV-visible Shimadzu UV-2401

La concentración de colorante índigo también se determinó mediante un valorador automático G20 de Mettler Toledo, equipado con un electrodo redox DM 140-SC (Figura 3.4).

Figura 3.4- Valorador automático G20

La conductividad y el pH fueron determinados usando un conductímetro GLP31 (Crison) y un pHmetro GLP21 (Crison), respectivamente (Figura 3.5)

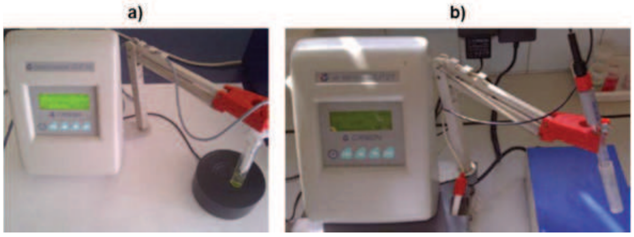

Figura 3.5- a) Conductímetro GLP31 y b) pHmetro GLP21

La determinación de aniones se llevó a cabo mediante el cromatógrafo iónico de Dionex ICS-1000 equipado con un automuestreador AS (Figura 3.6). Para la separación de los aniones se utilizó la columna IonPac AS23 (Dionex).

Figura 3.6- Cromatógrafo iónico Dionex ICS-1000

Las tinturas se llevaron a cabo en dos equipos: Ti-Color y Testherm 90-S. Para la determinación de las diferencias de color entre tinturas realizadas en los diferentes estudios de reutilización del permeado se utilizaron los espectrofotómetros Macbeth Colour Eye 7000A y MINOLTA CM 3600d (Figura 3.7).

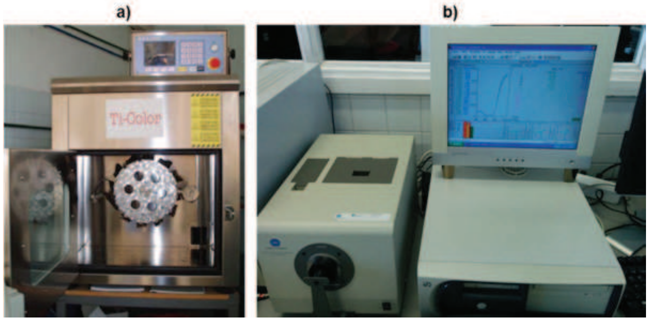

Figura 3.7- a) Máquina de tintura Ti-Color y b) Espectofotómetro Minolta CM 3600d

3.6- Bibliografía

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CHAPTER 4:

A critical comparison of methods for the analysis of indigo in dyeing liquors and effluents

A CRITICAL COMPARISON OF METHODS FOR THE ANALYSIS OF INDIGO IN DYEING LIQUORS AND EFFLUENTS

It was necessary to develop and validate an analytical method to determine the indigo dye concentration in dye baths both before and after the membrane treatment in order to establish the efficiency of the process. The method selected should be simple and easily automated for industrial application.

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Abstract

Indigo is one of the most important dyes in the textile industry. The control of the indigo concentration in dyeing liquors and effluents is an important tool to ensure the reproducibility of the dyed fabrics and also to establish the efficiency of the wastewater treatment. In this work, three analytical methods were studied and validated with the aim to select a reliable, fast and automated method for the indigo dye determination. The first method is based on the extraction of the dye, with chloroform, in its oxidized form. The organic solution is measured by Ultraviolet (UV)-visible spectrophotometry at 604 nm. The second method determines the concentration of indigo in its leuco form in aqueous medium by UV-visible spectrophotometry at 407 nm. Finally, in the last method, the concentration of indigo is determined by redox titration with potassium hexacyanoferrate [$K_3(Fe(CN)_6)$]. The results indicated that the three methods that we studied met the established acceptance criteria regarding accuracy and precision. However, the third method was considered the most adequate for application on an industrial scale due to its wider work range, which provides a significant advantage over the others.

Keywords: indigo dye; method validation; hexacyanoferrate titration; spectrophotometric; dye baths; effluent

4.1- Introduction

The denim industry constitutes an important part of the textile sector, with an estimated world production of 10^9 blue jeans annually [4.1, 4.2]. The characteristic blue colour of denim clothes is due to the indigo dye, which is used in the dyeing of cellulose fibres [4.3, 4.4]. Indigo is one of the oldest natural dyes, although nowadays, due to the high consumption of denim articles, most of them are dyed with synthetic indigo.

Indigo is insoluble in water, but soluble in polar organic solvents. Prior to the dyeing process, it has to be reduced into its leuco form (soluble in water). Currently, the dye reduction step is carried out with sodium dithionite in alkaline medium [4.3]. The chemical structures of indigo dye and its leuco form ($C_{16}H_{10}N_2O_2$) are shown in Figure 4.1.

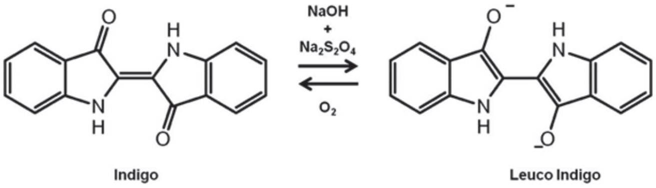

Figure 4.1- Chemical structure of indigo dye and its leuco form

The main disadvantage of indigo is the fast oxidation of its leuco form in contact with air. For this reason, some of the industrial dyeings are performed in nitrogen atmosphere. In order to ensure the reproducibility and regularity of dyed yarns, it is also important to evaluate the indigo concentration in the dye baths during the dyeing process. The concentration of leuco form should be constant and it is regulated by means of sodium dithionite addition [4.5].

It is estimated that at least 10 g of indigo are necessary for dyeing one pair of trousers [4.1, 4.2] and 20% of the dye used is discharged in the wastewater generated during the dyeing process. Based on this information, about two millions of tons are lost in the effluents each year. Several authors have studied the treatment of wastewater that contained indigo dye by either conventional techniques [4.6] or new proposals such as a stirred tank reactor combined with fixed bed bioreactor [4.7], electrochemical treatment with boron doped diamond anodes [4.8] and the use of ferrous oxalate as mediator in a photo-Fenton treatment [4.9]. In addition, interest in recycling waste products has been extended to indigo-containing effluents. In this way, the U.C.O Company from Belgium [4.10] and Porter *et al.* [4.11] studied the recovery of residual indigo from wastewater using ultrafiltration technology.

The aim of the present work was to establish a reliable analytical method for the determination of indigo dye concentration in both the dyeing baths and the residual effluents. In the first case, the indigo must be evaluated during the dyeing process in order to assess the level of dye oxidation. In the case of wastewaters, the analysis of indigo is useful to evaluate the effluent quality and to establish the treatment efficiency.

Since 1967, several studies, summarized in Section 4.1.1, have been published for the determination of indigo dye [4.12–4.17]. However, none of them were focused on dyeing baths and effluents control and studies about reliability, reproducibility and accuracy were not included.

4.1.1- Methods for the analysis of Indigo

As indicated, different analytical methods have been published for the analysis of indigo dye in aqueous media. The main challenge is the low solubility of the dye in water and common organic solvents. Generally, indigo is determined by UV-visible spectrophotometry using different methods that involve treatment of the sample and the addition of organic solvents such as dimethylsulfoxide [4.12], dichloromethane [4.13], and pyridine [4.14]. Indigo has also been determined spectrophotometrically in its leuco form [4.14] but an acceptable linearity was not obtained due to the fast oxidation of the dye in contact with the air. The solvent addition prevents the indigo dye oxidation in contact with the air and enables the analytical determination by UV-visible spectrophotometry. Amperometric [4.15] and voltametric [4.16] methods for the determination of indigo dye have also been reported. Among these methods, Gutierrez-Bouzán *et al.* [4.14] studied the indigo dye extraction with chloroform and its further determination at 605 nm by UV-visible spectrophotometry. This method is simple and affords good linearity (up to 10 mg·L^{-1}).

The use of FIA (Flow Injection Analysis) has also been proposed for the analysis of indigo in its leuco form by Merritt *et al.* [4.17] as a fast, simple and easy method.

However, the main disadvantages of this technique are that it involves a real-time analysis and requires specific equipment. In this study, three different solvents were tested to solubilize the dye: N-methylpyrrolidone (NMP), 2-ethoxyethanol (TEE) and triethanolamine (TEA). Although TEA provided good results, this method required the addition of ferric sulphate to achieve the dye reduction, which causes problems in the dyeing process. Both NMP and TEE solvents were found to be appropriate, but we selected NMP because its structure is rather similar to pyridine, which was successfully tested by Gutierrez *et al.* [4.12]

Moreover, Merritt *et al.* [4.17] investigated the method developed by the company BASF. This method enabled the simultaneous analysis of indigo dye and sodium dithionite, which is the main reducing agent used in the dyeing process. The concentration of both compounds was determined by redox titration using potassium hexacyanoferrate [$K_3(Fe(CN)_6$]. The semi-reactions that occur during the titration are shown in reactions 4.1-4.3:

$$S_2O_4^{2-} + 4OH^- \rightarrow 2SO_3^{2-} + 2H_2O + 2e^- \qquad (4.1)$$

$$C_{16}H_{10}O_2N_2^{2-} \rightarrow C_{16}H_{10}O_2N_2 + 2e^- \qquad (4.2)$$

$$4Fe(CN)_6^{3-} + 4e^- \rightarrow 4Fe(CN)_6^{4-} \qquad (4.3)$$

The titration curve shows two inflection points. The first point is due to sodium dithionite oxidation in the sample and the second one is attributed to indigo dye oxidation. The indigo concentration is calculated from the difference of titrant solution volume between the two points. This method was also selected and validated in this study due to its simplicity and to the advantage of the double titration. In addition, specific equipment is not required, although it can be used for automation purpose.

In the present work, three methods were studied for the determination of indigo dye in textile effluents in order to select an accurate, fast and easy method, adaptable to industrial processes.

The first one is based on the dye extraction with chloroform. The solution is subsequently measured by UV-visible spectrophotometry at its λ_{max} (604 nm). The second one is based on the determination of the indigo in its leuco form by UV-visible spectrophotometry at its λ_{max} (407 nm). In the third method, the concentration of indigo was determined by redox titration using $K_3(Fe(CN)_6)$ and an automatic titrator.

4.2- Experimental procedures

4.2.1- Reagents

Indigo dye (95%) and sodium dithionite (85%) were supplied by ACROS (Sentmenat, Spain). Sodium hydroxide (98.5%) and potassium hexacyanoferrate (99%) were obtained from Panreac (Castellar del Vallès, Spain). Chloroform (99%) and 1-methyl-2-pyrrolidine (99.5%) were purchased from Scharlau (Sentmenat, Spain).

4.2.2- Apparatus

For this study, a Shimadzu UV-visible spectrophotometer UV-2401 (Shimadzu Corporation, Kyoto, Japan) was used for all absorbance measurements. The titration method was carried out in an automatic titrator G20 from Mettler-Toledo equipped with a redox electrode DM 140-SC (Mettler-Toledo, L'Hospitalet de Llobregat, Spain), which is a standard platinum electrode filled with a solution of 3 M potassium chloride and saturated silver chloride. A nitrogen line was installed in order to exclude the oxygen during the titration.

4.2.3- Analytical methods

Three methods have been selected to determine the indigo dye in dyeing liquors and effluents.

Method 1: Determination of oxidized Indigo by chloroform extraction and UV-visible spectrophotometry

A calibration curve was made by dissolving the commercial dye powder in chloroform to obtain five known concentrations. The indigo was not immediately solubilized in chloroform; therefore standard solutions were placed in an ultrasonic bath for 10 min. Complete dissolution of dye was achieved. Then the absorbance values were recorded at λ_{max} = 604 nm.

For determination of indigo in the aqueous samples, an extraction with chloroform was previously performed. Then, the absorbance of the organic phase was measured at λ_{max} = 604 nm. The concentration was calculated from the calibration curve.

Method 2: UV-visible spectrophotometric determination of Indigo in its leuco form

This method involved the reduction of indigo using the following solution:

- 200 $mL \cdot L^{-1}$ 1-methyl-2-pyrrolidine
- 10 $g \cdot L^{-1}$ $Na_2S_2O_4$
- 13 $mL \cdot L^{-1}$ NaOH 33% (w/v)

The calibration curve was obtained from six known concentrations. The absorbance of the standard solutions was read at the maximum wavelength of the visible spectrum, λ_{max} = 407 nm.

The indigo content in the dyeing liquors and effluents was reduced, the absorbance of the solution was measured and the concentration calculated from the calibration curve.

Method 3: Redox titration

Indigo was determined in its reduced form. The reducing solution used for 1 g of indigo was:

- 4 g·L^{-1} $Na_2S_2O_4$
- 3 mL·L^{-1} NaOH 40% (w/v)

The solution was heated 50 ± 5 °C for 30 min.

The dye should remain in the reduced form for 24 h to ensure the complete reduction reaction. A few drops of anionic dispersant Setamol X-D were added to prevent the aggregation of oxidized indigo molecules. Finally, the sample was titrated with a solution of potassium hexacyanoferrate.

4.2.4- Validation method

The three methods were validated by means of several parameters [4.18–4.22]: Linearity, applicability range, limit of detection (LoD), limit of quantification (LoQ), accuracy and precision as repeatability and reproducibility.

A wide range of standard solutions of indigo dye (0 to 100 mg·L^{-1}) were prepared to establish the range of work. The absorbance was plotted versus concentration and only the standards which provide linear correlation were selected to establish the range of work.

The LoD and LoQ were determined from 10 replicates of standard solution with concentration close to the blank. They were calculated using the equations 4.4 and 4.5 [4.19]:

$$LoD = 3.3 \cdot \left(\frac{S_a}{b}\right) \qquad (4.4)$$

$$LoQ = 10 \cdot \left(\frac{S_a}{b}\right) \qquad (4.5)$$

where S_a is standard deviation of the standard solution and b is the slope of the calibration curve.

For methods 1 and 2 standard solutions of 0.12 $mg{\cdot}L^{-1}$ were prepared. For method 3 standard solutions of 50 $mg{\cdot}L^{-1}$ were prepared.

Accuracy was determined from the recovery of known amounts of indigo (200 and 300 $mg{\cdot}L^{-1}$) added to an industrial effluent containing 132 $mg{\cdot}L^{-1}$ indigo dye. Experiments were carried out in duplicate. The recovery percentage was calculated and evaluated.

Repeatability (r) was evaluated from 10 replicates of a standard solution in the same day. The standard solutions were 3.36 $mg{\cdot}L^{-1}$ for method 1, 4.60 $mg{\cdot}L^{-1}$ for method 2, and 531 $mg{\cdot}L^{-1}$ for method 3. The same procedures were carried out on three different days to test reproducibility (R). Repeatability and reproducibility were expressed as relative standard deviations (RSD_r and RSD_R, respectively).

Finally, the acceptance criteria were established before starting the validation analysis. In this study the acceptance criteria are shown in Table 4.1.

The theoretical RSD_r and RSD_R were calculated using Horwitz equation [4.23].

Table 4.1- Acceptance criteria established in the validation study

Parameter	Requirement
Linearity	$R^2 > 0.99$
Accuracy	Recovery 80%–115%
Repeatability	$RSD_r < 0.5\ RSD_r$ theoretical
Reproducibility	$RSD_R < 0.5\ RSD_R$ theoretical

4.3- Results and discussion

4.3.1- Validation test

Results of the validation are displayed in Table 4.2.

Table 4.2- Results obtained in the validation study

Parameter	Method 1	Method 2	Method 3
Range of linearity (mg·L^{-1})	0–5.0	0–10.0	>16.7
LoD (mg·L^{-1})	0.02	0.03	5.5
LoQ (mg·L^{-1})	0.08	0.10	16.7
Accuracy (%)	89.4	99.8	83.7
RSD_r (%)	5.17	1.37	2.65
RSD_R (%)	0.47	0.44	0.60

According to Table 2, the best results were obtained using method 2, which involved indigo determination in the leuco form using absorption spectroscopy.

Repeatability and reproducibility values obtained in the three studied methods were under 6% and 1% respectively. The repeatability of method 1 was higher than the others. This is probably due to the low solubility of the dye in chloroform.

Regarding the accuracy test, the recovery obtained is shown in Table 4.3.

Table 4.3- Accuracy obtained for each level of concentration studied

Sample (mg·L^{-1})	Indigo Added (mg·L^{-1})	Recovery (%)
132	200	Method 1: 96.7
		Method 2: 95.3
		Method 3: 84.2
132	300	Method 1: 82.1
		Method 2: 104.4
		Method 3: 83.4

Although method 3 gave lower dye recovery than methods 1 and 2, it did meet the established acceptance criteria. In method 2, about 100% of recovery was achieved, which demonstrates the high accuracy of this method. Method 3 showed similar recovery for each level of concentration. However, in method 1, when 300 mg·L^{-1} of indigo was added to the sample, the results exhibited lower recovery than when 200 mg·L^{-1} was used. The effect of high indigo dye concentration in results of method 1 is discussed in the Section 3.2.

The lowest range of linearity was obtained in method 1 due to the limited solubility of the indigo dye in chloroform. However, method 3 can only be applied with an indigo concentration above 16.7 mg·L^{-1}.

Finally, methods 1 and 2 exhibited similar LoD and LoQ. It is important to highlight the LoQ obtained in method 3. Industrially, about 3–4 g·L^{-1} of indigo dye are used; therefore, this method has an advantage with respect to the other ones: the samples do not need a dilution step. In addition, redox titration does not require a previous preparation of dye baths, because the dye is already in its leuco form due to the addition of sodium dithionite in alkaline medium. Consequently, this method is much faster than the other ones.

4.3.2- Application of the methods to the analysis of effluents and dyeing liquors

Five industrial effluents supplied by the denim yarn factory “Tejidos Royo” (Alcudia de Crespins, Valencia, Spain) were selected to evaluate the applicability of the three studied methods.

Sample 1 was the wastewater generated in first washing step after the dyeing process. Samples 2–5 were dye liquors collected during the dyeing process.

The indigo content in the samples was determined at least five times with each method. The average results are shown in Table 4.4.

Table 4.4- Results from application of methods 1–3 to industrial samples

Sample	**Indigo Dye Concentration (mg·L^{-1})**		
	Method 1	**Method 2**	**Method 3**
1	117	128	101
2	1300	1390	1290
3	780	940	800
4	1580	3080	3010
5	1700	4160	4060

The indigo concentration in industrial samples was unknown. As the validation tests (Section 3.1) showed high accuracy using method 2, values obtained with this method were selected as the reference levels.

From Table 3, it can be observed that method 2 provided the highest values for indigo dye concentration. With low indigo concentration, method 1 provided similar results to method 2. However, with high indigo concentration, method 3 exhibited similar results to method 2, whereas method 1 should be discarded. These differences are probably due to the high dilution rate, which produced errors in the determination and the low solubility of indigo in chloroform.

In summary, the three studied methods are suitable to be applied in the determination of indigo dye in textile effluents which have lower indigo concentration. In the case of dyeing liquors, methods 2 and 3 are more suitable (Figure 4.2).

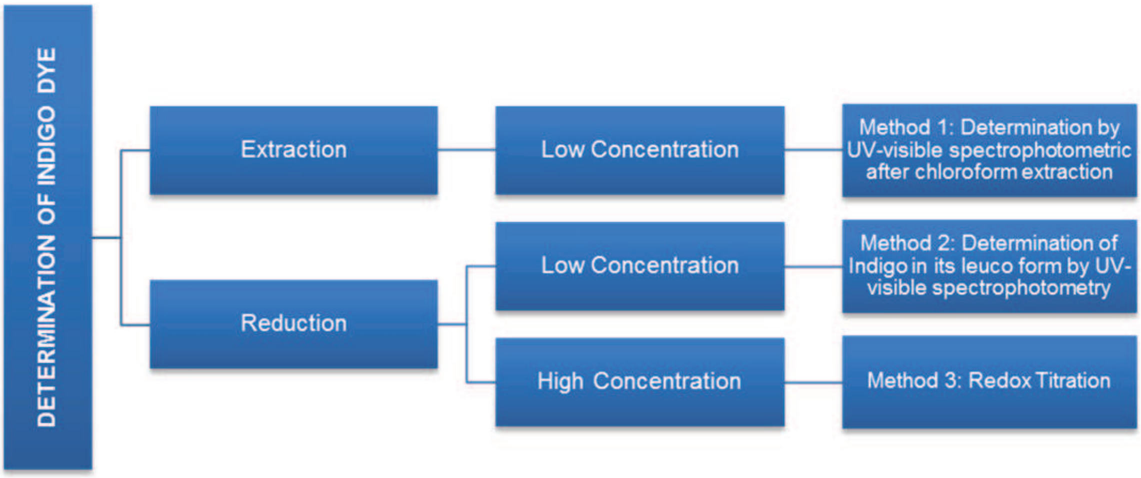

Figure 4.2- Scheme of the studied methods and their applicability

4.4- Conclusions

The validation process carried out in this work showed that all three studied methods can be applied to the determination of indigo dye in both dyeing baths and wastewater effluents.

Method 1 is the most laborious from the experimental point of view because it requires a previous extraction of the indigo in chloroform and a posterior stabilization of the sample in an ultrasonic bath. In addition, its low linearity range, between 0 and 5.0 $mg \cdot L^{-1}$, implies generally a sample dilution before the spectrophotometric analysis. Despite that, the method meets the acceptance criteria.

Method 2, based on the determination of indigo in its leuco form, exhibited the best results in terms of validation parameters. About 100% of recovery is achieved, which indicates the high accuracy of the method. In addition, the concentration range (0–10.0 $mg \cdot L^{-1}$) is higher than in method 1, although the sample still required a dilution for the determination.

Method 3 showed the lower recovery value (84%), but its high range of linearity (from 16.7 $mg \cdot L^{-1}$) provides a significant advantage respect the other two studied methods. Moreover, it enables the simultaneous determination of sodium dithionite and indigo dye concentrations, which are both important to ensure the reproducibility and repeatability of the dyeing process. For these reasons, we consider that method 3 is the most suitable for application on an industrial scale. It is also easy for automation and the installation of an automatic titration provides a fast and simple way to control the dyeing of liquors and efficiency of indigo removal after wastewater treatments.

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CHAPTER 5:

Sustainable dyeing of denim using indigo dye recovered with PVDF ultrafiltration membranes

SUSTAINABLE DYEING OF DENIM USING INDIGO DYE RECOVERED WITH PVDF ULTRAFILTRATION MEMBRANES

This chapter shows the results obtained in the treatment of effluents which contained indigo dye by means of ultrafiltration membranes. The concentrate was reused in new dyeings. Spectrophotometric colour difference, dry rubbing and washing fastness tests were determined to evaluate the feasibility of reusing indigo dye in new dyeing processes.

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Abstract

Indigo is one of the most consumed dyes in the textile sector, as it is widely used for the dyeing of denim clothes. About 15% of indigo used in the dyeing process is discharged to the wastewater treatment plants or sometimes into rivers, in countries where regulations are not strictly applied.

In this work, real effluents that contained indigo dye were treated by means of 4 different ultrafiltration membranes. The feasibility to recover the concentrated dye with lab and semi-industrial pilots was also investigated. The studied membranes achieved up to 99% colour removal and 80% chemical oxygen demand (COD) decrease. Finally, the concentrates containing 20 $g \cdot L^{-1}$ of indigo dye were reused in new dyeing processes. Colour differences (DE_{CMC}) and rubbing and washing fastnesses were evaluated. Fabrics dyed with the recovered indigo concentrates exhibited similar characteristics than the ones obtained with the commercial dye.

Keywords: dye recovery; indigo; reuse; membrane technology; ultrafiltration

5.1- Introduction

The textile industry consumes a large amount of water in their processes, especially in the dyeing and subsequent washing steps [5.1]. The wastewater generated is reported to be in the range of 21–377 m^3 per ton of textile products [5.2]. In addition, the wastewater generated from the textile industry is characterized by high colouration, biological oxygen demand (BOD), chemical oxygen demand (COD) and salinity [5.3].

Physico-chemical and biological processes are currently applied to treat textile wastewater [5.4]. In general, conventional biological treatment provides good COD removal, but low efficiencies in discoloration due to the chemical stability and resistance to microbiological attack of the dyes [5.5, 5.6]. Chemical coagulation is a very common treatment but this method generates a sludge which requires an additional treatment to be destroyed [5.7]. These methods are able to meet legislative requirements but they do not enable water reuse in textile processes [5.8].Recently, there are an increasing number of studies based on industrial waste reuse [5.9, 5.10] and on water reuse [5.11]. In particular, advanced oxidation treatments have been applied to achieve the reuse textile wastewater [5.12, 5.13].

Membrane technology is also an attractive alternative to treat and reuse textile wastewater [5.14, 5.15], because it is able to remove many kind of dyes.

In general, studies published on membrane technology applied to textile effluents are focused on the reuse of permeate [5.16-5.18]. Studies on concentrated dyes reuse are very scarce. Although some types of dyes cannot be reused, the sulphur dyes and vat dyes, especially indigo, are suitable to be recovered with membrane filtration because they are insoluble in water and can be easily separated from the effluent. This is especially interesting as the annual consumption of sulphur and vat dyes is about 120,000 t [5.19].

Indigo ($C_{16}H_{10}N_2O_2$) is one of the oldest known dyes and currently it still occupies an important place in textile dyeing. Its importance is especially due to the popularity of blue jeans, which are dyed with indigo [5.20, 5.21].

About 15% of the indigo used is lost during the dyeing process [5.22], but to our knowledge, only two studies have been published on indigo dye reuse after membrane technology treatment. Crespi [5.23] reported the recovery of the residual indigo from washing wastewater by ultrafiltration membranes in the Belgian company UCO. Porter *et al.* [5.24] studied the recovery of indigo dye with a vinyl-sulfone membrane using a multistage system, where the indigo concentration became progressively higher.

The aim of this work is to apply ultrafiltration membranes to effluents containing indigo in order to achieve the dye reuse. Nowadays, polyvinylidene difluoride (PVDF) is the most used material due to its thermal stability, high hydrophobicity, and resistance to corrosion from many chemicals [5.25]. As far as we know, this material has not still been applied to indigo wastewater treatment. Consequently, in this work different PVDF hollow fibre ultrafiltration membranes were tested to treat effluents containing indigo dye. The dye was firstly concentrated up to 20 $g \cdot L^{-1}$ and subsequently the concentrate was reused in a new dyeing process. Fabrics dyed with the recovered indigo were evaluated with respect to the reference ones (dyed with commercial indigo) by means of spectrophotometric colour difference, dry rubbing and washing fastness tests.

5.2- Experimental procedures

5.2.1- Reagents

Indigo dye (95%) and sodium dithionite (85%) were supplied by ACROS. Sodium hydroxide (98.5%) was obtained from Panreac. Sodium hypochlorite solution (6-14% chlorine active) was acquired from Sigma-Aldrich and 1-methyl-2-pyrrolidine (99.5%) from Scharlau.

5.2.2- Wastewater

Three industrial effluents supplied by the denim yarn factory “Tejidos Royo” (Alcudia de Crespins, Valencia, Spain) were selected to be treated. They were collected from the first washing tank, after the dyeing process, and correspond to different type of fibres and production periods.

The effluents used for the lab tests were preserved in a thermostated room at 20ºC. Before the membrane treatment, samples were pre-filtered (pore diameter 500 μm) in order to remove the higher size particles and fibres. The concentration of indigo was immediately determined before and after the ultrafiltration.

5.2.3- Ultrafiltration module

In this work, four hollow fiber membranes were selected to carry out the indigo dye recovery tests: ZeeWeed-1 (GE Power & Water, Canada), UOF-1b (Motimo Membrane Technology, China), UOF-4 (Motimo Membrane Technology, China) and FP-T0008 (Motimo Membrane Technology, China), referred herein after as ZW-1, U-1b, U-4 and FP-T, respectively. In Table 5.1 are described the main characteristics of these membranes.

Table 5.1- Membranes characteristics

Membrane	**Configuration**	**Pore size (µm)**	**Membrane Area (m^2)**
U-1b	External	0.04	0.5
ZW-1	Submerged	0.04	0.05
U-4	External	0.03	40
FP-T	Submerged	0.1	1

Three pilot plants were built to position the different membrane modules, according to their geometry and specific requirements.

Pilot 1 (Figure 5.1) was equipped with U-1b membrane. It was fed by a 100 L tank. Peristaltic pumps were used for feed, permeate, and concentrate effluents. Pilot 2 operated in cycles of 15 minutes of filtration and 30 seconds of backwashing with permeate.

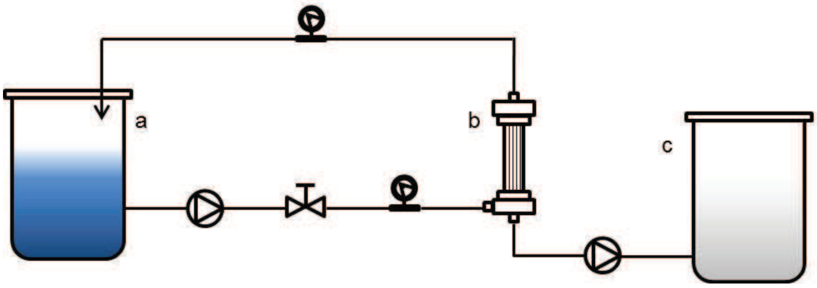

Figure 5.1- Pilot 1 with U-1b membrane. a) Feed tank, b) U-1b Membrane, c) Permeate tank

Pilot 2 (Figure 5.2) was designed to be equipped with ZW-1 module. The membrane reactor was a 20 L cylindrical vessel. It was fed from a 20 L tank by a centrifugal pump. A peristaltic pump was used for the permeate effluent. The membrane module had an air inlet with the purpose to decrease the fouling. This pilot also operated in cycles of 15 minutes of filtration and 30 seconds of backwashing with permeate.

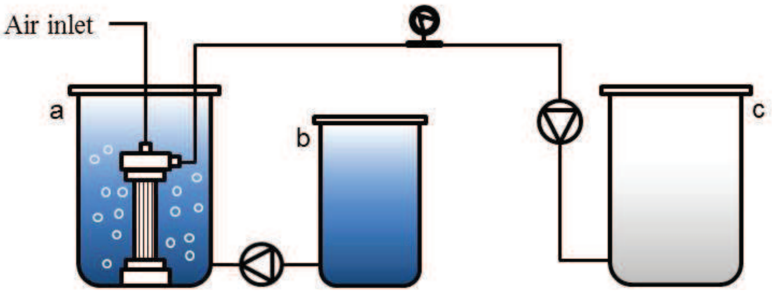

Figure 5.2- Pilot 2 with ZW-1 membrane. a) ZW-1 Membrane, b) Feed tank, c) Permeate tank

Pilot 3 (Figure 5.3) was a semi-industrial system designed to place two membrane modules. The first one was the U-4 membrane able to concentrating up to 3 g·L^{-1}. The volume of feeding tank was 1000L. The concentrate obtained was then applied as a feed to FP-T module which volume was 100 L. In this way, the indigo was concentrated until 20 g·L^{-1}. U-4 membrane operated in cycles of 30 minutes of filtration and 30 seconds of backwashing with permeate and FP-T membrane worked in cycles of 15 minutes of filtration and 30 second of backwashing.

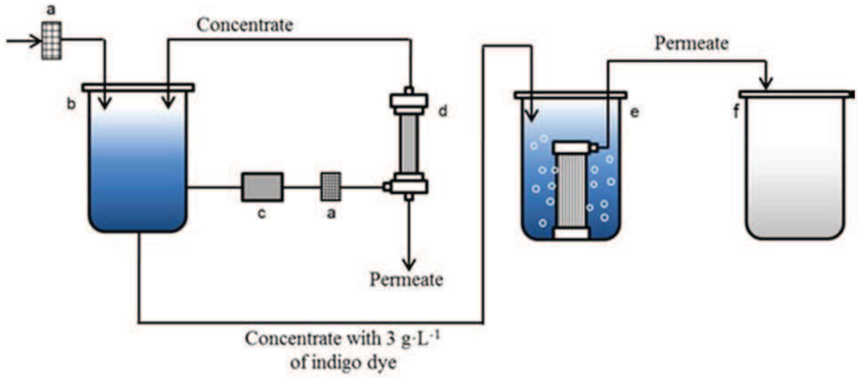

Figure 5.3- Semi-industrial system. a) Meshes, b) Feed tank, c) Control system, d) U-4 membrane, e) FP-T membrane, f) Permeate tank

Finally, after each filtration process, membranes were cleaned with a sodium dithionite alkaline solution (pH 11), followed by rinsing with a sodium hypochlorite solution (5 mg·L^{-1}).

5.2.4- Analytical methods and measurements

Permeate flux was determined by measuring the permeate volume collected in a certain period of time and using the following equation (5.1):

$$J = \frac{V}{A \cdot \Delta t} \tag{5.1}$$

Where J is the volumetric flux (L/m^2·h), A is the effective area of the membrane (m^2) and V is the collected volume in a time interval Δt (L/h).

Indigo removal (R_{indigo}) was calculated from concentrations of feed and permeates using the equation 5.2:

$$R_{indigo} = \left(\frac{C_f - C_p}{C_f}\right) \cdot 100 \tag{5.2}$$

where C_f and C_p are the concentrations of indigo in feed and permeate respectively. Indigo was reduced with a solution which contains sodium dithionite, sodium hydroxide and 1-methyl-2-pyrrolidine and determined by UV-Vis spectrophotometry (Shimadzu UV-2401) in the maximum of the visible spectrum (407 nm). The absorbance and dye concentration were linear in the range between 0.10 and 10 $mg \cdot L^{-1}$.

COD was determined according to the methods recommended by American Public Health Association [5.26]. The COD reduction (R_{COD}) was calculated using the equation 5.3:

$$R_{COD} = \left(\frac{COD_f - COD_p}{COD_f}\right) \cdot 100 \qquad (5.3)$$

where COD_f and COD_p are the COD values in feed and permeate respectively.

Finally, the conductivity and pH were determined using a Conductimeter GLP 31 (CRISON) and a pHmeter GLP 21 (CRISON) respectively [5.26].

5.2.5- Dyeing tests and dyed fabric evaluation

Dyeing experiments were carried out, with synthetic indigo dye and 100% recovered dye, in a foulard designed especially for laboratory tests by Tejidos Royo. Cotton fabrics were passed through a bath which contained the dyeing bath with 3 $g \cdot L^{-1}$ of reduced indigo and then exposed to the air.

The quality of fabrics dyed with indigo recovered was studied from colour differences ($DE_{CMC(l:c)}$) and fastness to rubbing and washing respect to fabrics dyed with commercial pre-reduced indigo dye.

Colour differences were measured using a Macbeth ColourEye 7000A spectrophotometer according to the Standard UNE-EN ISO 105-J03 [5.27].

The equation for $DE_{CMC(l:c)}$ describes an ellipsoidal volume with axes in the direction of lightness (L), chroma (C), and hue (H) centered about a standard. Colour difference is composed of three components:

- ♣ Lightness component (DL_{CMC}) that is weighted by the lightness tolerance (DL^*/lS_L). If DL_{CMC} is positive, the reused dyeing is lighter than the standard. If DL_{cmc} is negative, the reused dyeing is darker than the standard.

- ♣ Chroma component (DC_{CMC}) that is weighted by the chroma tolerance (DC^*_{ab}/cS_c). If DC_{CMC} is positive, the reused dyeing is more chromatic than the standard. If DL_{CMC} is negative the reused dyeing is less chromatic than the standard.

- ♣ Hue component (DH_{CMC}) that is weighted by the hue tolerance (DH^*_{ab}/S_H). It describes the difference between the hue angle of the standard and the hue angle of the reused dyeing in a polar coordinate.

Colour difference is calculated from the equation 5.4:

$$DE_{CMC(l:c)=} [(DL^*/lS_L)^2+(DC^*_{ab}/cS_c)^2+(DH^*_{ab}/S_H)^2]^{1/2} \qquad (5.4)$$

The lengths of the semi axes of the ellipsoid are calculated from the values L^*_r, $C^*_{ab,R}$ and $h_{ab,R,}$ that correspond to the reference as follows:

$S_L=0.040975\ L^*_R/(1+0.01765\ L^*_R)$ if $L^*_R \geq 16$ or $S_L= 0.511$ if $L^*_R < 16$

$S_C=[0.0638\ C^*_{ab,R}/(1+0.0131\ C^*_{ab,R})] + 0.638$

$S_H=(FT+1-F)S_c$

where

$F=((C^*_{ab,R})^4/((C^*_{ab,R})^4+1900))^{1/2}$

$T=0.36+|0.4\cos(35+h_{ab,R})|$ if $h_{ab,R} \geq 345^o$ or $h_{ab,R} \leq 164^o$

or $T=0.56+ |0.2\cos(168+ h_{ab,R})|$ if $164^o < h_{ab,R}< 345^o$

Colour fastness to rubbing was determined according to the Standard UNE-EN ISO 105-X12 [5.28]. This test determines the amount of colour transferred from the surface of dyed fabric to other surface by rubbing. Colour fastness to washing was determined following the Standard UNE-EN ISO 105-C10 [5.29]. Rubbing and washing fastnesses are evaluated on a scale of 1-5, where value 1 indicates very low fastness and 5 corresponds to high fastness.

5.3- Results and discussion

5.3.1- Wastewater characterization

Before the membrane filtration study, the effluents were characterized. The characteristics of each effluent (Table 5.2) depend mainly on the type of fibre and on dyeing conditions.

Table 5.2- Effluents characterization

Parameter	Effluent 1	Effluent 2	Effluent 3
Dyed Fibre	Cotton	Lyocell	Cotton
pH	8.6	9.5	10.4
COD ($mg \cdot L^{-1}$)	320	800	572
Conductivity ($\mu S \cdot cm^{-1}$)	6751	7266	4230
Indigo ($mg \cdot L^{-1}$)	58	118	82

As can be observed, the effluents generated by denim industry are mainly characterized by its high pH and conductivity. The alkaline pH is attributed to the dyeing process, as it requires pH between 11.5 and 12. The high conductivity is due to the presence of sulphates, which are generated from the oxidation of sodium dithionite. This reagent is used for the indigo reduction during the dyeing process.

The two lab pilots cannot run simultaneously as they share the same air inlet. For this reason, a different effluent was treated in each pilot. Effluent 1 was treated in U-1b membrane (pilot 1) and effluent 2 in ZW-1 membrane (pilot 2).

The effluent 3 was treated in situ in Tejidos Royo. The semi-industrial system, equipped with two ultrafiltration membranes, operated in the mill during 2 weeks.

5.3.2- Ultrafiltration experiments

Pilot 1 with U-1b membrane

The efficiency of the membrane process in the recovery of indigo dye from textile effluents was determined by means of permeates characterization. Permeate samples were taken and analysed daily.

It can be seen in Figure 5.4 that 96% dye removal was achieved. This result confirmed the almost full retention of the dye in the concentrate, which indicated the high efficiency of the ultrafiltration membranes in the recovery of indigo dye. In addition, the COD removal was about 40%, increasing at the end of the experiment. A layer of dye was formed on the membrane surface, which acted as a barrier and increased the process efficiency. The increase of colour and COD removal along the treatment has also been reported by different authors [5.30-5.33].

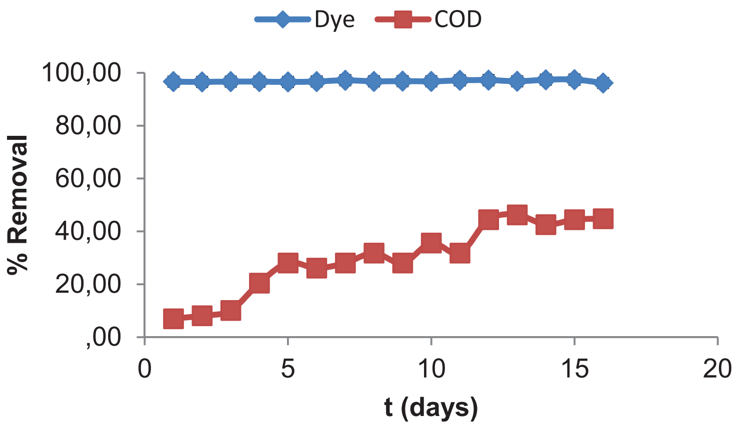

Figure 5.4- Dye and COD removal with U-1b membrane

The pH and conductivity values were 8.4 and 6720 µS·cm^{-1} respectively, which evidenced the low efficiency of the ultrafiltration membrane in ions removal. Ions such as sodium or sulphate pass through ultrafiltration membranes, therefore when the permeate has to be reused, nanofiltration or reverse osmosis membranes must be selected to remove inorganic ions.

After 5 days of operation, this pilot exhibited a remarkable membrane flux decrease up to 57% (Figure 5.5), which was mainly attributed to the indigo layer formed on the membrane surface. The classic washing was not able to remove this layer from the membrane surface and to restore the initial membrane flux.

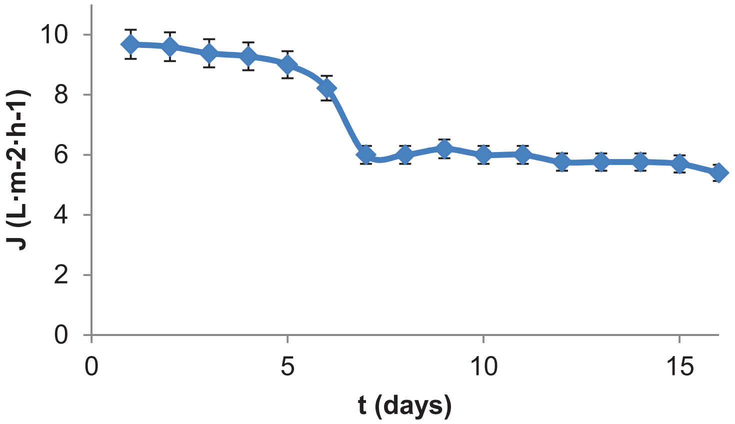

Figure 5.5- Flux values of U-1b membrane

Taking into account that higher size particles of effluent 1 were separated before ultrafiltration treatment, it was concluded that the fouling observed in U-1b membrane was due to its physical configuration as it is constituted by a packed column. This structure complicates the washing process and results in the production of a cake of indigo particles (Figure 5.6).

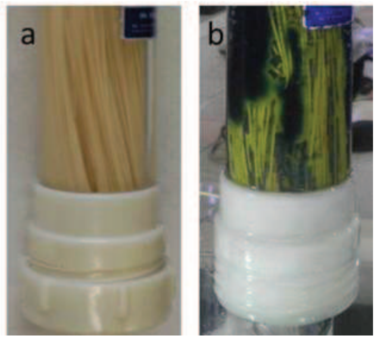

Figure 5.6- U-1b membrane: a) Before the study, b) After the study

Thus, this type of membrane was only considered able to obtain concentrates up to 3 g·L^{-1} indigo dye. This concentration is high enough to be directly reused in new dyeing processes. However, the automated dyeing process used in Tejidos Royo requires the dosage of an initial dye bath of 20 g·L^{-1}. For this reason, the dye reuse study was not carried out with the effluent treated with the U-1b membrane.

Pilot 2 with ZW-1 membrane

As in the previous section, permeate samples were taken and analysed daily. Along the filtration process, 99% dye removal was obtained and no coloration was observed in the permeate (Figure 5.7). In addition, at the end of the study, 80% COD removal was also achieved. This phenomenon was also observed with U-1b membrane and it was discussed in the previous section.

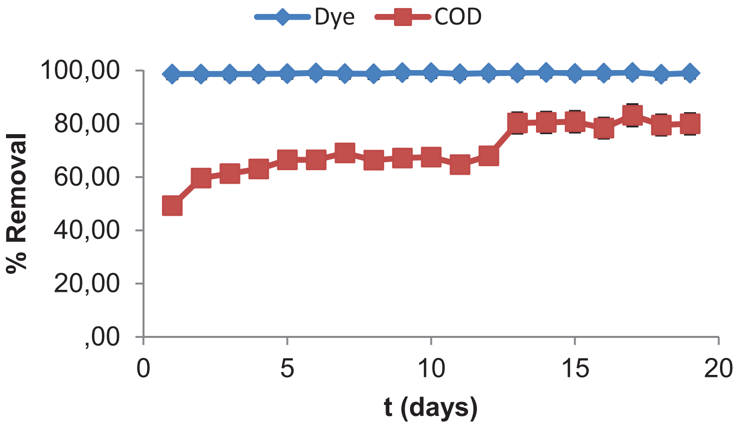

Figure 5.7- Dye and COD removal with ZW-1 membrane

The pH and conductivity values were 8.7 and 5027 μS·cm^{-1} respectively.

Regarding the membrane behaviour, the fouling was controlled by measuring the permeate flux during the treatment. The permeate flux was stable throughout the study, that indicated low fouling on the membrane. The importance of the fouling in a membrane process should be highlighted. In fact, membrane fouling has become in a major obstacle to the further application of UF technology in water treatment [5.34], because it causes a reduction in the permeability and therefore the maintenance cost of the membrane is increased and its life time is reduced [5.35]. The washing step was able to clean and recover the initial membrane flux value, which indicated that the cake formed on the membrane surface was fully removed, although at the end of the study, the membrane surface was just dyed with a blue coloration. The low fouling observed in this pilot shows the feasibility of applying this type of membranes to recover indigo dye.

The ZW-1 membrane enabled to obtain a concentrate containing 20 g·L^{-1} indigo dye. This concentration is adequate to be used in an automated dyeing process. Thus, the indigo dye reuse study was carried out with this concentrated effluent (section 3.3).

Semi-industrial system

In the lab tests, both membranes provided almost full retention of indigo. For this reason, in the semi-industrial study both membrane configurations were combined to evaluate their behaviour at semi-industrial scale. The design of the semi-industrial pilot was mainly based on practical considerations such as operational factors, maintenance, cleaning and membrane cost. The first membrane (U-4) was able to concentrate up to 3 g·L^{-1} and it was combined with a second membrane module (FP-T) in order to achieve the 20 g·L^{-1} as final concentration. The submerged configuration of the second membrane enabled to reach the required dye concentration for the automated dyeing process employed in Tejidos Royo.

Due to the high volume of effluent required, experiments of membrane characterization were not carried out, to avoid interference in the production process of the company.

Permeate was characterized and at the end of the process. It was obtained 98% of dye removal and 67% of COD decrease. As in the case of the first lab pilot; the layer of dye formed on the membranes surface increased the indigo dye rejection. The concentrated was kept for the reuse tests (section 3.3).

With the semi-industrial pilot, dye removal results (98%) were into the range of lab pilots (96-99%). COD removal (67%) was also found to be into the range of the lab pilots (40-80%).

5.3.3- Indigo dye reuse

Indigo dye reuse tests were performed from solutions containing 20 $g \cdot L^{-1}$ of indigo dye, which correspond to concentrates of pilots 2 (lab scale) and 3 (semi-industrial). The concentrate of pilot 1 was not included in this study as it did not meet the requirements for the automatic dosage of the mill.

Dyeings obtained from the two concentrates were evaluated with respect to a reference dyeing performed with commercial indigo. Their chromatic coordinates and colour differences ($DE_{CMC\ (2:1)}$) are shown in Table 5.3.

Table 5.3- Colour differences values

Pilot plant	**$DE_{CMC\ (2:1)}$**	**DL**	**DC**	**DH**
ZW-1 membrane	0.84	-0.76	-0.26	0.22
Semi-industrial	1.19	-1.19	-0.31	-0.35

From these values it can be concluded that the main differences between colour of the reference fabric and the ones dyed with reused indigo ($DE_{CMC\ (2:1)}$) were mainly due to the influence of DL. Thus reused dyeings had similar chroma (C) and hue (H), but they exhibited more differences on the intensity values (L). In addition, the negative value of DL means that dyeings with indigo recovered were darker than the reference. This fact was attributed to dispersant that can be retained with the indigo dye. It is necessary either determine the amount of dispersant in the concentrate and adjust it or decrease the dye concentration of the bath to obtain the same intensity. Both cases provide an important advantage from the economical point of view. This study is been currently carried out.

The indigo recovered with pilot ZW-1 membrane provided $DE_{CMC\ (2:1)}$ lower than 1, which is considered the acceptance limit of most industrial dyeing processes. However, in the denim industry the acceptance limit can be higher than 20% (1.2), as generally fabrics are submitted to subsequent bleaching or sandwashing processes. For this reason, $DE_{CMC\ (2:1)}$ corresponding to the semi-industrial test, is also considered acceptable.

Fastness properties are also an important factor to be considered in textiles. In this case, colour fastnesses to washing and rubbing were evaluated (Table 5.4).

Table 5.4- Colour fastnesses to washing and rubbing values

Pilot plant	**Washing**	**Rubbing**
Reference	4	2
ZW-1 membrane	5	2
Semi-industrial	5	2

Both, dyeings with reused and dyeings with commercial dye exhibited the same rubbing fastness. Fabrics dyed with recovered indigo showed higher values of washing fastness than the fabric dyed with commercial indigo. This difference could probably be attributed to the higher amount of dispersing agent in the recovered dyeing bath (part of the dispersant may probably be retained with the dye). This point is under research and should be confirmed by further investigations.

5.3.4- Permeate reuse

Although the aim of this work was the indigo dye reuse, it is important to highlight the quality of the permeate obtained after the membrane treatment (Table 5.5).

Table 5.5- Permeate characterization

Pilot Plant	**Dye concentration ($mg \cdot L^{-1}$)**	**pH**	**Conductivity ($\mu S \cdot cm^{-1}$)**	**COD ($mg\ O_2 \cdot L^{-1}$)**
U-1b membrane	1.8	8.6	6750	230
ZW-1 membrane	1.3	8.7	5028	239

Both membranes provided permeates with similar characteristics: very low dye concentration (<2 $mg \cdot L^{-1}$) and low organic matter content (<250 $mg \cdot L^{-1}$). According to the mill experience (Tejidos Royo), these values enable to reuse the effluent in a new indigo dyeing process directly or partially diluted.

Permeate reuse is an important challenge. It is estimated that the annual consumption of fresh water in the textile industry at the European level is 600 million m^3 [5.36]. Regarding the denim industry, Chico *et al.* [5.37] reported that about 3000 m^3 of water is needed per trouser from fibre production stage to fabric production. Despite the clear benefits of water reuse, its implementation is still not a common practice in the textile sector.

5.4- Conclusions

Indigo dye from wastewater can be successfully removed by means of PVDF ultrafiltration membranes.

Among the studied membranes, the external hollow fibre module (U-1b membrane) was able to treat wastewater containing indigo dye and it enabled to concentrate the dye up to 3 $g \cdot L^{-1}$. Higher concentration was discarded due to the fouling on the membrane surface. This concentration is acceptable when the effluent is directly reused. The U-1b membrane allowed obtain a permeate free of dye (96% dye removal) and a 40% COD reduction.

According to the results, the submersible hollow fibre module (ZW-1 membrane) enabled to obtain a concentrate with 20 $g{\cdot}L^{-1}$ indigo dye, which is the required concentration for automated dyeing processes. In addition, the permeate characterization showed 99% dye retention and 80% COD reduction.

The study in semi-industrial system showed that the combination of external and submerged PVDF membranes was able to treat wastewater that contained indigo dye. The COD and dye removal obtained was 67 and 98% respectively.

Finally, the study of indigo dye reuse carried out with the concentrate obtained in both submersible hollow fibre module and semi-industrial system, showed the feasibility of the membrane technology to recover indigo dye. The dyeing made with recovered dye exhibited similar characteristics than dyeing with commercial dye.

5.5- Acknowledgements

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CHAPTER 6:

Application of PVDF ultrafiltration membranes to treat and reuse textile wastewater

APPLICATION OF PVDF ULTRAFILTRATION MEMBRANES TO TREAT AND REUSE TEXTILE WASTEWATER

This chapter shows the results obtained in the treatment of synthetic effluents which contained disperse dyes by means of ultrafiltration membranes at laboratory scale. The permeate was reused in new dyeings. Fabrics dyed with the reused effluent were evaluated respect to references carried out with softened tap water by means of spectrophotometric colour differences.

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Abstract

In this work, the feasibility of polyvinylidene difluoride (PVDF) ultrafiltration membranes to treat textile wastewater was studied. The C.I. Disperse Orange 30 and C.I. Disperse Rubine 73 were selected as pollutant for the membrane filtration study.

The results showed about 90% and 96% of COD decrease and dye removal, respectively. In addition, very low fouling was observed which demonstrated the feasibility of applying this type of membranes to treat textile wastewater.

Finally, after the membrane treatment, 100% of the obtained permeate was reused. Fabrics dyed with the reused water were evaluated respect to references carried out with softened tap water. No significant colour differences were observed between reference fabrics and the fabrics dyed with the permeate.

Keywords: Textile wastewater; Disperse dyes; Water reuse; Colour removal; Membrane treatment

6.1- Introduction

Dyes are widely used in different industries such as textile, leather, paper, plastics, and food [6.1, 6.2]. There are more than 100,000 different synthetic dyes and their annual production is about 7·105 tons [6.3]. Particularly, the textile industry consumes 107 kg of dye per year [6.4] and 15% of dyes consumed are discharged into the textile wastewater [6.5] causing serious problems upon aquatic flora and fauna [6.6].

Dyes are classified according to their chemical structure and how they are applied in the dyeing process [6.7]. The most common dyes are reactive, acid, direct, vat and disperse [6.8, 6.9]. Disperse dyes are non-ionic aromatic compounds with low solubility in water [6.10]. They are widely used in the dyeing of polyester fibre. This fibre represents about the 50% of the total world textile fibre consumption [6.11].

In general, dyes are difficult to remove because they are stable to light and oxidizing agents, and with low biodegradability [6.12, 6.13]. The most used technologies to treat wastewater containing dyes are based on biological [6.14, 6.15] or/and physical-chemical processes [6.16–6.18]. Although these treatments are able to meet legislative requirements, they do not allow water reuse in textile processes [6.19, 6.20]. The reuse of textile wastewater is an important challenge since between 60 and 100 L of water are needed to produce a kilogram of textile product [6.21]. Other treatments such as photo-fenton [6.22], photocatalytic [6.23] and electrochemical [6.24] have been studied. These methods provided high colour removal but the generation of by-products and the high cost are their main limitations [6.25].

Membrane technology has shown great potential to treat textile wastewater as it can be applied to remove different kind of dyes. In addition, it allows both the reuse of auxiliary chemicals and some concentrate dyes [6.26] and produces a permeate with high quality, which can be reused in new textile processes [6.27]. In general, reverse osmosis (RO) [6.28, 6.29] and nanofiltration (NF) membranes [6.30, 6.31] are the most studied in the treatment of effluents containing dyes. The main limitation of membrane processes such as NF and RO is the decline of permeate flux caused by the accumulation of particles on the membrane surface [6.32]. This phenomenon is especially observed in RO membrane resulting in an increase of the treatment cost [6.33, 6.34]. Ultrafiltration membranes (UF) exhibit low fouling and high efficiency to separate chemicals with high molecular weight or insoluble dyes like disperse.

On the basis of these considerations, the aim of this work is study the feasibility of PVDF ultrafiltration membranes to treat textile wastewater containing disperse dyes. Two different disperse dyes, C.I. Disperse Orange 30 (DO30) and C.I. Disperse Rubine 73 (DR73) were selected for the membrane filtration study. Subsequently, the permeate was reused in new polyester dyeings. Finally, fabrics dyed with the reused effluent were evaluated respect to references carried out with softened tap water.

6.2- Experimental procedures

6.2.1- Reagents

Two disperse dyes provided by Archroma-Spain were selected for the study of permeate reuse: C.I. Disperse Orange 30 and C.I. Disperse Red 73. Figure 6.1 shows their chemical structures.

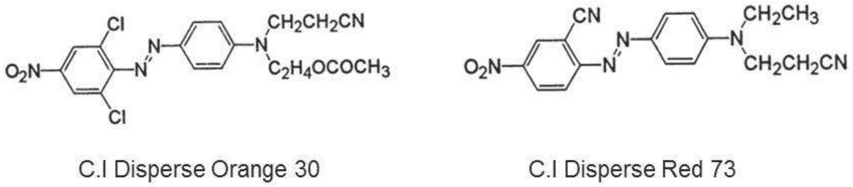

Figure 6.1- Chemical structure of C.I. Disperse Orange 30 and C.I. Disperse Red 73

To determine the dye concentration in the permeate, N,N-dimethylformamide (purity 99.5%, Scharlau) and softened tap water were used as solvents.

The pH of synthetic effluents dye baths was adjusted with NaOH and HCl.

Sodium hypochlorite solution (6-14% active chlorine) acquired from Sigma-Aldrich was used for the membrane cleaning.

6.2.2- Synthetic effluents preparation

To simulate the effluents discharged after the dyeing process, four solutions of either DO30 or DR73 were prepared in softened tap water. The pH of the effluents was adjusted at 6.0-6.5. The main characteristics of the effluents used in this study are shown in Table 6.1.

Table 6.1- Effluents characterization

Dye	pH	Conductivity (μS·cm^{-1})	COD (mg·L^{-1})	Dye concentration (mg·L^{-1})
DO30	6.4	1321	120.6	77.4
	6.2	1359	102.5	76.1
DR73	6.4	1557	106	77.2
	6.3	1438	109	77.8

6.2.3- Membrane treatment

In this work, a PVDF hollow fibre membrane module ZeeWeed-1 (ZW-1) (GE Power & Water, Canada) was used. Its main specifications and operation characteristics are shown in Table 6.2.

Table 6.2- ZW-1 Specifications

Model	ZW-1, Submersible Module
Configuration	Outside / In hollow Fiber
Membrane Surface	0.05 m^2
Pore size	0.04 μm
Maximum Transmembrane Pressure (TMP)	0.62 bar
Typical Operating TMP	0.1-0.5 bar
Maximum TMP Back Wash	0.55 bar
Operating pH range	5-9

A laboratory scale reactor was built to position the membrane module, according to its geometry and specific requirements (Figure 6.2). The membrane reactor was a 20 L cylindrical vessel. It was fed from a 20 L tank by a centrifugal pump. A peristaltic pump was used for the permeate effluent. The membrane module had an air inlet with the purpose to decrease the fouling. The laboratory scale reactor operated in cycles of 15 minutes of filtration and 30 seconds of backwashing with permeate.

Figure 6.2- Laboratory scale reactor

The membrane treatment was carried out at constant TMP (0.2 bar) and at room temperature. A concentration factor of 10 was selected for this study.

Finally, after each filtration process, the membranes were cleaned with a sodium hypochlorite solution (5 $mg \cdot L^{-1}$).

6.2.4- Permeate reuse

The reuse dyeing tests were performed in a laboratory Ti-Color dyeing machine (Integrated Color Line) under the following conditions: 10 g of polyester fabric, dye concentration 3% o.w.f (over weight of fibre) and liquor ratio 1:20 (1 g fibre/20 mL dye bath). The dyeing method conditions are shown in Figure 6.3.

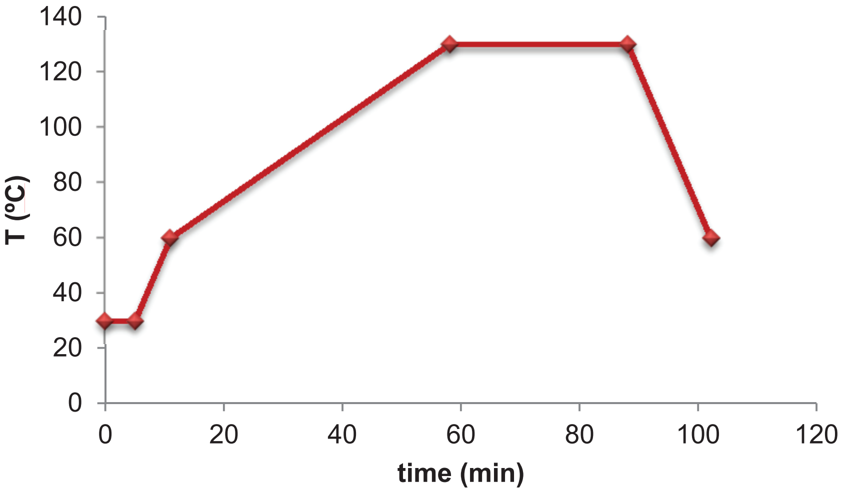

Figure 6.3- Dyeing method

6.2.5- Analytical methods and measurements

The permeate flux was determined to evaluate the membrane fouling. It was determined by measuring the permeate volume collected in a certain period of time (Equation 6.1)

$$J = \frac{V}{A \cdot \Delta t} \qquad (6.1)$$

Where J is the permeate flux ($L \cdot m^{-2} \cdot h^{-1}$), A is the effective area of the membrane (m^2) and V is the collected volume in a time interval Δt ($L \cdot h^{-1}$).

The dye removal ($\%R_{dye}$) was calculated from concentrations of feed and permeate using the Equation 6.2:

$$\%R_{dye} = \left(\frac{C_f - C_p}{C_f}\right) \cdot 100 \qquad (6.2)$$

where C_f and C_p are the concentrations of dye in feed and permeate, respectively. The dye was dissolved in an aqueous solution, which contained N,N-dimethylformamide 1:1, and determined with UV-Vis spectrophotometer UV-2401 (Shimadzu Corporation) at the maximum wavelength of the visible spectrum (430nm for DO30 and 528nm for RD73). For each dye, the calibration curve was:

DO30: Abs = 0.0235·conc – 0.0046 and R^2 = 0.9997

DR73: Abs = 0.0483·conc – 0.0087 and R^2 = 0.9996

COD was determined according to the methods recommended by American Public Health Association [6.35]. The COD reduction (%RCOD) was calculated using the Equation 6.3:

$$R_{COD} = \left(\frac{COD_f - COD_p}{COD_f}\right) \cdot 100 \qquad (6.3)$$

where CODf and CODp are the COD values in feed and permeate respectively.

The conductivity was measured following the method 2510 B [6.35] with a conductivity meter GLP 31 (CRISON). The pH was determined according to the method 4500 H+B [6.35] using a pH meter GLP 21 (CRISON).

The quality of dyed fabrics was studied from colour differences ($DE_{CMC(l:c)}$) using a MINOLTA CM 3600d spectrophotometer. The difference in colour was determined in conformity with the Standard UNE-EN ISO 105-J03 [6.36]. A dyeing is considered acceptable when the $DE_{CMC(l:c)}$ value is lower than 1, measured with Macbeth Colour Eye 7000A spectrophotometer with respect to a reference sample.

6.3- Results and discussion

6.3.1- Membrane treatment

The synthetic dye baths were treated by means of an ultrafiltration membrane laboratory scale reactor. The trans-membrane pressure was set at 0.2 bar. Along the filtration process, the permeate flux remained at 20.9 $L \cdot m^{-2} \cdot h^{-1}$ and 21.7 $L \cdot m^{-2} \cdot h^{-1}$ for DO30 and DR73 respectively. The low fouling observed in this laboratory scale reactor showed the feasibility of applying this type of membranes to treat textile effluents.

The efficiency of the membrane process in the treatment of textile effluents containing disperse dyes was determined by means of permeate characterization. Permeate samples were taken and analysed daily.

Both effluents showed similar behaviour producing high quality permeate. The pH and conductivity values did not change with respect to the initial effluent due to the low retention of inorganic ions by ultrafiltration membranes.

The treatment of DR73 showed 92% COD reduction and 97% dye removal (8.5 $mg \cdot L^{-1}$ and 2.8 $mg \cdot L^{-1}$ respectively). Similar results were also achieved for the DO30 effluent: 90% of COD decrease (10.5 $mg \cdot L^{-1}$) and 95% of dye removal (3.8 $mg \cdot L^{-1}$).

6.3.2- Selection of reference fabric

Replicates of same dyeing can exhibit slight differences in their colour coordinates. For this reason, before the permeate reuse study, it is important to select properly for each dye the reference fabric. With this purpose, colour differences were measured and compared between replicates. All experiments were run in triplicate.

Table 6.3 shows the values of $DE_{CMC(2:1)}$, DL, DC and DH for fabrics dyed with DO30 and softened tap water. As it was expected, low values of $DE_{CMC(2:1)}$ were found between replicates (<0.4). According to the results, the lowest $DE_{CMC(2:1)}$ were found when replicates 1 and 3 were compared with the replicate 2. For this reason, the replicate 2 was selected as the reference fabric for DO30 dye and it was used with this purpose in the permeate reuse study.

Table 6.3- Colour differences obtained in reference fabrics dyed with DO30

$DE_{CMC\ (2:1)}$	**1**	**2**	**3**		**DL**	**1**	**2**	**3**
1	*	0.18	0.38		**1**	*	-0.03	-0.13
2	0.13	*	0.21		**2**	0.03	*	-0.10
3	0.28	0.22	*		**3**	0.13	0.14	*
DC	**1**	**2**	**3**		**DH**	**1**	**2**	**3**
1	*	-0.06	-0.13		**1**	*	-0.17	-0.34
2	-0.10	*	-0.07		**2**	0.08	*	-0.17
3	-0.03	-0.11	*		**3**	0.24	0.12	*

The same procedure was carried out with DR73 dye (Table 6.4). In this case, DE$_{CMC(2:1)}$ were higher than DE$_{CMC(2:1)}$ with DO30 which means that the reproducibility of fabrics dyed with DR73 was lower. This fact was taken into account to evaluate the feasibility of permeate reuse. The replicate 1 was selected as the reference for DR73 dye.

Table 6.4- Colour differences obtained in reference fabrics dyed with DR73

$DE_{CMC\ (2:1)}$	**1**	**2**	**3**		**DL**	**1**	**2**	**3**
1	*	0.63	0.19		**1**	*	-0.41	-0.08
2	0.55	*	0.59		**2**	0.34	*	0.33
3	0.28	0.65	*		**3**	0.00	-0.29	*
DC	**1**	**2**	**3**		**DH**	**1**	**2**	**3**
1	*	-0.38	0.08		**1**	*	0.28	0.15
2	0.28	*	0.47		**2**	-0.33	*	-0.14
3	-0.19	-0.58	*		**3**	-0.20	-0.10	*

6.3.3- Permeate reuse

The treated effluents were used in order to study the feasibility of the permeate reuse. The dyeings were carried out with 100% of permeate. Dyeings obtained were evaluated with respect to a reference dyeing (selected in section 6.3.2).

Table 6.5 exhibits the values measured in the permeate reuse study. Fabrics referenced as 1-3 were dyed with the permeate obtained in the treatment of synthetic effluents containing DO30 dye. Fabrics referenced as 4-6 used permeate from synthetic effluents containing DR73 dye.

Table 6.5- Colour differences values in the permeate reuse study

	DO30 dye					**DR73 dye**			
	$DE_{CMC\ (2:1)}$	**DL**	**DC**	**DH**		**$DE_{CMC\ (2:1)}$**	**DL**	**DC**	**DH**
1	0.54	-0.23	-0.49	0.04		0.65	-0.29	-0.58	-0.10
2	0.55	-0.26	-0.32	-0.37		0.66	-0.41	-0.51	-0.09
3	0.64	-0.36	-0.39	-0.36		0.72	-0.37	-0.62	0.01
4	0.84	0.38	0.32	0.67		0.83	0.13	0.73	0.38
5	0.87	0.42	0.34	0.68		0.83	0.47	0.67	0.13
6	0.82	0.44	0.29	0.63		0.77	0.25	0.72	0.03

From Table 6.5, it can be observed that dyeings showed $DE_{CMC(2:1)}$ lower than 1, which is the maximum value accepted at industrial scale. For dyeings 1-3, $DE_{CMC(2:1)}$ values were mainly due to the influence of DC. The negative values of DC and DL mean that dyeings were less chromatic and darker than the replicates.

Regarding dyeings 4-6, fabrics dyed with permeate from synthetic effluents containing DR73 dye, exhibited $DE_{CMC(2:1)}$ higher than dyeings 1-3. This fact could be attributed to the reproducibility of the dyeings with this dye, which it was discussed in section 3.2. In this case, the three components (DL, DC and DH) have influenced in the value of

$DE_{CMC(2:1)}$. The positive values of DC and DL mean that dyeings were more chromatic and lighter than the replicates.

6.4- Conclusions

Synthetic textile effluents containing disperse dyes were treated by means of PVDF ultrafiltration membrane.

The membrane treatment provided up to 90% and 96% of COD decrease and dye removal, respectively. In addition, no fouling was observed during the experiments.

According to the results in the permeate reuse study, the dyeing performed with 100% of permeate exhibited similar characteristics than dyeing with softened tap water. The colour differences values were lower than 1 and therefore they met the established acceptance range. Due to the huge amounts of water consumed in the textile industry, the feasibility of UF membranes to treat and reuse textile effluents is a promising result.

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CHAPTER 7:

Reuse of textile wastewater after homogenization-decantation treatment coupled to PVDF ultrafiltration membranes

REUSE OF TEXTILE WASTEWATER AFTER HOMOGENIZATION-DECANTATION TREATMENT COUPLED TO PVDF ULTRAFILTRATION MEMBRANES

This chapter shows the results obtained in the treatment and reuse of wastewater generated by a textile mill specialized in polyester dyeing. The wastewater was treated by coupling a homogenization-decantation treatment with two polyvinylidene difluoride (PVDF) ultrafiltration membranes at laboratory and at semi-industrial scale. The permeate was reused in both monochromies and trichromies and fabrics dyed with the reused water were evaluated respect to references.

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Abstract

The textile industry is one of the largest consumers of water in the world and its wastewater is a serious problem when it is discharged without the proper treatment. In this work, wastewater generated by textile industry was treated coupling a homogenization-decantation treatment with polyvinylidene difluoride (PVDF) ultrafiltration membranes.

Initially, the wastewater was aerated in a homogenization-decantation tank where 17% colour and 10% chemical oxygen demand (COD) were removed. The aerated effluent was treated with an ultrafiltration membrane in order to reuse the permeate in new dyeing processes. Firstly, the ultrafiltration treatment was performed in a laboratory plant. The permeate analysis showed 20% colour removal and 60% COD decrease. On the basis of these results, a semi-industrial system was built. With this plant, the permeate characterization showed similar results. The system was found to be scalable and suitable for the treatment of this kind of effluents.

Finally, new dyeings were performed with both permeates. Monochromatic dyeings were carried out with 100% permeate whereas 50% permeate was reused for dyeings with a mixture of three dyes. The colour differences were found to be lower than 1.5, which was the acceptance value established.

Keywords: real textile wastewater; permeate reuse; ultrafiltration; dyeing process; membranes

7.1- Introduction

The textile industry is characterized by high water consumption. Up to 100 L of water are required to produce a kilogram of textile product [7.1]. Wastewater from textile industry contains different kind of dyes and chemical additives [7.2, 7.3], which cannot be easily degraded.

The most applied wastewater treatments are based on biological or physical-chemical processes. In general, conventional biological treatment provides good chemical oxygen demand (COD) removal, but low efficiencies in discoloration due to the chemical stability and resistance to microbiological attack of the dyes [7.4, 7.5]. Chemical coagulation can remove the colour completely, but it generates a sludge which requires an additional treatment to be destroyed [7.6, 7.7]. These methods are able to meet legislative requirements but they do not allow water reuse in textile processes [7.8].

Advanced oxidation treatments such as photo-fenton [7.9], photocatalytic [7.10] and electrochemical [7.11] have been studied in order to improve the efficiency in colour removal. Good results were obtained although they were found to be quite expensive [7.2]. Membrane technology is nowadays an attractive alternative to treat textile wastewater. In general, nanofiltration [7.12-7.14] and reverse osmosis [7.15] membranes have been studied to treat textile effluents. Its main advantage is that they can be applied to remove many kind of dyes, producing a concentrate, where dyes are retained, and a permeate free of dyes. Some studies have be focussed on the reuse of dyes concentrate [7.16] but the reuse of permeate in new processes is more advantageous.

Direct feed to membrane modules can produce irreversible fouling. As a result, the maintenance cost of the membrane is increased and its life time is reduced [7.17]. If advanced treatments like membrane technologies are combined with conventional processes, the quality of the effluent treated is good enough to be reused [7.18] and the fouling observed decreases. Generally, the combination of membranes process with coagulation-flocculation [7.19-7.22] and biological treatments [7.2, 7.3, 7.23] have been studied.

The reuse of textile wastewater is an important challenge, especially the effluents from polyester dyeing. In fact, the liquor ratio (amount of fibre/water) for conventional dyeing of polyester fabrics is generally 1:10 – 1:20, that implies the use of 10-20 ton water for each ton fabric. In addition, the consumption of polyester fibre has increased dramatically in the lasts years. Nowadays this fibre represents about the 50% of the total world textile fibre consumption and it still has an increasing demand [7.24]. Taking into account these considerations, this work is focused on the treatment and reuse of wastewater generated by a textile mill specialized in polyester dyeing. The wastewater was treated by coupling a homogenization-decantation treatment with two polyvinylidene difluoride (PVDF) ultrafiltration membranes. The permeate was reused in new polyester dyeings. Finally, fabrics dyed with the reused water were evaluated respect to references carried out with softened tap water.

Several authors have published studies about treatment of textile effluents by membranes technologies. In these studies, after exhaustive analyses of the treated effluents, they conclude the suitability of permeate to be reused. But, to the best of our knowledge, a complete study of permeate reuse in new dyeings, both at laboratory and industrial scale, has not been yet carried out for any of them.

7.2- Experimental procedures

7.2.1- Reagents

Nine Foron disperse dyes provided by Archroma-Spain were selected for the study of permeate reuse: Blue RD-S (referred as FB), Brilliant Red S-RGL 200 (FR), Brilliant Yellow RD-E 0.5 (FY), Marine Blue S-2GRL 200 (FM), Rubine RD-GFL 200 (FRU), Scarlet RD-S 0.5 (FS), Black BLN 200 (FBL), Yellow-Brown S-2RFL 150 (FYB) and Blue E-BL 150 (FB150). Figure 7.1 shows the available structures of the dyes FYB, FRU, FB150, and FR. The structures of the other dyes have not been already published.

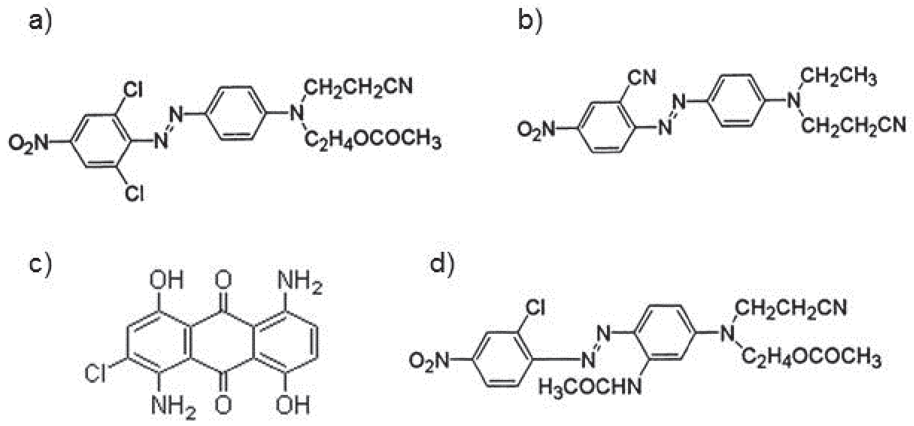

Figure 7.1- Chemical structure of a) Yellow-Brown S-2RFL 150 (FYB), b) Rubine RD-GFL 200 (FRU), c) Blue E-BL 150 (FB150), d) Brilliant Red S-RGL 200 (FR)

Sodium hypochlorite solution (6-14% active chlorine) acquired from Sigma-Aldrich was used for the membrane cleaning.

7.2.2- Wastewater

The textile effluents were supplied for the mill Vincolor (Terrassa, Spain). The effluents were collected after the dyeing processes during different days.

The dyeing process takes place in different steps as it is shown in Figure 7.2.

Figure 7.2- Scheme of the dyeing process

The main characteristics of the wastewater which was discharged into the homogenization-decantation treatment are presented in Table 7.1.

Table 7.1- Characteristics of wastewater discharged into the homogenization-decantation treatment

Parameter	Feed
pH	6.9
COD (mg·L^{-1})	806
Conductivity (µS·cm^{-1})	1825
Alkalinity (ºF)	15
Colour (mg Pt-Co·L^{-1})	300
SS (mg·L^{-1})	112
Hardness (ºF)	5
Cl^- (mg·L^{-1})	270
SO_4^{2-} (mg·L^{-1})	387

7.2.3- Homogenization-decantation treatment

The treatment was carried out in a homogenization tank (V=200m^3), where the wastewater generated in the different steps of the dyeing process, was discharged. The Hydraulic Retention Time (HRT) was 2.5 days. A screening process was applied to the effluents before the homogenization treatment in order to remove residual fibres.

A cylindro-conical clarifier (V=18 m^3) was placed after the treatment.

7.2.4- Ultrafiltration modules

In this study, two hollow fibre membranes modules were studied: UOF-1b (Motimo Membrane Technology, China) and UOF-4 (Motimo Membrane Technology, China), referred herein after as U-1b and U-4, respectively. In Table 7.2 are described the main characteristics of these membranes.

Table 7.2- Membrane characteristics

Membrane	Pore size (μm)	Membrane Surface (m^2)
U-1b	0.04	0.5
U-4	0.03	40

Two pilot plants were built to accommodate the membrane modules, according to the geometry and specifications of each membrane (Figure 7.3).

The pilot 1 was equipped with U-1b membrane. It was fed by a 100 L tank. Peristaltic pumps were used for feed, permeate, and concentrate effluents. The pilot operated in cycles of 15 minutes of filtration and 30 seconds of backwashing with permeate. The pilot 2 (Figure 4) was a semi-industrial system with U-4 membrane. Before the membrane module, two meshes (500 and 200 μm) were placed to remove the high particle size. The volume of feeding tank was 1000L. The membrane worked in cycles of 30 minutes of filtration and 30 seconds of backwashing with permeate.

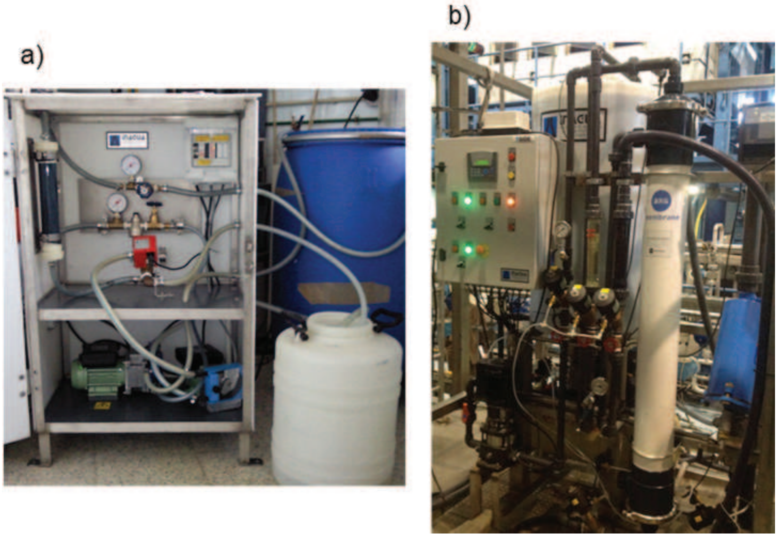

Figure 7.3 – Ultrafiltration modules: a) Pilot 1 with U-1b membrane, b) Semi-industrial system

Finally, after each filtration process, the membranes were cleaned with a sodium hypochlorite solution (5 mg·L^{-1}).

7.2.5- Analytical methods and measurements

The permeate flux was determined to evaluate the membrane fouling. It was determined by measuring the permeate volume collected in a certain period and using the equation 7.1:

$$J = \frac{V}{A \cdot \Delta t} \qquad (7.1)$$

Where J is the permeate flux (L·m^{-2}·h^{-1}), A is the effective area of the membrane (m^2) and V is the collected volume in a time interval Δt (L·h^{-1}).

COD was determined according to the method 5220C recommended by American Public Health Association [7.25]. The COD reduction (R_{COD}) was calculated using the equation 7.2:

$$R_{COD} = \left(\frac{COD_f - COD_p}{COD_f}\right) \cdot 100 \qquad (7.2)$$

where COD_f and COD_p are the COD values in feed and permeate respectively.

The conductivity was measured following the method 2510 B [7.25] with a Conductimeter GLP 31 (CRISON). The pH was determined according to the method 4500 H$^+$B [7.25] using a pHmeter GLP 21 (CRISON).

Suspended solids (SS), alkalinity and colour measurements were performed following standard methods (methods 2540D, 2320B and 2120B respectively) [7.25].

Water hardness was measured by complexometric titration with a standard solution of ethylenediamminetetraacetic acid (method 2340C) [7.25].

Finally, the determination of anions chloride (Cl^-) and sulphate (SO_4^{2-}) were carried out with Ion Chromatography ISC-1000 (Dionex) (method 4110B) [7.25].

7.2.6- Permeate reuse

The reuse dyeing tests were performed in a laboratory dyeing machine (Testherm 90-S) according to the mill procedure: 10 g of polyester fabric, dye concentration 0.5% o.w.f (over weight of fibre) and liquor ratio 1:15 (1 g fibre/15 mL dye bath).

Dyeings with only one dye (monochromies) were carried out with 100% permeate. For dyeings with a mixture of three dyes (trichromies), only 50% permeate was reused due to the different behaviour of each dye. Dyed fabrics were evaluated with respect to the corresponding reference (performed with softened tap water). The experiments were run in duplicate.

7.2.7- Dyed fabric evaluation

The quality of dyed fabrics was studied from colour differences ($DE_{CMC}(l:c)$) using a MINOLTA CM 3600d spectrophotometer. The difference in colour was determined in conformity with the Standard UNE-EN ISO 105-J03 [7.26]. Colour difference is calculated from the equation 7.3:

$$DE_{CMC(l:c)} = [(DL^*/lS_L)^2 + (DC^*_{ab}/cS_c)^2 + (DH^*_{ab}/S_H)^2]^{1/2} \qquad (7.3)$$

A dyeing is considered acceptable when the $DE_{CMC(l:c)}$ value is lower than 1.5, measured by MINOLTA CM 3600d spectrophotometer with respect to a reference sample.

7.3- Results and discussion

7.3.1- Homogenization-decantation treatment

Textile wastewater shows high variability and its main characteristics depend mainly on the dyeing process and on the type of fibre. Therefore, the homogenization-decantation treatment was applied to improve the membrane process as the membrane was exposed to a more homogenous feed.

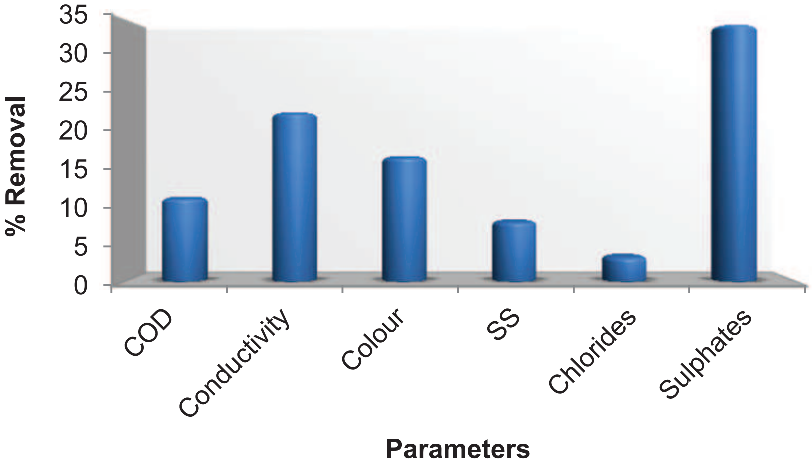

Figure 7.4- %Removal in the homogenization-decantation treatment

As can be seen in Figure 7.4, after the homogenization-decantation treatment, COD and colour removal were 10% and 17% respectively. This reduction is mainly due to the mixing of the different effluents, causing a dilution of the different compounds present in the wastewater. The Cl^- concentration remained almost constant and the SO_4^{2-} removal was 34%, which provided 23% conductivity reduction. This phenomenon could be attributed to the precipitation of sulphate and calcium ions present in the effluent producing the salt. The alkalinity and hardness values were also lower after the treatment.

The clarifier reduced 8% suspended solids. The low efficiency of the clarification process can be attributed to the effect of surfactants in the effluent, which are used as auxiliary agents for dyeing and washing processes.

The homogeneous effluent was finally treated with U-1b membrane.

7.3.2- Membrane treatment

Pilot 1 with U-1b membrane

After homogenization-decantation treatment, three effluents (referred as E1, E2 and E3) were treated by means of an ultrafiltration membrane lab pilot. The trans-membrane pressure was set at 0.2 bar. The permeate flux remained constant at 10 $L \cdot m^{-2} \cdot h^{-1}$ during the experiment (90 minutes). The membrane fouling has been reported as a major problem to the further application of UF technology in wastewater treatment [7.27], because it produces a reduction in the permeability and consequently the maintenance cost of the membrane is increased and its life time is reduced [7.17].

The membrane material is an important factor in the membrane fouling. In general, polymers such as PVDF, polysulfone (PS), polyacrylonitrile (PAN) and cellulose triacetate (CA) are employed to design membranes. The material provides different characteristics to the membranes: pore size, porosity and hydrophobicity [7.28, 7.29]. Although PVDF membranes have hydrophobic characteristics [7.30] and therefore they have a certain tendency of fouling, they have been widely used due to their thermal stability and resistance to corrosion from many chemicals and organic compounds [7.30, 7.31]. In addition, PVDF ultrafiltration membranes have shown percentage of dye retention and COD removal up to 90% when they are applied to treat textile wastewater [7.32]. In this study, the low fouling observed with this pilot showed the feasibility of applying PVDF membranes to treat textile wastewater.

The efficiency of the membrane process was determined with the permeate characterization (referred as P1, P2 and P3). Their main characteristics and the efficiency of the process are shown in Table 7.3.

Table 7.3- Effluents characterization and efficiency in the treatment with U-1b membrane

Parameter	**E1**	**P1**	**%**	**E2**	**P2**	**%**	**E3**	**P3**	**%**
pH	7.5	7.9	-	7.6	7.6	-	7.4	7.5	-
COD ($mg\cdot L^{-1}$)	732	237	67.6	553	319	42.3	864	275	68.2
Conductivity ($\mu S\cdot cm^{-1}$)	1426	1378	3.4	1383	1404	-	1429	1475	-
Alkalinity (ºF)	14	14	-	14	14	-	14	14	0.0
Colour (mg Pt-Co$\cdot L^{-1}$)	250	200	20.0	300	250	16.7	300	200	33.3
SS ($mg\cdot L^{-1}$)	161	2	98.8	44	2	95.5	309	2	99.4
Hardness (ºF)	2	2	-	2	2	-	2	2	-
Cl^- ($mg\cdot L^{-1}$)	254	249	2.0	291	284	2.4	256	242	5.5
SO_4^{2-} ($mg\cdot L^{-1}$)	250	237	5.2	276	259	6.2	244	236	3.3

From Table 7.3 it can be concluded that about 60% COD decrease and 20% colour removal were achieved. During the dyeing process different auxiliary products are employed. For example, a mixture of organic acids is added as a buffer, to maintain the pH constant. The membrane can retain these products resulting in a reduction of COD and also in an increase of pH. Also, suspended solids were completely removed with the membrane treatment. The Cl^- and SO_4^{2-} removals were about 3% and 5% respectively. It is important to highlight that the UF membranes cannot retain ions.

Finally, conductivity, hardness, alkalinity did not change with respect to the initial effluents.

According to results of section 3.1 and 3.2.1, the combination of homogenization-decantation and PVDF ultrafiltration was suitable to treat textile wastewater as it reduced all the studied parameters, except the pH which remained practically constant (Figure 7.5).

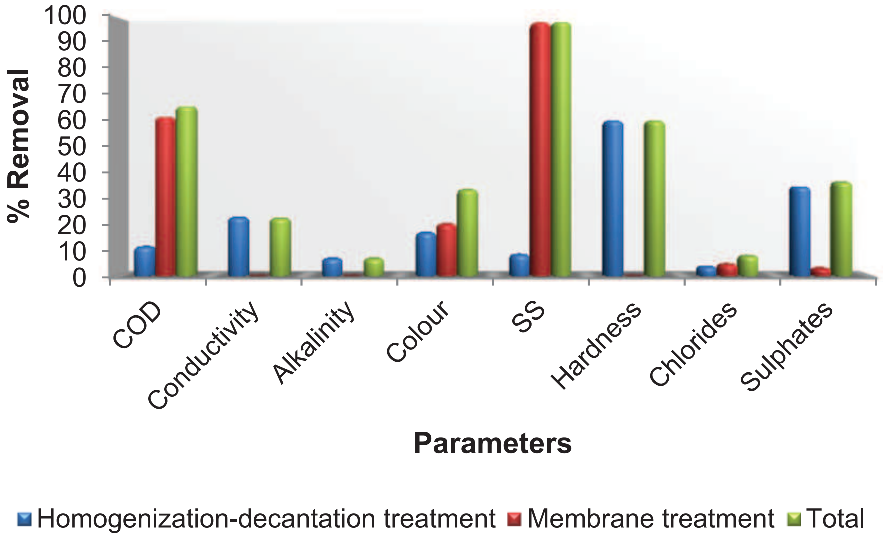

Figure 7.5- % Removal in the different treatments

At the end of both treatments, the COD removal was 66% and colour reduction was about 30%. The highest efficiency was obtained with the suspended solids (98%). The decrease in the conductivity was mainly due to the reduction of sulphate ions obtained in the homogenization-decantation treatment.

Semi-industrial system

On the basis of the promising results obtained at lab scale, the membrane behaviour was tested at semi-industrial scale during 2 days with the pilot 2. The trans-membrane pressure was also set up at 0.2 bar. A constant permeate flux of 15 $L \cdot m^{-2} \cdot h^{-1}$ was obtained. As in the case of pilot 1, membrane fouling was not observed at the working conditions.

During this study, two effluents (E4 and E5) were treated. The efficiency of the membrane process was also determined with the permeate characterization (P4 and P5). Their main characteristics and the efficiency of the process are shown in Table 7.4.

Table 7.4- Effluents characterization and efficiency in the membrane treatment with U-4 membrane

Parameter	**E4**	**P4**	**%**	**E5**	**P5**	**%**
pH	7.4	7.7	-	7.4	7.8	-
COD (mg·L^{-1})	509	236	53.6	648	236	63.6
Conductivity (µS·cm^{-1})	1521	1518	0.2	1557	1518	2.5
Alkalinity (ºF)	17	16	5.9	17	16	5.9
Colour (mg Pt-Co·L^{-1})	300	150	50.0	300	250	16.7
SS (mg·L^{-1})	74	2	97.3	118	2	98.3
Hardness (ºF)	3	2	33.3	2	2	-
Cl^- (mg·L^{-1})	226	218	3.5	270	264	2.2
SO_4^{2-} (mg·L^{-1})	240	229	4.6	268	253	5.6

At the end of the process, 60% of COD removal was achieved. Colour removal obtained was 33%, higher than with U-1b membrane. This was due to the pore size, which in this membrane is smaller. As in pilot 1, the suspended solid were effectively removed. Regarding the ions, they passed through the membrane to the permeate. It can be noticed that the permeate characterization showed similar results than the lab pilot (section 3.2.1), which indicated that the treatment could be scaled to industrial scale.

7.3.3- Permeate reuse

The treated effluents were used in order to study the feasibility of the permeate reuse. Monochromies were carried out with 100% of the permeate. Dyeings obtained were evaluated with respect to a reference dyeing (with softened tap water). Their colour differences ($DE_{CMC\ (2:1)}$) are shown in Table 7.5.

Table 7.5- Colour differences for monochromies

Dye	DL	DC	DH	$DE_{CMC(2:1)}$
FB	0.55 0.43	-0.09 -0.02	-0.40 -0.16	0.68 0.46
FS	-0.15 0.00	-0.11 -0.24	0.38 0.26	0.42 0.35
FY	-0.71 -0.60	-0.25 -0.65	-0.89 -0.52	1.16 1.03
FR	0.13 0.07	-0.27 -0.20	-0.59 -0.52	0.66 0.56
FYB	-0.35 -0.36	0.23 0.23	-0.49 -0.49	0.65 0.65
FB150	0.79 1.22	-0.96 -0.83	-1.76 -1.86	2.15 2.37
FM	-1.10 -0.89	-0.19 -0.12	0.92 0.78	1.45 1.19
FBL	0.24 -0.02	-0.34 -0.48	-0.31 -0.39	0.52 0.62
FRU	-0.65 -0.51	-0.22 -0.28	-0.15 0.03	0.70 0.58

As can be seen, all $DE_{CMC(2:1)}$ except the FB150 dye were lower than 1.5, which is the maximum value accepted by the quality control of mill. It is important to highlight that FB150 is an anthraquinone dye, with a compact aromatic ring structure, which may interact with the residual compounds of the permeate. FY and FM showed $DE_{CMC(2:1)}$ close to 1.5, mainly due to DL and DH values.

The reuse of the permeate in dyeing processes with trichromies was also studied. The trichromies were made with three of the following dyes: FR, FY, FRU, FYB and FB150. Taking into account the results of FB150 in monochromies, the trichromies dyeings were performed with 50% permeate and 50% clean water. Dyeings were found to be acceptable, as in all cases $DE_{CMC(2:1)}$ were clearly lower than 1.5 (Table 7.6). In this sense, further studies could be done to establish the maximum percentage of permeate that can be reused and fulfil the acceptance criteria.

Table 7.6- Colour differences for trichromies

Colour Dyed	**DL**	**DC**	**DH**	**$DE_{CMC(2:1)}$**
Purple	-0.41 0.37	-0.57 0.60	0.08 -0.07	0.71 0.70
Beige	-0.14 0.08	-0.30 -0.07	-0.70 -0.81	0.78 0.82
Red	-0.38 0.00	-0.63 -0.85	0.04 0.07	0.74 0.85
Blue-gray	-0.50 -0.20	0.15 -0.30	0.49 0.36	0.71 0.51
Light gray	-0.13 -0.26	-0.23 -0.32	-0.70 -0.46	0.75 0.62

The high water consumption in the industry and their scarcity in certain regions have caused the increase of water cost. In addition, the new environmental policies are focused on water recycling and reuse. Wastewater reuse involves both environmental and economic benefits. On the one hand it decreases the discharged of pollutant into the environment and on the other hand it allows to reduce water consumption and cost of depuration processes.

According to the company selected for this study, more than 5 m^3 are required to produce 160m of fabric. The price of municipal water is 2.64 €/m^3 (including wastewater discharge cost). Therefore, the permeate reuse can save up to 13€ per 160m of fabric produced.

7.4- Conclusions

Textile effluents were treated by means of homogenization-decantation and membrane treatments.

The combination of two treatments provided almost 66% and 30% of COD and colour removal respectively. The membrane treatment was shown to be scalable at semi-industrial scale and no fouling was observed during the experiments.

Finally, it can be stated that results of the permeate reuse are promising for the textile industry. When 100% permeate was reused, the colour differences for monochromies were into the acceptance range, except for the FB150 dye. With 50% permeate reuse, all trichromies fulfil the quality criteria. As the textile industry consumes large amounts of water, the homogenization-decantation followed by membrane treatment is an advantageous combination from both the environmental and economical points of view.

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CHAPTER 8:

Photocatalytic membrane reactor for the removal of C.I. Disperse Red 73

PHOTOCATALYTIC MEMBRANE REACTOR FOR THE REMOVAL OF C.I. DISPERSE RED 73

This chapter shows the results obtained in the treatment of synthetic effluents containing C.I. Disperse Red 73 by means of photocatalytic membrane treatment. To optimize the process, the treatment was carried out at different pH, initial dye concentrations and photocatalyst loading. The behaviour of the membrane was also tested.

This study was carried out in the European Institute of Membrane (Montpellier-France) with the financial support of AGAUR (CTP2012-00023). In addition, this work has been accepted for publication in Materials:

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Abstract

After the dyeing process, part of dyes used to colour textile materials are not fixed into the substrate and are discharged into wastewater as residual dyes. In this study, a heterogeneous photocatalytic process combined with microfiltration has been investigated for the removal of C.I. Disperse Red 73 from synthetic textile effluents. The titanium dioxide (TiO_2) Aeroxide P25 was selected as photocatalyst.

The photocatalytic treatment achieved between 60 and 90% of dye degradation and up to 98% chemical oxygen demand (COD) removal. The influence of different parameters on photocatalytic degradation was studied: pH, initial photocatalyst loading and dye concentration. The best conditions for dye degradation were pH 4, initial dye concentration of 50 $mg \cdot L^{-1}$ and a TiO_2 loading of 2 $g \cdot L^{-1}$.

The photocatalytic membrane treatment provided a high quality permeate, able to be reused.

Keywords: Photocatalytic membrane reactor; titanium dioxide; C.I. Disperse Red 73; UV light; polysulfone membrane; microfiltration

8.1- Introduction

Synthetic dyes are widely used in textile industry. Approximately 800,000 tons of dyes are produced annually worldwide [8.1]. However, about 15% of the dyes consumed are lost in the textile effluents [8.2]. Textile wastewater is characterized by its high chemical oxygen demand (COD), salinity, variable pH values and high temperature [8.3–8.6]. In addition, the presence of very low concentration of dyes in wastewater is highly visible [8.7].

The dyes are classified according to how they are applied in the dyeing process. The most common dyes are reactive, acid and disperse. Reactive dyes are water-soluble mainly applied to cotton. Acid dyes are water-soluble applied from an acidic solution to nylon, wool, silk, and some modified acrylic textiles. Finally, disperse dyes are used for polyesters fibres. They are not water-soluble, so they are applied as dispersion in the dyeing process [8.8].

Many processes have been studied to treat textile wastewater in order to remove colour. The most used treatments are physical and chemical techniques such as coagulation-flocculation, adsorption or membrane processes. Nonetheless, these treatments do not destroy the dye and a post treatment, such as incineration, is required [8.9].

In recent years, the interest for advanced oxidation processes (AOPs) has increased, especially heterogeneous photocatalytic processes. Titanium dioxide (TiO_2) is the most used photocatalyst due to its good photocatalytic activity, nontoxicity, chemical inertness and low cost [8.10].

Heterogeneous photocatalytic process starts when a semiconductor absorbs photons whose energy is equal or greater than its band gap (Eg = 3.2 eV for TiO_2). This adsorption enables the promotion of an electron (e^-) from the valence band (vb) of the semiconductor to the conduction band (cb), generating holes (h^+) in valence band [8.11]. The recombination of the electron and the hole must be prevented.

The electron can reduce the organic species or react with the O_2, which is either adsorbed on the semiconductor surface or dissolved in water, reducing it to superoxide radical anion ($O_2^{-\cdot}$). The hole can oxidize the organic molecule or react with OH^- or H_2O, oxidizing them into $OH^\cdot$ radicals [8.12].

The highly oxidant species generated during the photocatalytic process are responsible for the photodegradation of organic substrates such as dyes. The process can be expressed according to reactions (8.1)-(8.8) [8.11, 8.13]:

$$TiO_2 + h\nu(UV) \rightarrow TiO_2(e_{CB}^- + h_{VB}^+) \quad (8.1)$$

$$TiO_2(h_{VB}^+) + H_2O \rightarrow TiO_2 + H^+ + OH^\cdot \quad (8.2)$$

$$TiO_2(h_{VB}^+) + OH^- \rightarrow TiO_2 + OH^\cdot \quad (8.3)$$

$$TiO_2(e_{VB}^-) + O_2 \rightarrow TiO_2 + O_2^{-\cdot} \quad (8.4)$$

$$O_2^{-\cdot} + H^+ \rightarrow HO_2^\cdot \quad (8.5)$$

$$\text{Dye} + OH^\cdot \rightarrow \text{degradation products} \quad (8.6)$$

$$\text{Dye} + h_{VB}^+ \rightarrow \text{oxidation products} \quad (8.7)$$

$$\text{Dye} + e_{VB}^- \rightarrow \text{redeuction products} \quad (8.8)$$

The oxidation species responsible for organic substrates degradation depends on experimental conditions (pH, pollutant, concentration, etc.). The dominant oxidative species can be identified adding different specie quenchers [8.14].

The main limitation of the photocatalytic process is the recovery of the photocatalyst from the solution. This problem can be solved by doing a coupling of photocatalysis with membrane processes [8.15]. In addition, this coupling enable the confinement of the photocatalyst in the reaction environment, the control of the residence time of the molecule in the reactor by means of the transmembrane flux, and the achievement of a continuous process with simultaneous photocatalyst and products separation from the reaction environment. Heterogeneous photocatalytic oxidation may be combined with different membranes processes, such as microfiltration (MF) [8.16–8.19], ultrafiltration (UF) [8.20–8.22], nanofiltration (NF) [8.23, 8.24] and direct contact membrane distillation (DCMD, MD) [8.10, 8.25, 8.26]. Photocatalytic membrane reactors (PMRs) described in the literature can be divided into two groups: (I) reactors with photocatalyst suspended in a feed solution and (II) reactors with photocatalyst supported on the membrane [8.27]. A comparison between PMRs with photocatalyst in suspension and with photocatalyst supported on a membrane purification of water contaminated with dyes was reported by Grzechulska *et al.* [8.28]. The authors studied the degradation of three dyes: C.I. Acid Red 18, C.I. Acid Yellow 36 and C.I. Direct Green 99. Results showed that the time of discolouration was shorter in the suspended system than in case of the supported photocatalyst.

Several studies with photocatalyst in suspension have been reported to treat different solutions containing dyes. In general, colour removal of reactive dyes [8.10, 8.29] and acid dyes [8.16, 8.30] have been widely investigated, but fewer studies have been carried out on disperse dyes despite they are used for dyeing polyester fibres which is the most consumed fibre in the world. Due to the high worldwide consumption of polyester, the interest for the disperse dyes and their associated environmental problems has increased in the last years [8.31]. It is important to highlight that after the dyeing process, the dye is not totally adsorbed by polyester and it is discharged into wastewater. A proper removal of disperse dye in the effluent would allow reuse the water, which is an important advantage from the economic and environmental point of view.

Taking into account these considerations, this paper investigates the potential use of a photocatalytic membrane reactor for the degradation of C.I. Disperse Red 73 (DR73) using TiO_2 in suspension as photocatyst. In order to optimize the process, the effect of several parameters such as pH, initial dye concentration and TiO_2 loading on photodegradation efficiency was tested. As far as we know, no studies based on the degradation of disperse dyes by means of photocatalytic membrane reactor have been carried out.

8.2- Experimental procedures

8.2.1- Reagents

The photocatalyst used in this study was commercially available TiO_2 powder (Sigma-Aldrich). The average diameter of TiO_2 particles was 21 nm and BET was $50 \pm 15\ m^2 \cdot g^{-1}$.

C.I. Disperse Red 73 was supplied by Archroma (Figure 8.1). Its molecular weight is $348\ g \cdot mol^{-1}$.

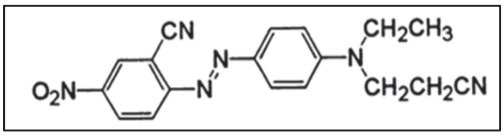

Figure 8.1- Chemical structure of Disperse Red 73 (DR73)

To determine the dye concentration, N,N-dimethylformamide (purity 99%, Merck) and deionised water were employed as solvents.

The pH of synthetic effluents containing DR73 with 1 M solutions of NaOH or HCl.

8.2.2- Photocatalytic membrane experiments

The photocatalytic membrane reactor was equipped with a photocatalytic reactor (2.2 L) and an outside membrane module (0.3 L) (Figure 8.2).

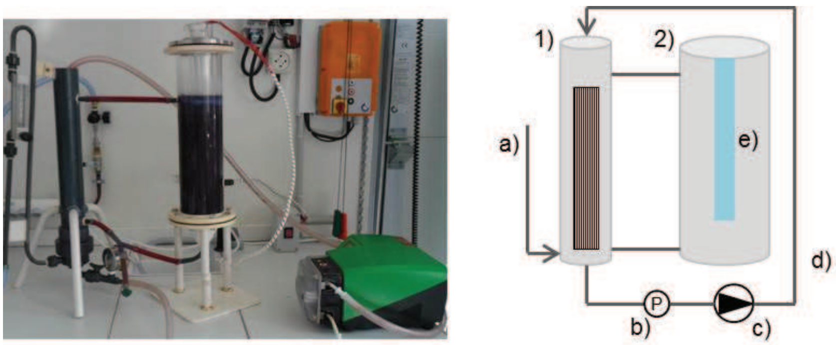

Figure 8.2- Membrane Photocatalytic Reactor: 1) Membrane reactor, 2) Photocatalytic reactor, a) air inlet, b) pressure measurement, c) peristaltic pump, d) permeate and e) UV lamp.

Hollow fibre membrane module manufactured by Polymem Company (Toulouse, France) was used. Its main specifications and operation characteristics are shown in Table 8.1.

Table 8.1- Membrane characteristics

Material	Polysulfone
Nominal pore size (µm)	0.2
External diameter (mm)	1.4
Fibre length (cm)	32
Surface area (m^2)	0.3
Hydraulic resistance (m^{-1})	$4 \cdot 10^{11}$
Pure water permeability at 20ºC ($L.h^{-1}.m^{-2}.bar$)	227

Air was injected at a flow rate of 200 $L \cdot h^{-1}$ through a diffuser placed at the bottom of membrane module. This injection of air enables to realize an air lift and then the liquid go from the membrane module to the photoreactor. This circulation allowed the homogenisation of the solution.

A peristaltic pump (Watson-Marlow) was used to fix the permeate flux at 20 $L \cdot h^{-1} \cdot m^{-2}$ and to recirculate the permeate to the membrane module.

The light source was a 24W UV lamp (Philips PL-L 24W/10/4P), with a maximum wavelength of 365nm, located in a quartz vessel in the centre of the photocatalytic reactor.

To simulate the effluents discharged after the dyeing process, solutions of DR73 were prepared in deionised water. Before photodegradation, the dye-TiO_2 mixture was kept for 30 min in the dark in order to allow adsorption of the dye molecules on the TiO_2 surface. The effect of different parameters on the process was tested. Photocatalytic experiments were conducted at different pH (4, 6 and 10), different amounts of TiO_2 (from 0.5 to 2 $g \cdot L^{-1}$) and different initial dye concentration (50, 75 and 100 $mg \cdot L^{-1}$).

8.2.3- Analytical methods and measurements

The membrane fouling was evaluated by recording the ΔP and measuring the normalized water permeability (equation 8.9).

$$Lp_{(20ºC)} = \frac{J}{\Delta P} \cdot \frac{\mu_{(20ºC)}}{\mu_T} \qquad (8.9)$$

where J is the permeate flux ($m^3 \cdot m^{-2} \cdot s^{-1}$), ΔP is the transmembrane pressure (Pa), $\mu_{(20ºC)}$ is the viscosity of the fluid at 20ºC (Pa·s) and μ_T is the viscosity of the fluid at working temperature (Pa·s).

Samples were taken from photocatalytic reactor and then centrifuged with Sigma 3-16k centrifuge in order to separate the TiO_2 particles from the solution.

Dye removal (R_{dye}) was calculated from concentrations of feed and photocatalytic reactor using Equation 8.10:

$$R_{dye} = \left(\frac{C_f - C_p}{C_f}\right) \cdot 100 \qquad (8.10)$$

where C_f and C_t are the concentrations of dye in feed and photocatalytic reactor at time t, respectively. The dye was dissolved in a solution of water/N,N-dimethylformamide (1/1, v/v), and its concentration was determined with UV-Vis spectrophotometer UV-2401 (Shimadzu Corporation) at the maximum wavelength of the visible spectrum (λ_{max}=528nm).

COD was determined according to the method 5220 D recommended by American Public Health Association [8.32]. The COD reduction (R_{COD}) was calculated using the Equation 8.11:

$$R_{COD} = \left(\frac{COD_f - COD_p}{COD_f}\right) \cdot 100 \qquad (8.11)$$

where COD_f and COD_p are the COD values in feed and permeate respectively.

The pH was determined according to the method 4500 H^+B [8.32] using a pH meter Ion 510 (Entech Instruments).

8.3- Results and discussion

8.3.1- Previous studies

Some dyes can be degraded under UV irradiation without photocatalyst. Before studying the photocatalytic degradation of DR73, the stability of the dye under UV light was tested (Fig. 8.3).

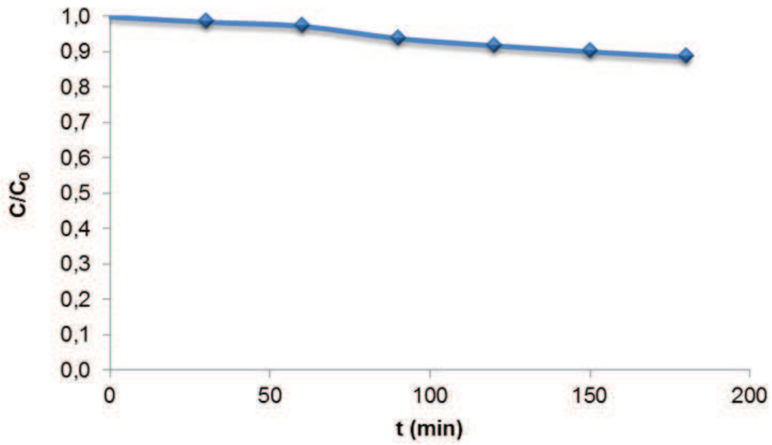

Figure 8.3- DR73 degradation after 180 minutes of UV irradiation (λ = 365 nm)

No significant dye degradation was observed after 180 minutes of UV irradiation. It is important to highlight that certain disperse dyes are generally characterized their high light fastness [8.33]. In the case of DR73 dye, its light fastness is 6 (value 1 indicates very low fastness and 8 corresponds to high fastness).

8.3.2 Photocatalytic degradation of DR73

<u>*Effect of initial pH*</u>

The pH affects both the surface properties of the photocatalyst and the physical properties of dye solution, such as dye aggregation or dispersion. The effect of the pH was studied using a solution of 75 mg·L^{-1} of DR73 and a TiO_2 dosage of 1 g·L^{-1}.

Comparing experiments carried out at different pH values (4, 6 and 10), it can be observed that, after 180 minutes of UV irradiation, the highest dye degradation (90%) was achieved at pH 4, whereas that at pH 10 only 61% of dye degradation was obtained (Figure 8.4).

The point of zero charge (pzc) of the TiO_2 Aeroxide P25 is reported to be at pH 6.5. Thus, the TiO_2 surface is positively charged in acidic medium (pH<6.5) and it is negatively charged in alkaline medium (pH>6.5) as is shown in Reactions 8.12 and 8.13 [8.34].

When pH<pzc: $TiOH + H^+ \leftrightarrow TiOH_2^+$ (8.12)

When pH>pzc: $TiOH + OH^- \leftrightarrow TiO^- + H_2O$ (8.13)

At pH lower than 6.5, the TiO_2 positively charged attracts the negatively charged species from the solution, facilitating their photodegradation. The dye studied in this project is negatively charged in water solution.

Although the mechanism of degradation was not the aim of this work, several studies [8.11, 8.14] have reported that in acidic medium holes are the major oxidation species whereas at high pH hydroxyl radicals are considered the predominant species.

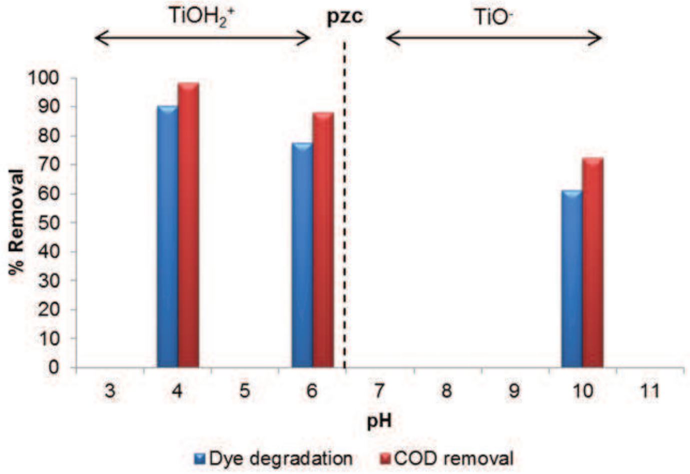

Figure 8.4- Influence of pH solution on the degradation of DR73

As expected, the COD removal followed the same trend that the degradation of dye. About 98% of COD removal was obtained at pH 4, 88% at pH 7 and 72% at pH 10.

Several authors [8.35, 8.36] reported that in very acidic medium, the strong adsorption of the dye particles on the TiO_2 surface could reduce the active centres on the photocatalyst surface. In the other hand, in alkaline medium, the dye particles are hardly adsorbed on the catalyst surface. In addition, the dyeing process with disperse dyes is carried out at pH between 5.5 and 6.5 [8.33]. A change of pH implies an increase in the conductivity of the effluents, which is one of the main problems of textile wastewater. For these reasons, the pH 6 was selected for the subsequent studies.

Effect of photocatalyst loading

To determine the influence of the photocatalyst loading in the process, a solution of 75 $mg \cdot L^{-1}$ at pH 6 was used.

As can be observed in Figure 8.5, the COD removal ranged from 70 to 90% for the tested concentration of TiO_2. The photocatalyst loading of 0.5 $g \cdot L^{-1}$ and 1 $g \cdot L^{-1}$ provided similar dye degradation (about 75%). However, when 2 $g \cdot L^{-1}$ of TiO_2 was used, a remarkable increase of the dye degradation (90%) was observed.

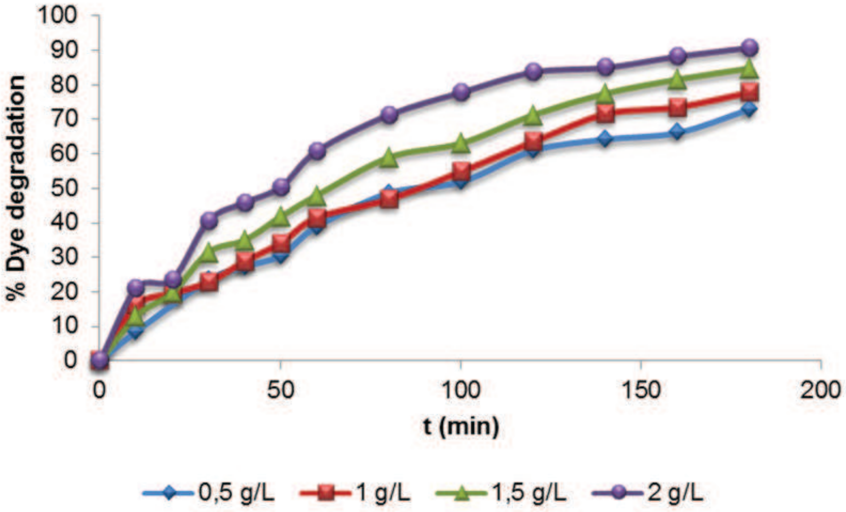

Figure 8.5- Evolution of the dye degradation for different TiO_2 loading (initial dye concentration=75 mg·L^{-1})

Nonetheless, it is important to highlight that an excess of photocatalyst can produce a light screening, which causes a reduction in the surface area exposed to irradiation and thus could reduce the photocatalytic efficiency of the process [8.37].

Taking into account these considerations and to prevent membrane fouling, 1 g·L^{-1} of TiO_2 was selected for subsequent experiments.

Effect of initial dye concentration

The effect of the dye initial concentration was tested at constant TiO_2 dosage (1 g·L^{-1}) and pH 6, with dye concentrations ranging from 50 to 100 mg·L^{-1}. As can be observed in Figure 8.6, the dye degradation decreased (from 87% to 62%) when the dye concentration increased.

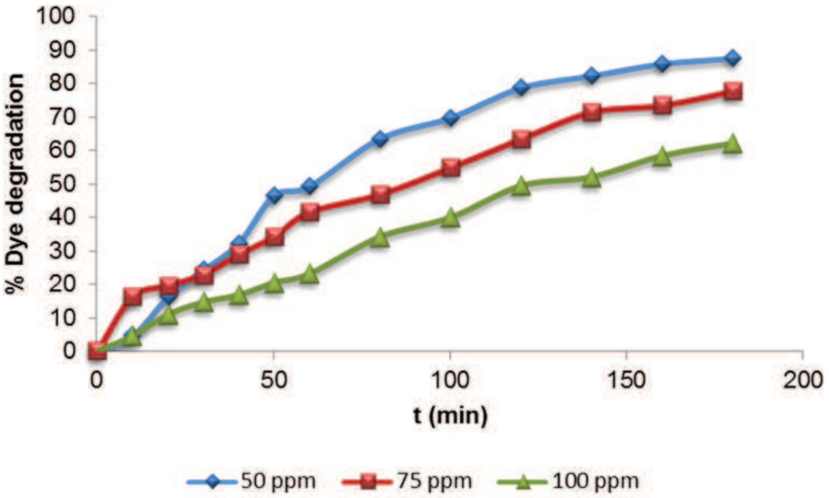

Figure 8.6- Influence of the initial dye concentration on dye degradation (1 g·L^{-1} TiO$_2$)

The higher the dye concentration, the higher the adsorption of the dye on the photocatalyst surface, which produced a decrease of OH$^-$ adsorption and, consequently, diminished the formation of OH$^\cdot$ radical, the principal oxidant in the photocatalysis process [8.38]. In addition, at high dye concentration, the UV light might be absorbed by dye instead of the TiO$_2$ particles. Similar results have been reported for the photocatalytic degradation of reactive [8.29, 8.39] and direct dyes [8.40, 8.41] and pharmaceutical compounds [8.42, 8.43]. Liang *et al.* [8.42] observed that the photodegradation reached a saturation limit at high reactant concentration.

Regarding the COD removal (Fig. 8.7), all experiments showed COD decrease higher than 80%.

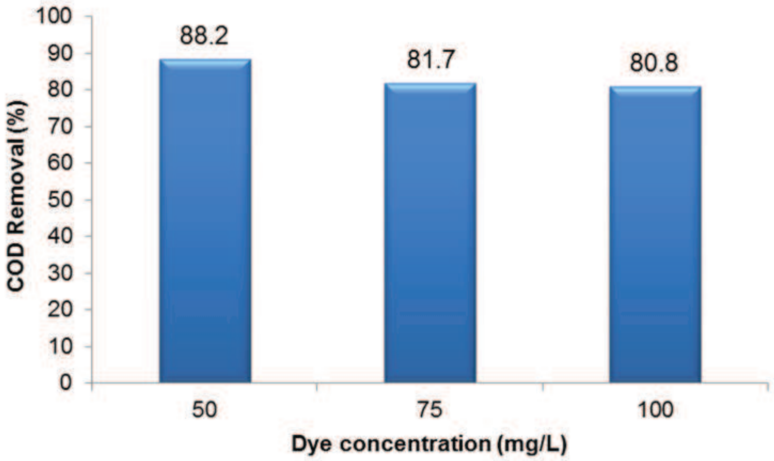

Figure 8.7- Influence of the dye concentration COD removal (1 g·L^{-1} TiO$_2$)

The effect of the initial concentration of dye on the photocatalytic process can be described by pseudo-first-order kinetic with respect to the dye concentration. In general, photocatalytic degradation has a kinetic according to Langmuir-Hinshelwood (Equation 8.14) [8.15, 8.16]:

$$r = \frac{dC}{dt} = -k \cdot C \qquad (8.14)$$

Integrating Equation (8.14) with respect to time t, it can be simplified to the pseudo-first order kinetic model equation (8.15):

$$ln\left(\frac{C_0}{C_t}\right) = k_{app} \cdot t \qquad (8.15)$$

Where, dC/dt is the rate of dye degradation (mg·L^{-1}·min^{-1}), C_0 and C_t are initial concentration and concentration at time t of the dye (mg·L^{-1}) respectively and k_{app} is the degradation kinetic rate (min^{-1}) [8.44]. The k_{app} was calculated from the slope of logarithmic concentration values versus time of treatment (Figure 8.8).

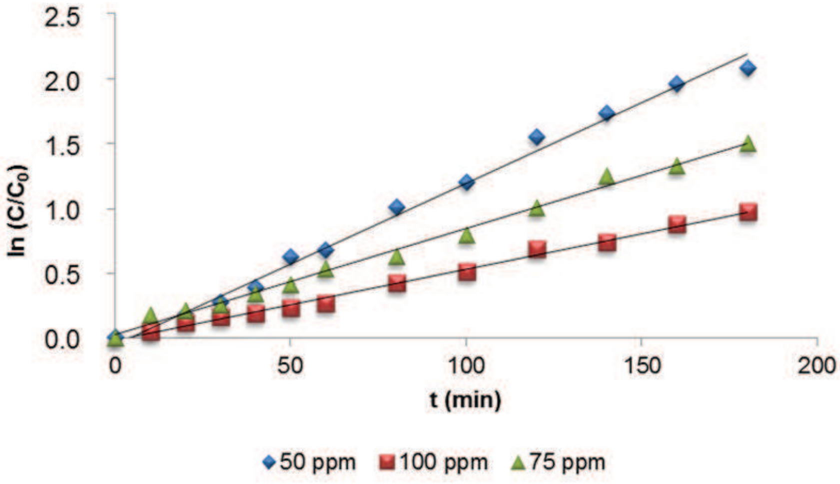

Figure 8.8- Relationship between ln (C/C_0) and treatment time (t=180min)

The results indicated that the degradation of DR73 fitted first order kinetics and it followed the Langmuir-Hinshelwood model (Table 8.2). The value of k_{app} decreased with the increasing of the dye concentration.

Table 8.2- The pseudo-first-order degradation rate constants of DR73 at different initial dye concentrations

Dye concentration (mg·L^{-1})	**K_{app} (min^{-1})**	**r^2**
50	0.0124	0.9937
75	0.0082	0.9934
100	0.0055	0.9943

8.3.3 Photocatalytic membrane treatment

Permeate quality

A synthetic effluent containing 75 mg·L^{-1} DR73 and 119 mgO$_2$·L^{-1} COD was treated by means of a photocatalytic membrane reactor. The characterization of the permeate after 180 min of treatment showed dye concentrations lower than 0.5 mg·L^{-1} and COD values of about 10 mg·L^{-1}. A full mineralization of the dye would probably be achieved with longer treatment, but with high associated cost. However, our previous studies

[8.45] have shown that permeates with higher residual organic matter content are able to be successfully reused in new dyeing processes with disperse dyes. Due to the high water consumption in the textile industry, water reuse is an important challenge with advantage from both economic and environmental points of view.

Effect of photocatalytic treatment on membrane fouling

The maintenance of the membrane is also an important point to take into account for the industrial application of the technology.

Generally, a significant fouling is observed when photocatalysis process is combined with pressure driven membrane processes, such as MF and UF [8.46, 8.47] which results in either a flux decrease or a ΔP increase. To establish the factor affecting the membrane fouling, the ΔP was recorded with three effluents: pure water, water containing 1 $g \cdot L^{-1}$ of TiO_2 and a dye solution of 75 $mg \cdot L^{-1}$.

It was observed that when the solution with photocatalyst was treated, the pressure increased with respect to the ΔP obtained with pure water, although it remained constant during the whole experiment. Thus, the presence of the photocatalyst produced an initial fouling on the membrane that did not increase along the experiment. According to Damodar *et al.* [8.29] this result could indicate that the TiO_2 particles formed a very porous cake layer on the membrane surface. Finally, when the dye solution was treated, an increase of pressure was observed during the experiment indicating the formation of a dye deposit.

During the photocatalytic treatment the pH was found to be the most influent parameter on the membrane fouling. At pH 10, an important increase of the ΔP was observed whereas that at pH 4 the fouling decreased. The high pH could influence the stability of the dye dispersion producing an agglomeration of the dye particles which size has an influence on fouling.

The efficiency of the cleaning process was determined from the normalized water permeability (NWP) after hydraulic cleaning carried out at the end of each experiment.

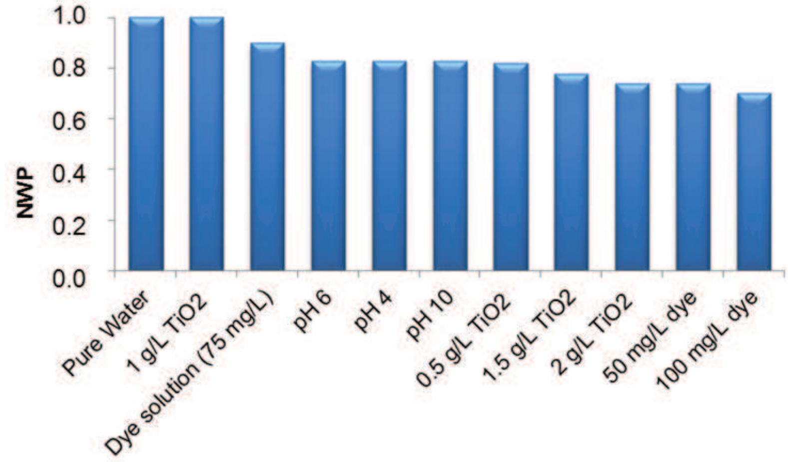

Figure 8.9- Evolution of normalized water permeability (NWP) for different experimental conditions

According to results shown in Figure 8.9, it can be stated that after the treatment of the dye solution, the water permeability of the membrane decreased about 10%. The dye particles were adsorbed on the membrane surface and they only could be completely removed after a chemical washing.

Despite the increase of ΔP observed in the experiment carried out at pH 10, the water permeability remained constant at any of the studied pH. This phenomenon indicated that the fouling observed in alkaline medium was only a physical process.

At the end of all experiments, the membrane water permeability was reduced of about 30%.

8.4- Conclusions

For C.I. Disperse Red 73 dye, the photocatalytic treatment provided degradation in the range of 60% to 90% and COD removal from 70% to 98%.

The effect of pH in the photocatalytic degradation of DR73 was tested and shows that the highest dye degradation was achieved at pH 4 whereas the lowest was at pH 10, which is in accordance with photocatalyst charge. The experiments carried out at different photocatalyst loading indicated that dye degradation increased when the photocatalyst concentration increased. From 50 to 100 mg·L^{-1}, the best results were obtained when the initial dye concentration was 50 mg·L^{-1}. As expected, the photocatalytic dye degradation followed the Langmuir-Hinshelwood model.

Finally, the photocatalytic membrane treatment provided an uncolored permeate (dye concentration lower than 0.5 mg·L^{-1}) with a low concentration of residual organic matter, which could be reused in new dyeing processes. This study thus demonstrates the feasibility of the coupling of photocatalysis and filtration for the treatment of azo dye wastewater.

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CHAPTER 9:

Conclusions

CONCLUSIONS

The different studies carried out in this work have demonstrated the feasibility of PVDF ultrafiltration membranes to both reuse permeates in new dyeing processes and recover concentrate in the case of indigo dye.

The main conclusions of this thesis are divided according to the type of dye studied:

1) Indigo dye

- ♣ In the analytical study, three methods were developed and validated for indigo dye determination. All of them met the established acceptance criteria regarding accuracy and precision.
- ♣ Among the three studied methods, the redox titration method was considered the most adequate for application at industrial scale due to its wider work range. In addition, it can be easily automated and enables the simultaneous quantitative determination of sodium dithionite and indigo dye.
- ♣ The membrane treatment showed to be efficient for the removal of indigo dye from wastewater.
- ♣ Successful recovery of indigo was achieved by means of PVDF ultrafiltration membranes. No fouling was observed with any of the studied membranes.
- ♣ The external hollow fibre module enabled to concentrate the dye up to 3 $g \cdot L^{-1}$. The submerged hollow fibre module allowed to obtain a concentrate with 20 $g \cdot L^{-1}$ indigo dye, which is the required concentration for automated dyeing processes.

- The laboratory study was extended to a semi-industrial system, which demonstrated that the combination of external and submerged PVDF membranes was able to treat industrial wastewater containing indigo dye.

- The dyeing study using the filtration concentrates completed the reuse cycle. Different dyeings were carried out with the indigo concentrated effluents. Fabrics dyed with 100% recovered indigo exhibited similar colour coordinates and fastness properties than the ones obtained with commercial dye.

2) Disperse dyes

- Synthetic effluents containing C.I. Disperse Orange 30 and C.I. Disperse Rubine 73 dyes were treated by means of PVDF ultrafiltration membrane at laboratory scale. No fouling was observed and results showed 97% dye removal and up to 92% COD decrease.

- Industrial textile effluents were treated by means of homogenization-decantation and laboratory PVDF ultrafiltration pilot plant. This hybrid treatment provided 68% COD reduction 33% and colour removal. As in the case of synthetic effluents, no fouling was observed in laboratory pilot plant after the ultrafiltration of industrial effluents.

- The membrane treatment showed to be scalable at semi-industrial level. Also in this case, no fouling was observed during the experiments with the semi-industrial pilot.

- The study of permeates reuse was carried out by performing fabric dyeings with nine different disperse dyes. When dyeing liquor was constituted by 100% permeate, the colour differences of dyed fabrics, with respect to references, were into the acceptance range for all monochromies, except the dye FB150. The reuse of 50% permeate, achieved to fulfil the quality criteria for the trichromies.

- ♣ Consequently, results of dyeings carried out with reused permeate are a very promising way to achieve a significant reduction of water consumption in the textile industry, which is one of the major water footprint sectors.

- ♣ Finally, a new hybrid treatment based on the combination of polysulphone membrane microfiltration and heterogeneous photocatalytic process was evaluated. The combined photocatalytic-membrane treatment was applied to the study of synthetic effluents containing C.I. Disperse Red 73.

- ♣ The best conditions for photocatalytic degradation of the dye were established: pH 4, initial dye concentration of 50 $mg \cdot L^{-1}$ and a TiO_2 loading of 2 $g \cdot L^{-1}$.

- ♣ The photocatalytic treatment provided a 60-90% dye degradation and COD removal from 70% to 98%.

- ♣ The efficiency of the photocatalytic treatment was clearly improved by combination with a membrane treatment. The membrane treatment enabled to separate the TiO_2 particles and provided very high quality permeate.

CAPÍTULO 10:

Recomendaciones

RECOMENDACIONES

Teniendo en cuenta los resultados obtenidos en esta tesis, se proponen las siguientes líneas de trabajo para futuras investigaciones:

1. Automatización del método analítico y del proceso de recuperación de índigo a escala industrial.
2. Estudio de otros materiales de membranas para la recuperación de índigo y estudio de su vida útil con el fin de comparar los resultados con los materiales usados en esta tesis y evaluar el material más adecuado para este proceso.
3. Ampliación del estudio a efluentes que contengan mezclas de colorantes sulfurosos y colorante índigo. Para ello serán necesarias las siguientes etapas:
    - Puesta a un punto de un método analítico que permita determinar la concentración de cada colorante en los efluentes.
    - Recuperación y separación de mezclas con colorante índigo y colorantes sulfurosos mediante combinación de membranas.
    - Estudio de la reutilización de los colorantes recuperados en nuevos procesos de tintura.
4. Estudio de la reducción electroquímica del colorante índigo con vistas a sustituir parcial o totalmente el empleo de hidrosulfito sódico.
5. Estudio de la influencia de la presencia de dispersantes en la reutilización de efluentes que contengan colorantes dispersos.
6. Tratamiento de colorantes reactivos mediante membranas de nanofiltración. Reutilización del permeado y tratamiento del concentrado obtenido mediante técnicas electroquímicas.

7. Estudio de los mecanismos de degradación de los colorantes textiles en los procesos fotocatalíticos.

8. Estudio de la combinación de procesos fotocatalíticos con técnicas electroquímicas para la degradación de colorantes. Evaluación de su reutilización.

9. Estudio de recuperación, regeneración y reutilización del TiO_2.

10. Degradación de colorantes textiles mediante procesos fotocatalíticos que utilicen luz solar.

11. Ampliación del estudio a otras industrias que generen efluentes poco biodegradables (farmacéutica, química...) y comparación con los tratamientos actuales. Evaluación de su reutilización en los diferentes procesos de la industria (fabricación del producto, refrigeración, lavado, etc.).

CAPÍTULO 11:

Bibliografía general

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