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

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A B S T R A C T

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 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.

1. Introduction

The textile industry consumes a large amount of water in their processes, especially in the dyeing and subsequent washing steps (Fersi et al., 2005). The wastewater generated is reported to be in the range of 21–377 m^3 per ton of textile products (Asghar et al., 2014). In addition, the wastewater generated from the textile industry is characterized by high colouration, biological oxygen demand (BOD), chemical oxygen demand (COD) and salinity (Riera-Torres et al., 2010).

Physico-chemical and biological processes are currently applied to treat textile wastewater (Blanco et al., 2013). 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 (Bes-Piá et al., 2005; Robinson et al., 2001). Chemical coagulation is a very common treatment but this method generates a sludge which requires an additional treatment to be destroyed (Sala and Gutiérrez-Bouzán, 2012). These methods are able to meet legislative requirements but they do not enable water reuse in textile processes (Barredo-Damas et al., 2010). Recently, there are an increasing number of studies based on industrial waste reuse (Huber et al., 2014; Sathishkumar et al., 2012) and on water reuse (Othman et al., 2014). In particular, advanced oxidation treatments have been applied to achieve the reuse textile wastewater (Li and He, 2013; Sala and Gutiérrez-Bouzán, 2014).

Membrane technology is also an attractive alternative to treat and reuse textile wastewater (Tahri et al., 2012; Zheng et al., 2013), 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 (Arnal et al., 2008; He et al., 2013; Sahinkaya et al., 2008). 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 (Roessler, 2004).

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 (Meksi et al., 2012; Vuorema et al., 2008).

About 15% of the indigo used is lost during the dyeing process (Vedrenne et al., 2012), but to our knowledge, only two studies have been published on indigo dye reuse after membrane technology

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treatment. Crespi (1989) reported the recovery of the residual indigo from washing wastewater by ultrafiltration membranes in the Belgian company UCO. Porter (1990) 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 (Zhang et al., 2014). 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 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.

2. Experimental

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.

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 20 °C. 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.

2.3. Ultrafiltration module

In this work, four hollow fibre 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 1 are described the main characteristics of these membranes.

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

Pilot 1 (Fig. 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 min of filtration and 30 s of backwashing with permeate.

Pilot 2 (Fig. 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 min of filtration and 30 s of backwashing with permeate.

Pilot 3 (Fig. 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 1000 L. 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 min of filtration and 30 s of backwashing with permeate and FP-T membrane worked in cycles of 15 min of filtration and 30 s of backwashing.

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}).

Table 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

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:

$$J\left(L/m^2\cdot h\right) = V/A\cdot\Delta t$$

where J is the volumetric flux, A is the effective area of the membrane and V is the collected volume in a time interval Δt.

Indigo removal was calculated from concentrations of feed and permeates using the following equation:

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

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 L^{-1}.

COD was determined according to the methods recommended by American Public Health Association (Standard Methods for the Examination of Water and Wastewater, 2012). The COD reduction was calculated using the following equation:

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

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

Finally, the conductivity and pH were determined using a conductivity meter GLP 31 (CRISON) and a pH meter GLP 21 (CRISON) respectively (Standard Methods for the Examination of Water and Wastewater, 2012).

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