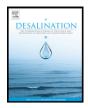
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Reactive dyes rejection and textile effluent treatment study using ultrafiltration and nanofiltration processes

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1. Introduction

The characteristics of wastewater from textile processing operations are comprehensively reviewed. The categorisation of wastewaters proceeds through a consideration of the nature of the various industrial processes employed by the industry and the chemicals associated with these operations. Chemical pollutants arise both from the raw material itself and a broad range of additives used to produce the finished product. The industrial categories considered include sizing and weaving, scouring, bleaching, mercerising, carbonising, dyeing and finishing. Pollutants of concern range from non-biodegradable highly-coloured organic dyes to pesticides from special finishes such as insect-proofing [1].

Textile industries consume large volumes of water and chemicals for wet processing of textiles. The chemical reagents used are very diverse in chemical composition, ranging from inorganic compounds to polymers and organic products [2,3]. Chitin and chitosan were used in lobster shell wastes for colour removal from aqueous solutions [4]. The presence of very low concentrations of dyes in effluent is highly visible and undesirable [5]. Due to their chemical structure, dyes are resistant to fading on exposure to light, water and many chemicals [6,7].

ABSTRACT

Ultrafiltration and nanofiltration processes were used to treat synthetic reactive dyes aqueous solutions and a raw textile effluent supplied from rinsing baths of Spanish textile industry. The influence of the reactive dyes molecular weights and the effect of the used membranes types and cut-offs were investigated with regard to the permeate flux at different transmembrane pressures (2–7 bar for UF and 4–15 bar for NF). The extent of colour retention, COD and conductivity was determined in order to monitor the membrane's separation efficiencies aiming at waste water treatment, water reuse and chemical usage minimisation. High COD retentions (80–100%) were achieved using UF and NF processes. Good conductivity rates (80%) and high COD and colour retention rates (>90%) were obtained for both NF 200 and NF 270 membranes for all studied dyes solutions. An improvement of the rinsing wastewater quality was obtained using UF and NF processes. © 2012 Elsevier B.V. All rights reserved.

Many dyes are difficult to decolourise due to their complex structure and synthetic origin.

There are many structural varieties, such as, azo, diazo, anthroquinone, triphenylmethane, phetalocyanine, stilbene, and metal complex dyes. Decolouration of textile dye effluent does not occur when treated aerobically by municipal sewerage systems [8].

The conventional method of textile wastewater treatment consists of chemical coagulation (using ferrous, lime and polyelectrolytes), biological treatment followed by activated carbon adsorption. The conventional coagulation process generates huge volume of hazardous sludge and poses a problem of sludge disposal. In order to meet the legal requirements for the discharge of textile wastewater, researchers are attempting a combination of two or more treatment methods for the complete and successful removal. Combination of electrochemical treatment and chemical coagulation [9], combined chemical coagulation, electrochemical oxidation, and activated sludge process [10], and combination of electrochemical method, chemical coagulation, and ion exchange [11] were reported for textile effluent treatment to comply with the legal requirements or for reuse standards. Each treatment method has its own advantages and disadvantages, and the selection of the method mainly depends on the treatment target to be achieved.

The fluctuating compound concentrations and flow rates make the conventional processes quite insufficient for the treatment of textile wastewaters, especially for colour removal [12,13].

The discharge regulations are becoming more stringent, and there is a growing tendency and interest in the advanced treatment methods like ozonation, photo catalysis, and membrane processes for a better treatment of the textile wastewaters [14].



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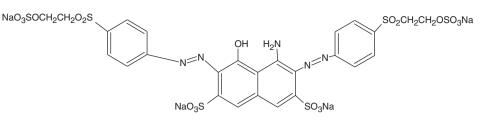


Fig. 1. Chemical structure of Everzol Black (M_{Black} = 991 g mol⁻¹).

The recovery and reuse of textile wastewaters have been studied extensively by membrane researchers [15–24]. Membrane techniques hold great promise in this field, as they have the potential to either remove the dyes stuffs or allow reuse of the auxiliary chemicals used for dyeing or to concentrate the dyestuffs and auxiliaries and produce purified water.

In fact, membrane processes can be used for the purification of these complex wastewater streams [21–25]. There have been many investigations on the treatment of the dye house effluents using microfiltration [26,27], ultrafiltration [26,28–32], nanofiltration [26,33–39], and reverse osmosis membranes [26,40–44].

Several applications of the ultrafiltration process (UF) have been reported for the separation of certain dyes, such as indigo, direct, disperse and reactive dyes [25–30]. A special attention was given to the application of membrane processes; especially the nanofiltration (NF), on the rejection of reactive dyes, whose fixation rates on the fabric is one of the lowest (60–90%) [31–33].

In this work, different UF and NF membranes were used to treat three synthetic reactive dyes aqueous solutions (using black, blue and red EVERZOL dyes). The effect the of dye molecular weight (MW), the cut-off and the type of used membranes were investigated with regard to the permeate flux and separation efficiency.

These processes were also used to treat a rinsing textile effluent supplied from rinsing baths of Spanish textile industry. The extent of colour retention, COD and conductivity were determined in order to monitor the membrane's separation efficiencies aiming at waste treatment, water reuse and chemical usage minimisation.

2. Materials and methods

2.1. Synthetic model solutions

Experiments were conducted using three reactive azo dyes (Everzol Black, Everzol Blue and Everzol Red) which are known to contain anionic sulphonate groups to various degrees.

Three synthetic model solutions were prepared using reactive azo dyes and chloride sodium. The three synthetic solutions of azo reactive dyes were prepared by dissolving 15 g of Everzol dye powder in a flask containing two liters of ultrapure water. This mixture was heated for 30 min at a temperature of 80 °C to ensure complete dissolution of the dye. After cooling, the contents of the flask were poured

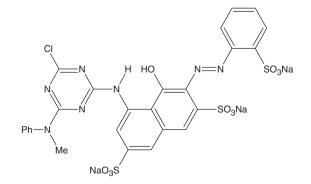


Fig. 2. Chemical structure of Everzol Red ($M_{Red} = 788 \text{ g mol}^{-1}$).

into a tank of 25 L. Then, an amount of 12.5 g of NaCl was added and supplemented with ultrapure water up to the mark.

Just after, pH was adjusted to 10 with 5 M sodium hydroxide solution and the solutions prepared were homogenised by simple magnetic stirrer. The dye concentration and NaCl concentration are equal to 600 mg L^{-1} and 500 mg L^{-1} respectively.

The choice of pH value is in relation with the simulation of dies solutions to a real textile wastewater.

In fact, the real textile wastewater is highly alkaline (pH 10.0–12.5) and is characterised by strong colour and high pH. The textile industry plant consists mainly of printing and dying processes. In these processes, the use of substances such as NaCl and Na₂CO₃ is required to improve the aggregation of dye ions on the fiber to fix the dyestuffs.

The molecular structures and weights of the three dyes are presented in Figs. 1, 2 and 3.

The main characteristics of these solutions are shown in Table 1.

2.2. Textile wastewater characteristics

The study was conducted with a textile wastewater sample supplied from the rinsing baths of COLORTEX textile industry, Spain.

The main characteristics of this sample are given in Table 2.

2.3. Analytical methods

pH values were determined by means of a GLP 22 pH-meter (Crison). The conductivities were measured by a Crison (GLP 32) instrument type conductivitymeter. Both conductivity and pH sensors used for these analyses allowed automatic and continuous correction of the values by taking into account the sample temperature. Turbidity was measured with a DINKO D-112 turbidimeter according to the ISO 7027:1999. Turbidity and conductivity were measured with accuracies of ± 2 NTU and $\pm 1.0\%$, respectively. The COD concentrations were obtained using a Spectroquant Nova 60 from MERCK (Germany) type COD-meter, whereas SAC (spectral absorption coefficient) values were obtained by UV-vis absorption using a HP 8453 spectrophotometer (1 cm cell width) after samples filtration with a 0.45 µm filter, according to the ISO 7887:1994 method [45].

COD analyses were carried out in a cell tests from MERCK (denominated kits). These tubes contain the required reagents for the oxidation (potassium dichromate, sulphuric acid and silver sulphate).

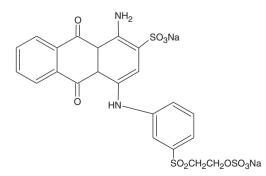


Fig. 3. Chemical structure of Everzol Blue ($M_{Blue} = 626 \text{ g mol}^{-1}$).

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