Journal of Cleaner Production 65 (2014) 458–464

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Electrochemical treatment of industrial wastewater and effluent reuse at laboratory and semi-industrial scale

Mireia Sala, M. Carmen Gutiérrez-Bouzán*

Institut d'Investigació Tèxtil i Cooperació Industrial de Terrassa (INTEXTER), Universitat Politècnica de Catalunya (UPC), C/Colom 15, 08222 Terrassa, Spain

ARTICLE INFO

Article history:
Received 16 April 2013
Received in revised form
2 August 2013
Accepted 3 August 2013
Available online 14 August 2013

Keywords:
Electrochemical treatment
Decolouration
Bath reconstitution
Effluents reuse
Colour removal
Salt reuse

ABSTRACT

This study is based on the electrochemical decolouration of exhausted dyeing effluents which contain dyes and salts. The treated effluents were reconstituted and reused in a new dyeing process.

Initially, synthetic effluents containing one of the reactive dyes Novacron Yellow, Ruby and Deepnight were treated in the laboratory pilot. In all cases, the dye decolouration follows a pseudo-first order reaction.

Subsequently, seven industrial effluents which contain mixtures of these dyes were collected in a Spanish mill and treated in the laboratory pilot. Two methods for the electrochemical treatment and further effluent reconstitution and reuse were studied. The first method consisted of an electrochemical treatment followed by an acidification and a stripping step to remove the carbonate ions. In the second method, the acidification was carried out before the electrochemical treatment; subsequently, the generated CO_2 was removed during the decolouration process.

Finally, the optimised process was applied in situ in a Spanish mill by means of a semi-industrial pilot plant (400 L). No significant colour differences were appreciated between reference dyeings and the fabrics dyed with the treated exhausted effluents. The reuse of the dyeing effluent achieves the reduction of 70% process water consumption and 60% salt discharge.

1. Introduction

Textile processing industry which comprises different operations such as pre-treatment, dyeing, printing and finishing, is one of major environmental polluters. In order to process a ton of textile, one might have to use as much as 230–270 t of water (Tahri et al., 2012). For this reason, environmental issues are being increasingly taken into account in textile dyeing and finishing industries because of strict legislations and a growing ecological concern (Hoque and Clarke, 2013). Main environmental impacts of textile dyeing and finishing industries involve high water consumption, high energy use and also input of wide range of chemicals such as dyes, surfactants, salts... (Pasquet et al., 2013).

This work is focused on reactive dyes effluents, especially on the spent dyeing and first washing baths because they contain higher amount of residual dyes and salts. Reactive dyes were selected because of their high worldwide consumption: they represent about 20–30% of the total market (Carneiro et al., 2005). They are extensively used in the cotton industry due to their washing fastness and brilliant colour. In their structure, they contain one or several *reactive groups* (able to react with the fibre) and a *chromophore group* (which is the main responsible of the colour). The most extensive chromophore group is the azo (R–N=N–R′), followed by the anthraquinone group (Lee and Pavlostathis, 2004). The azo group constitutes more than half of worldwide dyes production (Oliveira et al., 2010). In particular, Guaratini and Zanoni (2000) indicate that approximately 65% of dyes production corresponds to azo dyes and this finding was also supported by and Carneiro et al. (2010).

The conventional biological treatments are not effective in reactive effluents colour removal because this type of dyes have aromatic rings in their large molecules that provide chemical stability but also resistance to the microorganisms attack (Dos Santos et al., 2007). Although the effluent colour regulations are very variable depending on the country, the biological treatments are always insufficient to degrade reactive dyes (Reemtsma and Jakobs, 2001) and to satisfy current regulation. Consequently, in all cases, the application of tertiary treatments to remove colour is required because dyes are usually toxic (Baliarsingh et al., 2012) and, in addition, small amount of them (ppm) are sufficient to produce an intense colouration which can impact or even impede the aquatic life in the riverbeds. Current methods for colour removal are based

* Corresponding author. Tel.: +34 93 739 80 08; fax: +34 93 739 82 72.
E-mail addresses: mireia.sala@intexter.upc.edu (M. Sala), gutierrez@intexter.upc.edu (M.C. Gutiérrez-Bouzán).

0959-6526/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jclepro.2013.08.006

on the separation between dye and effluents: physico-chemical methods (coagulation-flocculation), absorbent materials (such as active carbon, silica gel or alumina) or filtration with membranes. However, these methods produce a residue which requires an additional treatment to be destroyed and in some cases, regeneration or cleaning step (López-Grimau et al., 2011). With the increased awareness of environmental protection, the need for green wastewater technologies is growing fast. Advanced oxidation methods such as ozonation, Fenton, photoFenton, photocatalysis are an advanced alternative, as residues are not produced (Chon et al., 2012), but they are rather expensive and involve some operational difficulties. Enzymatic decomposition of dyes requires an exhaustive control of temperature and pressure to avoid enzymes denaturalisation. For these reasons, the electrochemical methods are nowadays the subject of a wide range of investigations at laboratory and pilot plant scale, as the electron is a clean reagent and they do not generate residues.

As some industrial wastewaters contain large amounts of chloride ions, the indirect electrochemical oxidation method with active chlorine is a very suitable technique to treat this kind of effluents. The indirect electro-oxidation occurs when strong oxidants are generated in situ during the electrolysis and react with the organic pollutants such as dyestuffs, producing its total or partial degradation, according to the reactions 1–3:

$$2Cl^- \rightarrow Cl_{2(aq)} + 2e^- \quad (1)$$

$$Cl_{2(aq)} + H_2O \rightarrow ClO^- + Cl^- + 2H^+ \quad (2)$$

$$\text{Dye (C, H, O, N)} + ClO^- \rightarrow \text{intermediate compounds} \rightarrow CO_2 + H_2O + Cl^- + N_2 \quad (3)$$

Sanjay et al. (2005) suggested a mechanism involved in decolouration and chemical oxygen demand (COD) reduction for the azo dyes, according to the reactions 4–6:

$$R{-}N{=}N{-}R' + 2ClO^- \rightarrow R{-}N(ClO) = N(ClO){-}R' \text{ (intermediate)} \quad (4)$$

$$R{-}N(ClO) = N(ClO){-}R' \rightarrow R{-}N(O) = N(O){-}R' \text{ (intermediate)} \quad (5)$$

$$R{-}N(O) = N(O){-}R' \rightarrow RO + R'O + N_2 \quad (6)$$

On the other hand, McCallum et al. (2000) discussed the possible reaction pathways of anthraquinone textile dyes through the oxidative degradation process of Uniblue A. In the case of reactive dyes effluents, the addition of any chemical product in the electrolysis is not required because the chloride ion contained in the effluents acts as electrolyte. The electrochemistry method using chlorine as indirect oxidant has noted to be effective in the degradation of several kinds of dyes, such as azo dyes (Lopez-Grimau and Gutierrez, 2006), acid dyes (Oliveira et al., 2007) or disperse dyes (Osugi et al., 2009). Its combination with photo-electrochemistry has also provided good results for phtalocyanine dyes degradation (Osugi et al., 2006), but in this case, the metal ions liberated (i.e. copper) have to be removed.

Del Rio et al. (2009a) studied the efficiency of electrochemical treatment with DSA, both in a divided cell (for oxidation and reductions processes separately) and in an undivided cell (oxide-reduction processes). The greatest decolouration rates were obtained with the second process (Del Rio et al., 2009b). According to those results, in the current study the studies are focused on an oxide-reduction process carried out in an undivided cell.

Moreover, the current policies concerning water and energy consumption conduce to the recycling and reuse treatments (Kurta et al., 2013). In this sense, recent studies on textile effluents (Riera-Torres et al., 2011) demonstrated the possibility of reusing these discoloured effluents for new dyeing processes. The reuse of 70% discoloured dyebaths after the electrochemical treatment assisted by UV irradiation provides, in most of cases, acceptable colour differences (limit of acceptance in the textile industry: $DE_{CMC\ (2:1)} \leq 1$) with respect to the original dyeing with decalcified tap water.

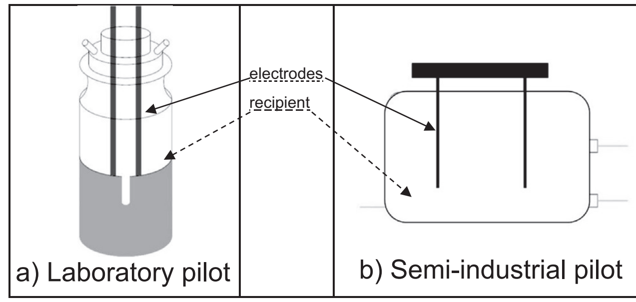

Fig. 1. Electrolytic cells.

The current study was carried out with the support and assistance of a Spanish mill focussed on knitwear dyeing and finishing processes. According to environmental policies, the main interest of this enterprise was to reduce the salts content in their wastewater. In this sense, the electrochemical treatment-reuse system was a promising alternative to avoid the discharge of the reactive dyeing effluents due to their high salinity.

The main goal of this study is to optimise the electrochemical method for the treatment of dyeing effluents (dyeing and first washing effluents) and their reuse in a new dyeing process, with the aim to reduce the water consumption and the salts discharge in the industrial effluents. Several authors have published studies about dyeing effluents treatment but reuse experiments have not been included in their manuscripts (Kim et al., 2005). As far as we know, in addition to our research group, only Lu et al. (2009) reused printing and dyeing effluents after biological-filtration treatments and Tahri et al. (2012) achieved the reuse of 50% of water and 30% of salt after microfiltration–nanofiltration treatment of reactive dye effluents. With respect to these studies, the main advantage of the electrochemical treatment is the possibility of reusing higher amounts of water and salt without the generation of wastes.

2. Experimental

2.1. Dyes and reagents

Three azo dyes containing three reactive groups in their molecule, kindly provided by the mill Hidrocolor SA were selected: Novacron Deepnight (ND), Ruby (NR) and Yellow (NY). Their maximum absorption wavelengths are 583 nm, 543 nm and 417 nm, respectively (see calibration curves in section *2.4.1)*.

These three dyes, used at different rates, are the basis of many industrial trichromies as they provide a wide range of colour shades.

For the effluents and the dyebath preparation, analysis quality reagents were used: Na_2CO_3 (Merck) and NaCl (Fluka).

Dyeing was performed on 100% cotton fabrics, kindly provided by the mills TIPSA and Hidrocolor SA.

The industrial effluents studied correspond to 3 trichromies collected at the mill, namely: Purple (PpT), Violet (ViT) and Midnight Blue MbT). Their dyeing formulas were not specified.

2.2. Electrochemical treatment

The industrial effluents were treated in the undividable electrolytic cells shown in Fig. 1.