Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2015.1031185

57 (2016) 2685–2692
February

Taylor & Francis
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Comparison of different wastewater treatments for colour removal of reactive dye baths

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Received 15 October 2014; Accepted 12 March 2015

ABSTRACT

The generation of high-coloured wastewater is one of the main environmental problems of the textile industry. Reactive dyes are widely used in the dyeing of cellulosic fibres. However, they have low exhaustion degree (70–90%). The degradation of residual dyes by aerobic biological treatment is very poor, being necessary the application of specific treatments. In this work, three different methods for the removal of reactive dyes were compared: electrochemical treatment, coagulation with *Moringa oleifera* waste and enzymatic treatment with laccase. Two azo bifunctional dyes with different reactive groups were selected: C.I. Reactive Black 5 (vinyl sulphone) and C.I. Reactive Red 231 (chlorotriazine). The influence of pH (5 and 9) and dye hydrolysis on the decolourisation yield was studied. The electrochemical treatment was the most efficient, with 95–100% colour removal yield. The coagulation with *M. oleifera* waste also achieved high colour removal efficiency (91–94%). Both methods showed an independent behaviour with respect to pH or dye hydrolysis. The enzymatic treatment should be performed at pH 5. This method was suitable to remove the chlorotriazine dye (92–93% efficiency), whereas the vinyl sulphone one showed a marked dependence on dye hydrolysis: moderately efficient for the hydrolysed dye and highly efficient without hydrolysis. The activity of laccase was not modified by the usual salinity of the reactive dyeing effluent (20 g/L NaCl). Nevertheless, the effluent salinity enhanced the electrochemical and *M. oleifera* treatment yield.

Keywords: Colour removal; Reactive dyes; Electrochemical treatment; *Moringa oleifera*; Natural coagulant; Enzymatic treatment; Laccase

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1. Introduction

Worldwide, 280,000 tons of textile dyes are discharged in industrial effluents every year, being azo dyes the most widely used with more than 60% of the total dye production [1]. The aromatic amines generated from dye reduction can be harmful, and some of them have been classified as carcinogenic and genotoxic by the International Agency for Research on Cancer [2]. The presence of toxic and carcinogenic

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Presented at the International Congress on Water, Waste and Energy Management
16–18 July 2014, Porto, Portugal

products in textile dyeing effluents is a problem added to the high colouration inherent to this type of effluents [3], mainly taking into account the large volume of wastewater generated by textile industry.

Among the different kind of textile dyes, reactive ones are widely used in the dyeing of cotton and other cellulosic fibres since they offer high washing fastness and brilliant colours. Reactive dyes represent the 25% of the total world market [4]. In opposite, these dyes have a low degree of exhaustion and fixation, from 70 to 90% [5]. Therefore, an important percentage of dye remains in its hydrolysed and unfixed form in the exhausted dye bath, or it is removed in the washing liquors.

The degradation of residual dyes by aerobic biological treatment by activated sludge is very poor, since they have low biodegradability and they are also poorly adsorbed in the activated sludge [6]. As biological treatments are not able to remove colour properly, the application of specific treatments is required in order to accomplish current regulations. There are different techniques to achieve colour removal, and the most used are activated carbon adsorption [7,8], membrane filtration [9,10], coagulation–flocculation processes [11,12] and treatment with ozone [13,14].

These technologies have been applied at industrial scale, offering a good colour removal, but they have a high cost of operation and maintenance in the case of membrane technologies and ozonolysis or high cost of chemical products in the case of activated carbon and coagulation–flocculation reagents [5]. Different research groups are working, at laboratory and pilot plant scale, on diverse new methods: low-cost adsorbents [15,16], natural coagulants [17,18], enzymatic action of specific micro-organisms [19,20], anaerobic bioreactors [21] or advanced oxidation methods (AOMs) (Fenton and photo-Fenton reactions [22,23], heterogeneous photocatalysis [24,25] or electrochemical oxidation [26,27]).

The electrochemical oxidation is an AOM which provides great advantages in the treatment of high-coloured textile wastewater: wastes are not generated, and the addition of chemical compounds (organic or inorganic) is not required. In fact, the salt added during the dyeing process with reactive dyes acts as support electrolyte during the electrolysis. The only requirement is the power supply which can be minimised by optimising operational conditions [27].

On the other hand, the use of agricultural by-products as coagulants is a low-cost alternative to traditional chemical coagulants (aluminium and ferrum salts). This is the case of the residues generated after oil extraction of *Moringa oleifera* seeds. These residues have a high content of positive-charged protein which acts as coagulant. *M. oleifera* has been widely applied to eliminate turbidity in drinking water [28] and more recently to eliminate colour of industrial wastewater [29].

Moreover, some bacteria and fungi are able to degrade recalcitrant compounds such as reactive dyes by enzymatic action [30]. This is the case of laccase from the ascomycete *Myceliophthora thermophila* [31]. Enzymes are highly selective and may be affected by changes in pH and salinity. Furthermore, in many cases, the enzyme action requires the addition of an organic mediator, such as ABTS (2,2′-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid)) or HBT (1-hydroxybenzotriazole) [32].

In this work, these three methods (electrochemical, *M. oleifera* waste and laccase) were applied to the removal of colour from reactive dye baths. Two azo-reactive dyes were selected: C.I. Reactive Black 5 and C.I. Reactive Red 231. These dyes have different reactive groups (vinyl sulphone and chlorotriazine, respectively) in order to study their influence on the treatment efficiency. The effect of pH and dye hydrolysis on the decolourisation yield was also studied. In addition, the influence of high salt concentration was evaluated, due to the high salinity characteristic of reactive dye effluents.

2. Experimental

2.1. Dye solutions

Two azo-reactive dyes widely used in cotton dyeing industries were selected in this study: Colour Index (C.I.) Reactive Black 5 (referred as RB5) and C.I. Reactive Red 231 (RR231). Both are bifunctional: RB5 has two vinyl sulphonic groups, whereas RR231 has two monochlorotriazinic ones. The chemical structure of dyes is shown in Fig. 1.

Simulated dye baths were prepared at a dye concentration of 0.1 g/L in decalcified water. Decolourisation

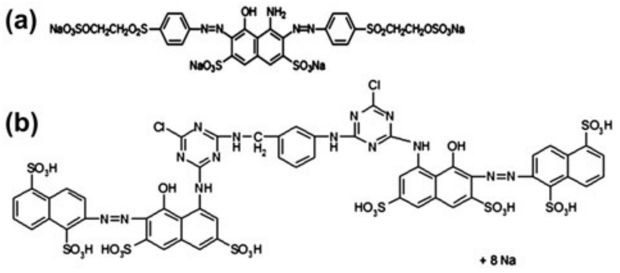

Fig. 1. Chemical structure of the two selected dyes: (a) C.I. Reactive Black 5 (RB5) and (b) C.I. Reactive Red 231 (RR231).

tests were carried out at pH 5 and 9, adjusted with HCl 1 M or NaOH 1 M. To simulate residual reactive dyeing baths, 20 g/L NaCl was added to all dye solutions.

The effect of dye hydrolysis on the efficiency of the three decolourisation methods was studied with the two dyes since they contain different reactive groups. The general reactions of hydrolysis for vinyl sulphonic dyes (react. (1)) and chlorotriazinic dyes (react. (2)) are as follows:

$$\begin{aligned}&\mathrm{Dye-SO_2-CH_2-CH_2-OSO_3Na\ +^{-}OH}\\&\quad\rightarrow \mathrm{Dye-SO_2-CH_2-CH_2-OH\ +^{-}OSO_3Na}\end{aligned}\qquad(1)$$

$$\mathrm{Dye-Cl+^{-}OH\rightarrow Dye-OH+Cl^{-}}\qquad(2)$$

The hydrolysis of chlorotriazinic dyes only implies the substitution of Cl^- by OH^-, whereas the hydrolysis of vinyl sulphonic dyes supposes the loss of a sulphonic group which can affect the dye removal efficiency. Dye hydrolysis was carried out by boiling for 2 h the dye solutions at pH 12.

2.2. *Electrochemical treatment*

Electrochemical treatments were conducted in an electrolytic cell, which was undivided. The cathodes were constituted by titanium, and the anodes were made of titanium, covered by platinum oxides (Ti/PtOx anodes). The total surface area of each electrode was 486 cm^2, and the distance between the electrodes was 2 mm. The volume of the vessel was 1 L.

The experimental plant was completed by a pump to feed the cell and a tank to store the treated wastewater. This plant operated continuously at a flow rate of 20 L/h [27]. The current was regulated by the source supply among 0 and 25 A (current density range: 0–50 mA/cm^2). The electrical consumption was registered during the treatment as Wh/L taking into account the time of treatment and the volume of the sample.

2.3. M. oleifera *coagulation*

Dry *M. oleifera* seeds were supplied by the Centre National de Semences Forestières of Burkina Faso. Shells were removed manually, and kernels were reduced to powder using a domestic grinder (Moulinex). 1 g of *M. oleifera* powder was fed to a Soxhlet extractor fitted with a 250-mL round-bottom flask and a condenser. The extraction was run for 2 h with 100 mL of hexane (Sharlab). After the extraction, the solvent was distilled off under vacuum in a rotary evaporator. The oil extraction yield was 36.1%. Protein content of the *M. oleifera* seeds was determined by analysis of nitrogen Kjeldahl (protein = N (%) × 6.25). The protein content of seeds before extraction was 25.0% and after extraction with ethanol was 34.4%. This increase in the protein content should favour the coagulant effect of *M. oleifera* solutions.

Oilseed residues were used to prepare a suspension at 5% (w/v) in distilled water by stirring at room temperature for 2 h. Later, the suspension was filtered with 0.45-μm glass filter (Millipore). Colour removal tests were carried out with solutions of *M. oleifera* at different concentrations, ranging from 250 to 1,250 mg/L. Trials with 1 L of dye solution samples were performed in a jar test. The samples were first submitted to a fast stirring at 150 rpm for 10 min; subsequently, they were stirred slowly at 20 rpm for 30 min [33], and finally, they were allowed to stand 1 h in Imhoff cones to promote natural decantation [34].

2.4. *Enzymatic treatment*

Laccase from the ascomycete *M. thermophila* was selected for the enzymatic treatments. Laccase solutions were supplied by Novozymes (Davis, CA, USA). Commercial solutions were initially filtered with a cartridge Sep-Pack C18 (Waters Associates, Milford, USA). Lacasse activity was determined spectrophotometrically by oxidation of ABTS (2,2´-azino-di-[3-ethyl-benzothiazoline-(6)-sulphonic acid]) supplied by Sigma-Aldrich (Madrid, Spain). The reaction was monitored at room temperature by measuring the change in absorbance at 436 nm for 2 min. One activity unit was defined as the amount of enzyme that oxidised 1 μmol of ABTS per minute, and the activities were reported as U/mL. The laccase enzyme solution showed 400 U/mL of activity.

The pH of dye solutions was fixed at 5 by addition of 0.1 M acetate/acid acetic buffer solution pH 5, as it is a common procedure in previous literature focused on the removal of Reactive Black 5 solutions [35,36]. According to our previous studies, no organic mediator was added to dye solutions and all the experiments were performed at 50˚C for 24–48 h with the addition of 4 U/mL of enzyme concentration.

2.5. *Colour removal measurements*

Colour removal values were calculated from absorbance measurements at the maximum absorbance wavelength of each dye (599 for RB5 dye and 522 nm for RR231 dye). The absorbance measurements were carried out with a UV–visible spectrophotometer

Shimadzu UV-2401 PC model (Japan). The linearity interval was previously established. All dye removal tests were carried out in triplicate.

3. Results and discussion

3.1. *Electrochemical treatment*

The results of colour removal obtained in the electrochemical treatment are shown in Fig. 2. Current density was initially fixed at 24 mA/cm^2 according to previous studies [27]. As can be seen, the same experiments were performed with dyes not hydrolysed and with solutions of dyes previously hydrolysed.

Fig. 2 evidences that colour removal results were almost independent on pH. Dye oxidation mainly occurs through the action of oxidant species generated in the anode (Cl2, Cl$^{\cdot}$, Cl2$^{\cdot}$, ClOH$^{\cdot-}$), which are independent of the pH [27]. The electrochemical treatment reached 98–100% of colour removal for RR231 dye and 95–96% for RB5. On the other hand, the dye hydrolysis did not have any significant effect on the efficiency of the electrochemical treatment. Decolourisation is mainly caused by the breakage of the chromophore (azo bond) [37]. The hydrolysis of the reactive group, located in different points of the dye molecule, is not a decisive factor in this reaction and does not have effect on the efficiency of the electrochemical treatment.

Consequently, solutions with hydrolysed dye at pH 9 were selected to optimise the current to be applied during the electrochemical treatment, as these conditions are similar to those of industrial residual dye baths. With this purpose, experiments at different current densities were carried out (Fig. 3).

As is shown in Fig. 3, colour removal results were better for RR231 than for RB5. In this sense, almost total decolourisation was obtained for RR231 at 12 mA/cm^2 and 94% colour removal was reached for RB5, in which electrical consumption corresponded to 12.4 Wh/L. However, it can be underlined that in the case of RR231, 6 mA/cm^2 current density was sufficient to obtain more than 90% colour removal, which implied that the electrical consumption was drastically reduced to 6.7 Wh/L. Between the two dyes, the differences in colour removal can be attributed to their different molecule structure. Both dyes have two azo chromophore groups to be degraded, so the difference between their decolourisation yields is attributed to the rest of their molecular structure [38]. RB5 degradation can produce any intermediate capable of giving slight colour to the water.

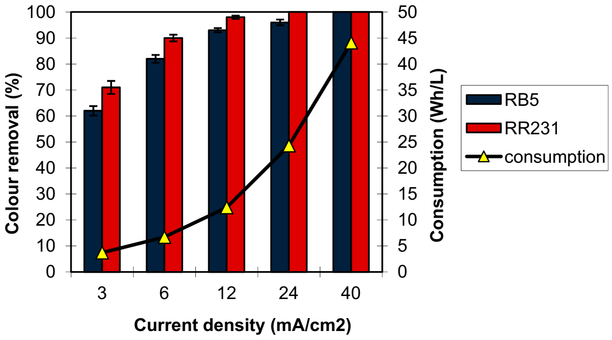

Fig. 3. Optimisation of the electrochemical treatment (0.1 g/L hydrolysed dye, pH 9, 20 g/L NaCl).

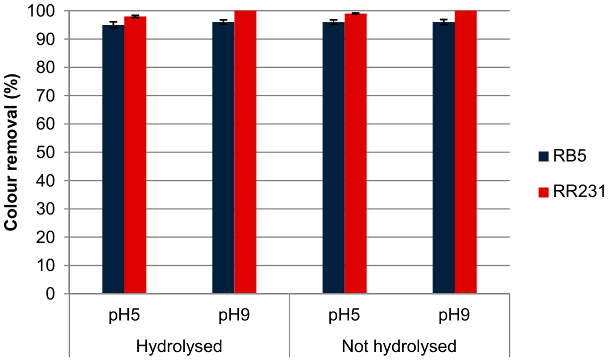

Fig. 2. Colour removal by electrochemical treatment (0.1 g/L dye, 20 g/L NaCl; current density 24 mA/cm^2).

3.2. M. oleifera *coagulation*

Results of coagulation with *M. oleifera* suspensions are shown in Fig. 4. Initially, the concentration of *M. oleifera* was fixed at 1,000 mg/L, which is a

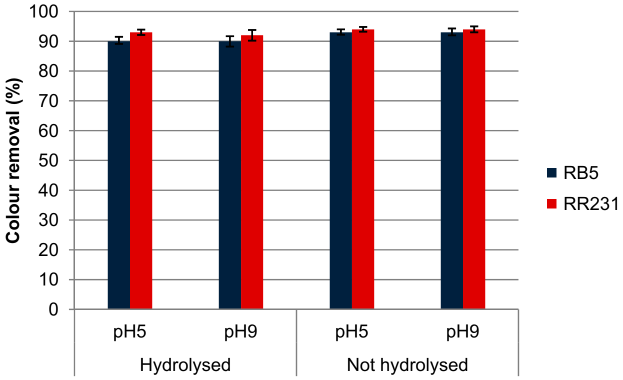

Fig. 4. Colour removal by *M. oleifera* coagulation (0.1 g/L dye, 20 g/L NaCl; *M. oleifera* 1,000 mg/L).

common concentration of coagulant for this type of industrial wastewater [39].

As can be seen in Fig. 4, *M. oleifera* waste had high coagulation action (90–94% of colour removal) for all experimental conditions, independently of the pH or the dye hydrolysis. Previous studies reported the interaction between the sulphonic groups of the dyes and the positive-charged proteins of *M. oleifera* [29,33]. This interaction is independent of the pH. *M. oleifera* provided good colour removal yield for RR231 whether or not the dye was hydrolysed. However, for RB5, the efficiency was slightly lower when the dye was hydrolysed. This fact could be attributed to the loss of two sulphonic groups due to the hydrolysis of vinyl sulphonic dyes.

In order to optimise the addition of coagulant to the dye solutions, decolourisation tests were performed with solutions of hydrolysed dye at pH9 to simulate the industrial reactive dye baths. Several *M. oleifera* suspensions were prepared in a range of 250–1,250 mg/L. Dye removal results are shown in Fig. 5.

Fig. 5 evidences slightly better performance of *M. oleifera* suspensions to remove RR231 than RB5. RR231 removal reached 90% with the 750 mg/L Moringa solution, whereas RB5 required the addition of 1,000 mg/L *M. oleifera* to achieve the same level of colour removal. The higher efficiency on the removal of RR231 respect to RB5 could be attributed to its higher number of negative sulphonic groups (8 groups for RR231 respect to 4 groups for RB5.

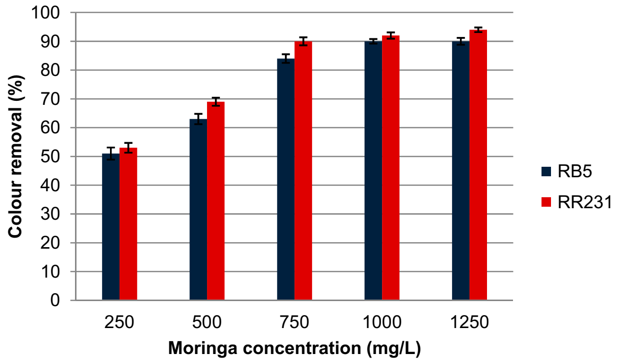

Fig. 5. Coagulation dose optimisation for *M. oleifera* waste suspensions (0.1 g/L hydrolysed dye, pH 9, 20 g/L NaCl).

3.3. Enzymatic treatment

Results of colour removal obtained by applying enzymatic treatment are shown in Fig. 6. In any case, laccase provided good colour removal yield for RR231 dye (88–93%). For RB5, the efficiency was highly dependent on dye hydrolysis (53–61% vs. 88–91%). This can probably be attributed to the effect of vinyl sulphone-reactive groups on the enzyme activity. Zille et al. [35] stated that laccase reacts with dyes by electrostatic interaction between negative-charged sulphonic groups of the dyes and amino acids of the enzymes. The hydrolysis of the two vinyl sulphone groups of RB5 implied the loss of two sulphonic groups which did not occur in the case of hydrolysis of the RR231 triazine groups. In fact, RR231 dye maintains its 8 sulphonic groups after dye hydrolysis. On the other hand, 48-h reaction time provided slightly better results than 24 h. These results were in accordance with previous studies where an increase of decolourisation was reported when the incubation time was extended from 24 to 48 h [36].

Finally, it is important to underline that inhibitory phenomena were not observed in the enzymatic treatments although all the experiments were carried out in high saline medium. Furthermore, the addition of electron transfer mediator or co-substrate was not necessary, unlike other enzymes reported for decolourisation studies [20].

3.4. Comparison of the treatment methods

The three technologies studied in this work demonstrated to be effective for the removal of reactive dyes in simulated residual dye baths. As can be seen in Table 1, despite the very different chemical constitution (molecular size and reactive groups) of the two selected dyes, for each type of treatment, it was possible to find experimental conditions which enabled to remove at least 90% dye.

The electrochemical treatment provided excellent results: colour removal in the range 95–100%, almost independent of dye hydrolysis and pH. The

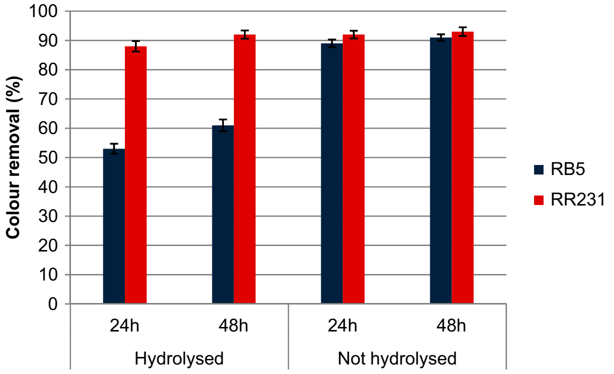

Fig. 6. Dye removal by enzymatic treatment (0.1 g/L dye, 20 g/L NaCl, pH fixed at 5, enzyme concentration 4 U/mL).

Table 1
Colour removal yield (%) of the different treatments

	Electrochemical				*Moringa oleifera*				Enzymatic	
	Hydrolysed		Not hydrolysed		Hydrolysed		Not hydrolysed		Hydrolysed	Not hydrolysed
Dye	pH 5	pH 9	pH 5	pH 9	pH 5	pH 9	pH 5	pH 9	pH 5	pH 5
RB5	95	96	96	96	90	90	93	94	61	90
RR231	98	100	99	100	93	92	93	94	92	93

characteristic high salinity of the industrial reactive dye effluents is a factor that enhances the performance of the electrochemical treatment and reduces the electrical consumption and consequently the cost of the treatment. An additional advantage of the electrochemical method is that it can be considered as a clean technology because the addition of chemical reagents is not required, no wastes are generated and dyes are degraded, which enables the reuse of the treated effluent.

The *M. oleifera* waste applied to the coagulation of reactive dyes has also shown to be an interesting option. Both dyes exhibited removal yield results in the range 90–94%. As in the previous case, the salinity of the effluent also demonstrated to be a positive factor for the treatment efficiency (see Section 3.2). In addition, results are also almost independent of the other variables: pH and dye hydrolysis. For these reasons, the use of *M. oleifera* waste as reactive dye coagulant constitutes an interesting low-cost and natural alternative to substitute the conventional chemical coagulants–flocculants. On another hand, the addition of *M. oleifera* supposes a low increase of COD which can be easily eliminated in the subsequent biological treatment plant. The increase of COD is slight in comparison with the organic content of industrial textile waste waters. In this sense, the use of *M. oleifera* as well as the other two methods described in this work is thought as specific methods to remove nonbiodegradable dyes, and they are proposed as a previous step to biological aerobic treatment. Once the dye is eliminated, the water can be discharged to the biological plant to follow up with the degradation of the rest of organic matter.

With respect to enzymatic treatment, results can be considered in general very positive because laccase activity is not influenced by the salinity of the effluent, as it was shown in Section 3.3, opposite to previous studies which reported inhibitory effects caused by the high salinity of the dye effluents [40]. However, the treatment is very sensitive to pH variations: the effluent should be buffered at pH 5. This implies an additional cost and an increase of wastewater salinity as reactive dye effluents which are typically alkaline. In addition, the dye hydrolysis constitutes also an important factor to take into account in the case of vinyl sulphonic dyes.

4. Conclusions

The comparison of the three decolourisation methods studied in this work leads to the conclusion that the electrochemical treatment was the most efficient (95–100% colour removal yield). The coagulation with *M. oleifera* also achieved high colour removal efficiency for both dyes (91–94%). Enzymatic treatment provided good colour removal yield for RR231 (92–93%), whereas for RB5, the efficiency was highly dependent on dye hydrolysis (61–90%). Electrochemical and *M. oleifera* treatments were almost independent on pH, whereas in the case of the enzymatic treatment, the pH should be carefully controlled (pH buffered at 5). Therefore, both electrochemical and *M. oleifera* treatments have shown to be attractive as new alternative methods for colour removal, whereas laccase can only be applied for the removal of reactive dyes under controlled conditions.

Acknowledgements

The authors thank the Spanish Ministry of Economy (MINECO) for its financial support (Project CTM2012-31461).

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