



COMPARISON OF DIFFERENT WASTEWATER TREATMENTS FOR COLOUR REMOVAL OF REACTIVE DYE BATHS

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COMPARISON OF ~~DIFFERENT NEW~~ WASTEWATER TREATMENTS FOR COLOUR REMOVAL OF REACTIVE DYE BATHS

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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 conventional~~ 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 (vinylsulfone) 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 Moringa 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 vinylsulfone 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, This factor~~ the effluent salinity enhanced the electrochemical and Moringa oleifera treatment yield.

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

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 dyes 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 products in textile dyeing effluents is a problem added to the high coloration 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 conventional 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 among them, the most used are: activated carbon adsorption [7-86-7], membrane filtration [9-108-9], coagulation-flocculation processes [11-1210-11] and treatment with ozone [13-1412-13].

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63 These technologies have been applied at industrial scale, offering a good colour
64 removal, but they have a high cost of operation and maintenance in the case of
65 membrane technologies and ozonolysis or high cost of chemical products in the
66 case of activated carbon and coagulation-flocculation reagents [5]. Different
67 research groups are working, at laboratory and pilot plant scale, on diverse new
68 methods: low cost adsorbents [15-1614-15], natural coagulants [17-1816-17],
69 enzymatic action of specific microorganisms [19-2018-19], anaerobic
70 bioreactors [2120] or advanced oxidation methods (Fenton and Photo-Fenton
71 reactions [22-2321, 22], heterogeneous photocatalysis [24-2523, 24] or
72 electrochemical oxidation [26-2725, 26]).

~~73 In this work, three different methods for the removal of reactive dyes were
74 compared: electrochemical degradation, coagulation with an agricultural by-
75 product and enzymatic treatment.~~

76 The electrochemical oxidation is an advanced oxidation method (AOM) which
77 provides great advantages in the treatment of high coloured textile wastewater:
78 wastes are not generated and the addition of chemical compounds (organic or
79 inorganic) is not required. In fact, the salt added during the dyeing process with
80 reactive dyes acts as support electrolyte during the electrolysis. The only
81 requirement is the power supply which can be minimized by optimizing
82 operational conditions [2726].

83 On the other hand, the use of agricultural by-products as coagulants is a low
84 cost alternative to traditional chemical coagulants (aluminum and ferrum salts).
85 This is the case of the residues generated after oil extraction of *Moringa oleifera*
86 seeds. These residues have a high content of positive charged protein which
87 acts as coagulant. *Moringa oleifera* has been widely applied to eliminate
88 turbidity in drinking water [2827] and more recently to eliminate colour of
89 industrial wastewater [2928].

90 Moreover, some bacteria and fungi are able to degrade recalcitrant compounds
91 such as reactive dyes by enzymatic action [3029]. This is the case of laccase
92 from the ascomycete *Myceliophthora thermophila* [3130]. Enzymes are highly
93 selective and may be affected by changes in pH and salinity. Furthermore, in
94 many cases the enzyme action requires the addition of an organic mediator,

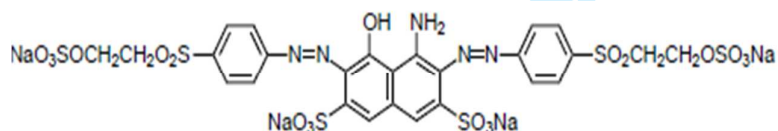
such as ABTS (2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid)) or HBT (1-hydroxybenzotriazole) [32].

In this work, these three methods (electrochemical, *Moringa oleifera* waste and laccase) were applied to the removal of colour from reactive dyebaths. Two azo reactive dyes were selected: C.I. Reactive Black 5 and C.I. Reactive Red 231. These dyes have with different reactive groups (vinylsulfone and chlorotriazine respectively) were selected 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.

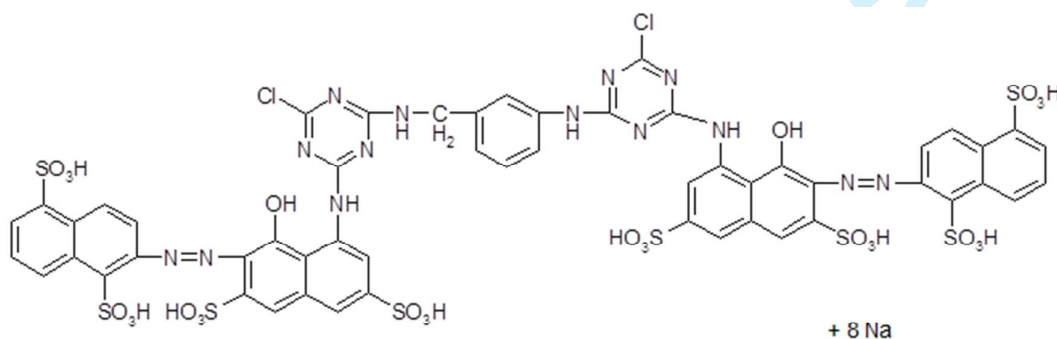
2. EXPERIMENTAL

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 vinylsulfonic groups whereas RR231 has two monochlorotriazinic ones. The chemical structure of dyes is shown in Figure 1.



(a)

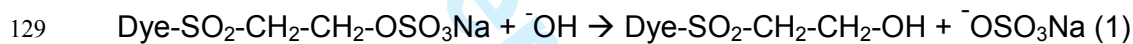


(b)

117
118 **Figure 1.** Chemical structure of the two selected dyes: (a) C.I. Reactive Black 5
119 (RB5), (b) C.I. Reactive Red 231 (RR231).

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121 Simulated dye baths were prepared at a dye concentration of 0.1 g/L in
122 decalcified water. Decolourisation tests were carried out at pH 5 and 9, adjusted
123 with HCl 1M or NaOH 1M. To simulate a residual reactive dyeing baths, ~~up to~~
124 20 g/L NaCl was added to all dye solutions.

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



131 The hydrolysis of chlorotriazinic dyes only implies the substitution of Cl⁻ by OH⁻,
132 whereas the hydrolysis of vinyl sulfonic dyes suppose the loss of a sulfonic
133 group which can affect to the dye removal efficiency. Dye hydrolysis was carried
134 out by boiling for 2h the dye solutions at pH 12.

136 2.2 Electrochemical treatment

137 Electrochemical treatments were conducted in an electrolytic cell, which was
138 undivided. The cathodes were constituted by titanium and the anodes were
139 made of titanium, covered by platinum oxides (Ti/PtOx anodes). The total
140 surface area of each electrode was 486 cm² and the distance between the
141 electrodes was 2 mm. The volume of the vessel was 1 L.

142 The experimental plant was completed by a pump to feed the cell and a tank to
143 store the treated wastewater. This plant operated continuously at a flow rate of
144 20 L/h [27]. The current was regulated by the source supply among 0 and 25 A
145 (current density range: 0- 50 mA/cm²). The electrical consumption was

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3 146 registered during the treatment [as Wh/L taking into account the time of](#)
4 [treatment and the volume of the sample.](#)
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10 11 150 **2.3 Moringa oleifera coagulation**

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13 151 Dry Moringa oleifera seeds were supplied by the *Centre National de Semences*
14 *Forestières* of Burkina Faso. Shells were removed manually and kernels were
15 reduced to powder using a domestic grinder (Moulinex). 1g of M. oleifera
16 powder fed to a Soxhlet extractor fitted with a 250 mL round-bottom flask and a
17 condenser. The extraction was run for 2 hours with 100 mL of hexane (Sharlab).
18 154 After the extraction, the solvent was distilled off under vacuum in a rotary
19 evaporator. The oil extraction yield was 36.1%. Protein content of the Moringa
20 oleifera seeds was determined by analysis of Nitrogen Kjeldahl (protein= N(%) x
21 6.25). The protein content of seeds before extraction was 25.0% and after
22 extraction with ethanol was 34.4%. This increase in the protein content should
23 favour the coagulant effect of Moringa oleifera solutions.
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32 162 Oilseed residues were used to prepare a suspension at 5% (w/v) in distilled
33 water by stirring at room temperature for 2 hours. [Later the suspension was](#)
34 [filtered with 0.45 µm glass filter \(Millipore\).](#) Colour removal tests were carried
35 out with [solutions of Moringa oleifera](#) at different concentrations ~~of Moringseed~~
36 ~~extraction waste~~, ranging from 250 to 1,250 mg/L. [Trials with 1 liter of dye](#)
37 [solution samples were performed in a Jar Test.](#) The samples were first
38 submitted to a fast stirring at 150 rpm for 10 minutes, subsequently they were
39 stirred slowly at 20 rpm for 30 minutes [33] and finally they were allowed to
40 stand 1 hour [in Imhoff cones](#) to promote natural decantation [34].
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49 172 **2.4 Enzymatic treatment**

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51 173 Laccase from the ascomycete *Myceliophthora thermophila* was selected for the
52 enzymatic treatments. Laccase solutions were supplied by Novozymes (Davis,
53 CA, USA). Commercial solutions were initially filtered with a cartridge Sep-Pack
54 C18 (Waters Associates, Milford, USA). Laccase activity was determined
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3 177 spectrophotometrically by oxidation of ABTS (2, 2'-azino-di-[3-ethyl-
4 178 benzothiazoline-(6)-sulfonic acid]) supplied by Sigma-Aldrich (Madrid, Spain).
5
6 179 The reaction was monitored at room temperature by measuring the change in
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8 180 absorbance at 436 nm for 2 min. One activity unit was defined as the amount of
9
10 181 enzyme that oxidized 1 μmol of ABTS per minute and the activities were
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12 182 reported as U/mL. The Laccase enzyme solution showed 400 U/mL of activity.

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14 183 The pH of dye solutions was fixed at 5 by addition of 0.1M acetate/acid acetic
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16 184 buffer solution pH 5, [as it is a common procedure in previous literature focused](#)
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18 185 [on the removal of Reactive Black 5 solutions \[35-36\]](#). According to our previous
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20 186 studies no organic mediator was added to dye solutions and all the experiments
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22 187 were performed at 50 °C for 24-48h with the addition of 4 U/mL of enzyme
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24 188 concentration.

25 26 190 **2.5 Colour removal measurements**

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28 191 Colour removal values were calculated from absorbance measurements at the
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30 192 maximum absorbance wavelength of each dye (599 for RB5 dye and 522 nm
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32 193 for RR231 dye). The absorbance measurements were carried out with a UV-
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34 194 visible spectrophotometer Shimadzu UV-2401 PC model (Japan). The linearity
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36 195 interval was previously established. All dye removal tests were carried out in
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38 196 triplicate.

39 40 41 198 **3. RESULTS AND DISCUSION**

42 43 199 **3.1 Electrochemical treatment**

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45 200 The results of colour removal obtained in the electrochemical treatment are
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47 201 shown in Figure 2. Current density was initially fixed at 24 mA/cm^2 according to
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49 202 previous studies [\[27\]](#). As can be seen, the same experiments were performed
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51 203 with dyes not hydrolysed and with solutions of dyes previously hydrolysed.

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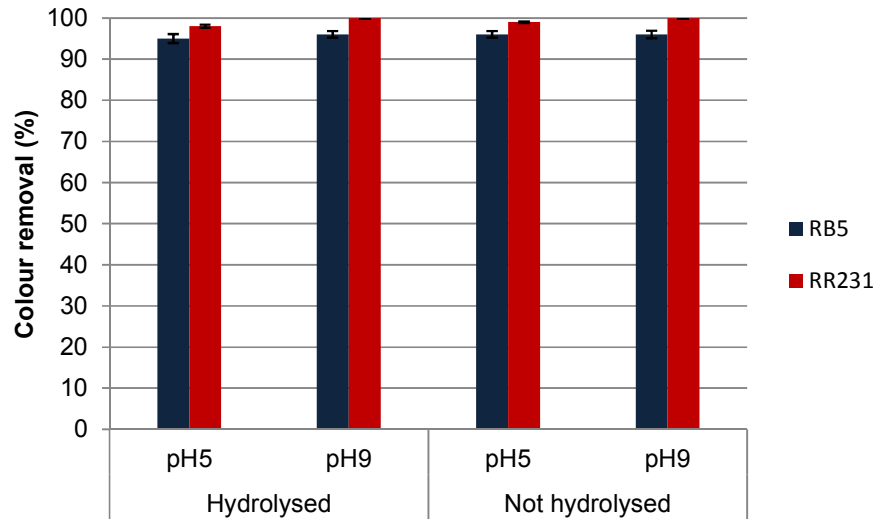


Figure 2. Colour removal by electrochemical treatment (0.1 g/L dye, 20 g/L NaCl; Current density 24 mA/cm²).

Figure 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 \(Cl₂, Cl•, Cl₂•, ClOH•-\) which are independent on 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 (Figure 3).

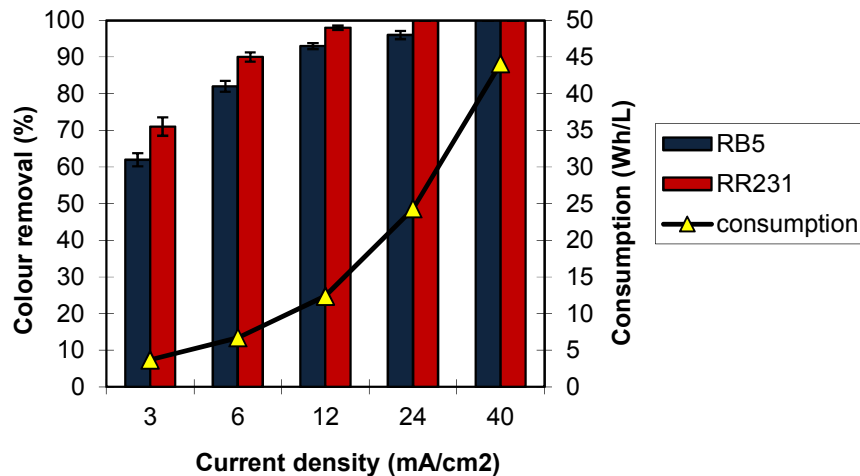


Figure 3. Optimisation of the electrochemical treatment (0.1 g/L hydrolysed dye, pH9, 20 g/L NaCl).

As is shown in Figure 3, colour removal results were better for RR231 than for RB5. In this sense, almost total decolourisation was obtained for RR231 at 12 mA/cm² and 94% colour removal was reached for RB5, which electrical consumption corresponded to 12.4 Wh/L. However, it can be underlined that in the case of RR231, 6 mA/cm² 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 yield is attributed to the rest of their molecular structure [38]. RB5 degradation can produce any intermediate capable of giving slight colour to the water.

3.2 Moringa oleifera coagulation

Results of coagulation with Moringa oleifera suspensions are shown in Figure 4. Initially, the concentration of Moringa oleifera was fixed at 1,000 mg/L, which is a common concentration of coagulant for this type of industrial wastewater [39].

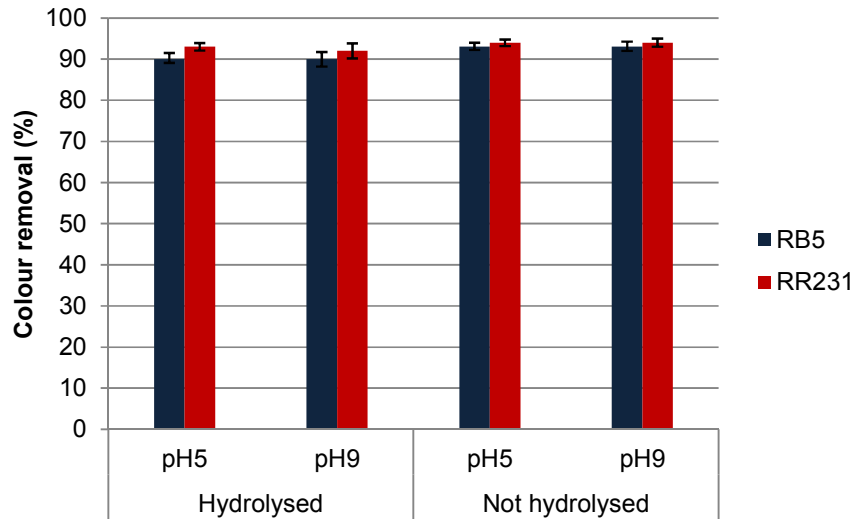


Figure 4. Colour removal by *Moringa Oleifera* coagulation (0.1 g/L dye, 20 g/L NaCl; *Moringa oleifera* 1,000 mg/L).

As can be seen in Figure 4, *Moringa 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 sulfonic groups of the dyes and the positive charged proteins of *Moringa oleifera* [29, 33]. This interaction is independent of the pH. *Moringa 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 sulfonic groups due to the hydrolysis of vinyl sulfonic dyes.

As can be seen in Figure 4, *Moringa oleifera* waste had high coagulating action whether or not the dye is hydrolysed for both dyes. The dye molecule size or reactive group do not show any influence on the treatment yield (RB5: smaller molecule and two vinyl sulfone reactive groups; RR231: larger molecule and two monochlorotriazine reactive groups). In this sense, the loss of two sulfonic groups due to the hydrolysis of vinyl sulfonic dyes did not affect the efficiency of the *Moringa oleifera* treatment. Moreover, colour removal yield higher than 90% was achieved for both dyes, independently of the pH.

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 *Moringa oleifera* suspensions were prepared in a range 250 mg/L - 1250 mg/L. Dye removal results are shown in Figure 5.

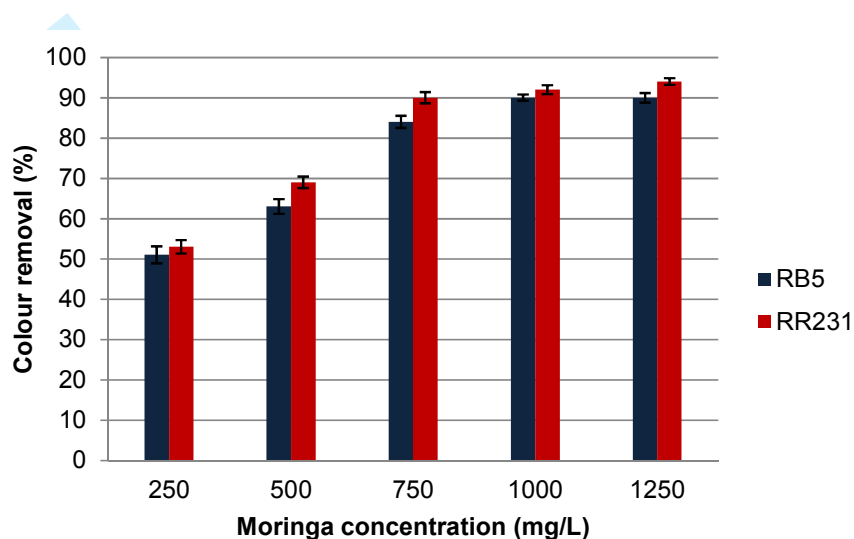


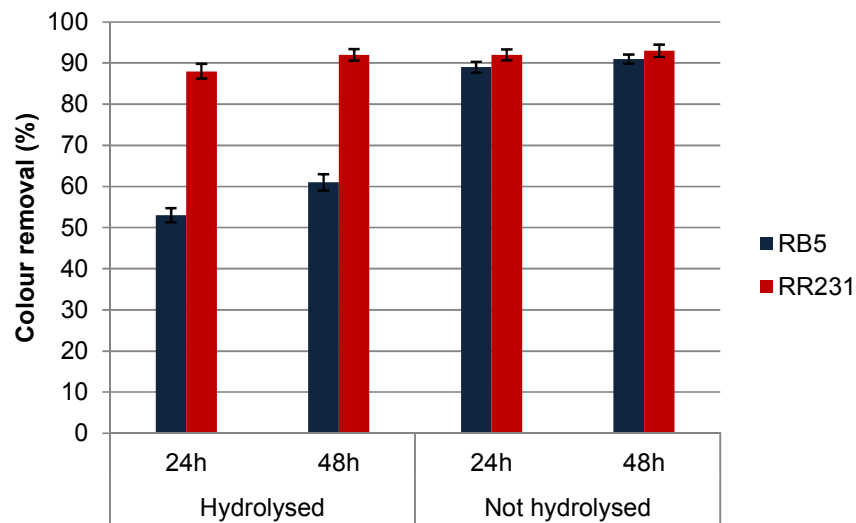
Figure 5. Coagulation dose optimisation for *Moringa oleifera* waste suspensions (0.1 g/L hydrolysed dye, pH9, 20 g/L NaCl).

Figure 5 evidences slightly better performance of *Moringa 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 *Moringa 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 sulfonic groups \(8 groups for RR231 respect to 4 groups for RB5\).](#)

3.3 Enzymatic treatment

Results of colour removal obtained by applying enzymatic treatment are shown in Figure 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

289 | vinylsulfone reactive groups on the enzyme activity. Zille et al. [35] stated that
 290 | Laccase reacts with dyes by electrostatic interaction between negative charged
 291 | sulfonic groups of the dyes and amino acids of the enzymes. The hydrolysis of
 292 | the two vinylsulfone groups of RB5 implied the loss of two sulfonic groups which
 293 | did not occur in the case of hydrolysis of the RR231 triazine groups. In fact,
 294 | RR231 dye maintain their 8 sulfonic groups after dye hydrolysis. On the other
 295 | hand, 48h reaction time provided slightly better results than 24h. This results
 296 | were in accordance with previous studies where an increase of decolourisation
 297 | was reported when the incubation time was extended from 24h to 48h [36].
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 300 | **Figure 6.** Dye removal by enzymatic treatment (0.1 g/L dye, 20 g/L
 301 | NaCl, pH fixed at 5, enzyme concentration 4 U/mL).
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303 | Finally, it is important to underline that inhibitory phenomena were not observed
 304 | in the enzymatic treatments although all the experiments were carried out in
 305 | high saline medium. Furthermore, the addition of electron transfer mediator or
 306 | co-substrate was not necessary; unlike other enzymes reported for
 307 | decolourisation studies [20][49].
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309 | 3.4. Comparison of the treatment methods

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3 310 The three technologies studied in this work demonstrated to be effective for the
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5 311 removal of reactive dyes in simulated residual dyebaths. As can be seen in
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7 312 Table 1, despite the very different chemical constitution (molecular size and
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9 313 reactive groups) of the two selected dyes, for each type of treatment it was
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11 314 possible to find experimental conditions which enabled to remove at least 90%
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13 315 dye.

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

Dye	Electrochemical				Moringa Oleifera				Enzymatic	
	Hydrolysed		Not hydrolysed		Hydrolysed		Not hydrolysed		Hydrolysed	Not hydrolysed
	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

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319 The electrochemical treatment provided excellent results: colour removal in the
320 range 95-100%, almost independent on dye hydrolysis and pH. The
321 characteristic high salinity of the industrial reactive dye effluents is a factor that
322 enhances the performance of the electrochemical treatment and reduces the
323 electrical consumption and consequently, the cost of the treatment. An
324 additional advantage of the electrochemical method is that it can be considered
325 as a clean technology because the addition of chemical reagents is not
326 required, no wastes are generated and dyes are degraded, which enables the
327 reuse of the treated effluent.

328 The Moringa Oleifera waste applied to the coagulation of reactive dyes has also
329 shown to be an interesting option. Both dyes exhibited removal yield results in
330 the range 90-94 %. As in the previous case, the salinity of the effluent also
331 demonstrated to be a positive factor for the treatment efficiency (see section
332 3.2). In addition, results are also almost independent of the other variables: pH
333 and dye hydrolysis. For these reasons, to the use of Moringa Oleifera waste as
334 reactive dye coagulant constitutes an interesting low-cost and natural
335 alternative to substitute the conventional chemical coagulants-flocculants. [On
336 another hand, the addition of Moringa oleifera supposes a low increase of COD
337 which can be easily eliminated in the subsequent biological treatment plant. The
338 increase of COD is slight in comparison with the organic content of industrial
339 textile waste waters. In this sense, the use of Moringa oleifera as well as the](#)

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3 340 [other two methods described in this work are thought as specific methods to](#)
4 341 [remove non biodegradable dyes and they are proposed as a previous step to](#)
5 342 [biological aerobic treatment. Once the dye is eliminated the water can be](#)
6 343 [discharged to the biological plant to follow up with the degradation of the rest of](#)
7 344 [organic matter.](#)

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11 345 With respect to enzymatic treatment, results can be considered in general very
12 346 positive because Laccase activity is not influenced by the salinity of the effluent,
13 347 as it was shown in section 3.3, [in opposite to previous studies which reported](#)
14 348 [inhibitory effects caused by the high salinity of the dye effluents \[40\]](#). However,
15 349 the treatment is very sensitive to pH variations: the effluent should be buffered
16 350 at pH 5. This implies an additional cost and an increase of wastewater salinity
17 351 as reactive dye effluents which are typically alkaline. In addition, the dye
18 352 hydrolysis constitutes also an important factor to take into account in the case of
19 353 vinylsulfonic dyes.

20 21 22 23 24 25 26 27 28 29 355 **4. CONCLUSIONS**

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31 356 The comparison of the three decolourisation methods studied in this work leads
32 357 to the conclusion that the electrochemical treatment was the most efficient (95-
33 358 100% colour removal yield).

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37 359 The coagulation with *Moringa oleifera* also achieved high colour removal
38 360 efficiency for both dyes (91-94%).

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41 361 Enzymatic treatment provided good colour removal yield for RR231 (92-93%)
42 362 whereas for RB5 the efficiency was highly dependent on dye hydrolysis (61-
43 363 90%). ~~That is to say, in the case of the vinylsulfone dye, this treatment showed~~
44 364 ~~a marked dependence on dye hydrolysis, being moderately efficient for the~~
45 365 ~~hydrolysed dye and highly efficient without hydrolysis. This difference can~~
46 366 ~~probably be attributed to the effect of sulfonic groups on the enzyme activity~~
47 367 ~~when the vinylsulfone dye is not hydrolysed.~~

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53 368 ~~On the other hand, results of E~~electrochemical and *Moringa oleifera* treatments
54 369 were almost independent on pH whereas in the case of the enzymatic
55 370 treatment, the pH should be carefully controlled (pH buffered at 5).

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3 371 ~~In addition, both electrochemical and Moringa oleifera treatments promising to~~
4 372 ~~remove colour of industrial effluents containing reactive dyes, because they~~
5 373 ~~were very efficient independently on pH range and dye hydrolysis conditions~~
6 374 ~~and because their yield is enhanced by the effluent salinity.~~

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10 375 Therefore, both electrochemical and Moringa Oleifera treatments have shown to
11 376 be attractive as new alternative methods for colour removal, whereas Laccase
12 377 can only be applied for the removal of reactive dyes under controlled conditions.
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17 379 **ACKNOWLEDGEMENTS**

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20 380 The authors thanks the Spanish Ministry of Economy (MINECO) for its financial
21 381 support (Project CTM2012-31461).
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