

Article

## Valorization of Waste Obtained from Oil Extraction in *Moringa Oleifera* Seeds: Coagulation of Reactive Dyes in Textile Effluents

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**Abstract:** *Moringa oleifera* seeds contain about 40% of highly valued oil due to its wide range of applications, from nutritional issues to cosmetics or biodiesel production. The extraction of *Moringa* oil generates a waste (65%–75% of seeds weight) which contains a water soluble protein able to be used either in drinking water clarification or wastewater treatment. In this paper, the waste of *Moringa oleifera* extraction was used as coagulant to remove five reactive dyes from synthetic textile effluents. This waste constitutes a natural coagulant which was demonstrated to be effective for the treatment of industrial reactive dyestuff effluents, characterized by alkaline pH, high NaCl content and hydrolyzed dyes. The coagulation yield increased at high NaCl concentration, whereas the pH did not show any significant effect on dye removal. *Moringa oleifera* showed better results for dye removal than the conventional treatment of coagulation-flocculation with FeCl<sub>3</sub> and polyelectrolyte. Treated water can be reused in new dyeing processes of cotton fabrics with high quality results.

**Keywords:** *Moringa oleifera*; natural coagulant; reactive dyes; color removal; textile wastewater; water reuse; cotton dyeing

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## 1. Introduction

*Moringa oleifera* Lam. (synonym *Moringa pterygosperma* Gaertn.) is a tropical multipurpose tree originally growing in India, Pakistan, Asia Minor, Africa and Arabia [1] and that has been later distributed to Central America, North and South America, and the Caribbean Islands [2]. Almost every part of the plant (leaves, flowers, seeds, roots and bark) can be used as food or for medicinal and therapeutic purposes [3].

Interest in the oil extracted from *Moringa oleifera* seeds has grown significantly over the years. This vegetable oil, known commercially as “Ben” or “Behen” oil, is suitable for edible purposes as it contains high levels of oleic acid (closer to 80%) [4]. Apart from nutritional purposes, other applications of Ben Oil have been reported in cosmetics, lubricants for fine machinery and lately for biodiesel production [5].

The powder of *Moringa oleifera* seeds is also reported as coagulant/flocculant agent for drinking water clarification due to its high content of a water soluble cationic protein able to reduce turbidity [6,7]. The defatted residues generated from *Moringa oleifera* oil extraction can be valorized as water treatment agent, not only for drinking water clarification, but also for municipal wastewater treatment [8,9]. The use of natural coagulant/flocculant agents is especially prominent in developing countries, in substitution of external chemical coagulants (aluminum sulfate, ferric chloride) [10,11]. These natural coagulant/flocculants can also be applied in industrial wastewater treatment, as is in the case of wastewater generated in textile dyeing and finishing processes [12]. In recent years, the valorization of natural waste as low-cost materials for the treatment of textile effluents has garnered interest [13–15].

In this work, the use of waste from *Moringa oleifera* oil extraction is proposed for the removal of dyes from textile wastewater in substitution of more expensive decolorization methods which require the use of chemical reagents or higher operation and maintenance technologies, namely: coagulation/flocculation with Fe or Al salts [16,17], adsorption with active carbon [18,19], membrane technology [20–23], and advanced oxidation methods (ozonation [24,25], Fenton and Photo-Fenton reactions [26,27], heterogeneous photocatalysis [28,29] or electrochemical techniques [30,31]). In some cases, hybrid systems are applied to treat highly concentrated dyebaths, as is the case of combined process of coagulation/flocculation and nanofiltration [32].

Valorization of *Moringa oleifera* wastes to treat textile wastewater could be of special interest for the Asian, African and American regions where the plant is grown, as there are many countries with a strong textile sector, for example China, India, or Brazil [33].

The textile industry is characterized by the large volume and variability of wastewater produced in their dyeing and finishing processes. 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 [34]. Azo dyes can be fragmented by reduction reactions of the azo group, generating aromatic amines. The aromatic amines can be harmful and some of them have been classified as carcinogenic and genotoxic by the International Agency for Research on Cancer [35]. 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 [36].

Among the different kinds of textile dyes, reactive ones are widely used in the dyeing of cotton and other cellulosic fibers since they offer high washing fastness and brilliant colors. Reactive dyes represent

25% of the total world market [37]. On the other hand, these dyes have a relatively low degree of exhaustion and fixation, from 70% to 90% [38]. The unfixed dyes are hydrolyzed and cannot be reused because they are unable to be covalently fixed to the cellulosic fibers. Consequently, substantial amounts of unfixed dyes are released in the wastewater.

Another environmental concern associated to dyeing with reactive dyes is the generation of highly saline effluents due to the amount of electrolyte, generally NaCl, required to increase the dye exhaustion and fixation. About 50–80 g·L<sup>-1</sup> of salt is added during the reactive dyeing [38] which is almost completely discharged into the wastewater after the dyeing process. The presence of high concentration of salts is very harmful for aquatic ecosystems. Moreover, its elimination is only possible through applying costly treatments as reverse osmosis [39] or electrodialysis [40]. These environmental problems draw attention to residual reactive dyebath discoloration. In addition, the reuse of discolored salt-containing effluents in new dyeing processes can also be considered. This approach entails a significant saving of water and electrolyte.

This work is focused on the use of the waste of oil extraction from *Moringa oleifera* seeds to eliminate five azo reactive dyes from synthetic effluents. In recent years, some studies have been published about the treatment of acid dyes (anionic dyes) with *Moringa oleifera* seeds [41,42] but to our knowledge there is no previous literature centered on the use of *Moringa oleifera* to remove reactive dyes, nor on the use of waste from seed extraction. The effect of pH, dye hydrolysis and salt content in simulated dye baths are studied with the aim to evaluate the viability of *Moringa oleifera* waste to treat industrial reactive dyeing effluents. The efficiency of dye removal with *Moringa oleifera* waste is compared with the use of the chemical coagulation-flocculation. Finally, the feasibility of reusing the treated water to carry out new dyeing of cotton fabrics was verified.

## 2. Experimental Section

### 2.1. *Moringa oleifera* Oil Extraction

Dry *Moringa 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, Groupe SEB Ibérica, Barcelona, Spain).

One g of *M. oleifera* crushed seeds fed to a Soxhlet extractor fitted with a 250 mL round-bottom flask and a condenser. The extraction was run for 2 h in triplicate ( $n = 3$ ) with 100 mL of two different solvents: hexane and ethanol (Sharlau, Sharlab S.L., Sentmenat, Barcelona, Spain). After the extraction, the solvent was distilled off under vacuum in a rotary evaporator. The extracted oil yield was expressed as percentage in weight (mean  $\pm$  standard deviation). Oil yield extraction was higher for ethanol (36.1%  $\pm$  1.83%) than for hexane (24.6%  $\pm$  2.19%). The ethanol extraction yield is in accordance with results of other authors [43] whereas hexane only achieves a partial oil extraction. For this reason, in this work, ethanol was selected as solvent for oil extraction.

Protein content of the *Moringa oleifera* seeds before and after oil extraction was determined by analysis of Nitrogen Kjeldahl (protein = N(%)  $\times$  6.25). The protein content of seeds before extraction was 25.0%  $\pm$  1.45% (mean  $\pm$  standard deviation,  $n = 3$ ). The protein content of the defatted residues after

extraction with ethanol was  $34.38\% \pm 2.03\%$ . This increase in the protein content should favor the coagulant effect of *Moringa oleifera* solutions.

## 2.2. Preparation of Coagulant from *Moringa oleifera*

Residues obtained after the extraction of oil from the seeds, also called *Moringa oleifera* meal, were dried at 60 °C for 24 h and latter were kept at room temperature. In order to evaluate the influence of salt on the extraction of the coagulant protein, two different suspensions at 5% (w/v) were prepared by stirring at room temperature (for 2 h) a portion of the oilseed residue: one with distilled water (referred as Mw) and another one with NaCl 1 M (referred as Ms). In order to evaluate the influence of coagulant filtration on dye removal efficiency, each coagulant solution (Mw and Ms) was divided again in two fractions: the first one was kept to be used directly (Mwd and Msd, respectively) and the second one was filtered (Mwf and Msf) with 0.45 µm glass filter (Millipore, Madrid, Spain).

## 2.3. Preparation of Reactive Dye Solutions

Five azo reactive dyes widely used on cotton dyeing industries were selected in this study. They were supplied by DyStar. Their chemical structures are shown in Figure 1. In the literature, these five dyes have been the target of several studies of elimination by different technologies [29,30,44].

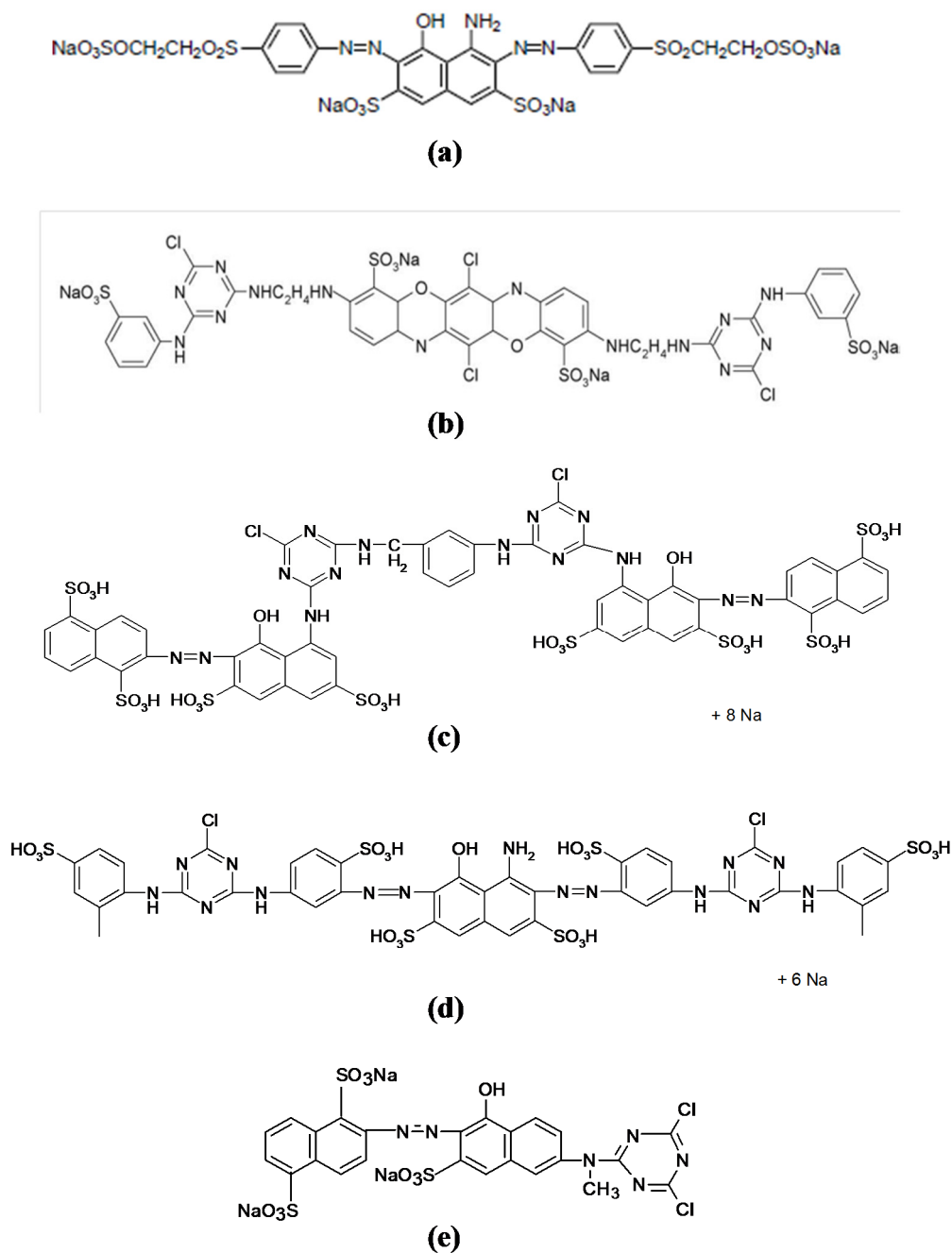
The Orange Procion MX-2R has the smallest structure with only one azo group as chromophore and one reactive group (dichlorotriazine). All the other dyes have two azo groups and are bi-functional. Procion H-EXL dyes have two monochlorotriazine reactive groups whereas Remazol Black dye has two vinyl sulfone groups. All dyes have several sulfonic groups in their chemical structure to increase their solubility in water. The negative charge of sulfonic groups will probably favor the coagulation of dyes with the positive charged proteins of *Moringa oleifera*.

Simulated dye baths were prepared at a dye concentration of 0.1 g/L in decalcified water. In the textile industry the dyeing process with reactive dyes is carried out with the addition of salt as electrolyte and at alkaline pH. This procedure generates alkaline and saline residual dye baths which contain the reactive dye in its hydrolyzed form.

The range of pH was selected from 5 to 11 (5, 7, 9 and 11) and it was adjusted with HCl 1 M or NaOH 1 M. The lower pH was established in previous published studies [41,42] and the more alkaline corresponds to the usual value in industrial effluents. The NaCl concentration in dye solutions was fixed at 60 g/L (1 M), as it is usual in dyeing process with reactive dyes [45].

To ensure the dye hydrolysis, all solutions were initially prepared at pH 12, boiled for 2 h and settled for 24 h. After this process, the solution was adjusted to the corresponding experimental conditions (pH and NaCl concentration).

**Figure 1.** Chemical structures of the selected reactive dyes: (a) Remazol Black B-133 (b) Procion Blue H-EXL (c) Procion Crimson H-EXL (c) and (d) mixture: Procion Navy H-EXL (e) Procion Orange MX-2R.



#### 2.4. Dye Removal Tests

Tests of dye removal were carried out with 50 mL dye solution samples by adding different concentrations of *Moringa oleifera* seed extract at ranging from 1250 to 250 mg/L of *Moringa oleifera*, in order to optimize this parameter.

Samples were first submitted to a fast stirring at 150 rpm for 10 min and subsequently they were stirred slowly at 20 rpm for 30 min. Finally, the treated samples were allowed to stand 24 h to promote natural decantation.

Dye removal values were calculated by UV-visible spectrophotometric measurements (Shimadzu UV-2401 PC, Shimadzu Corp., Kyoto, Japan), from the absorbance values at the maximum dye absorption wavelength (indicated in Table S1 of Supplementary Information). For each dye, the interval of linear relationship absorbance vs. dye concentration was previously established. All dye removal tests were carried out in quintuplicate.

Once the optimal conditions were selected (type of extraction, concentration of *Moringa Oleifera* and pH), trials with 1 L of dye solution samples were performed in a Jar Test which is designed for the small scale reproduction of industrial coagulation-flocculation treatments.

Conventional coagulation/flocculation tests were also carried out in Jar Test with 750 mg/L Iron (III) chloride solution (10%) and 1 mg/L polyelectrolyte TS140 (Deripol, Barcelona, Spain) solution (1 g/L) as coagulant and flocculant, respectively, which are the common values for this type of water.

For Jar Test trials, dye removal measurements were performed after 30 min (V30 min) and 24 h (V24 h) decantation times in Imhoff cones.

### 2.5. Cotton Dyeing with Decolorized Water

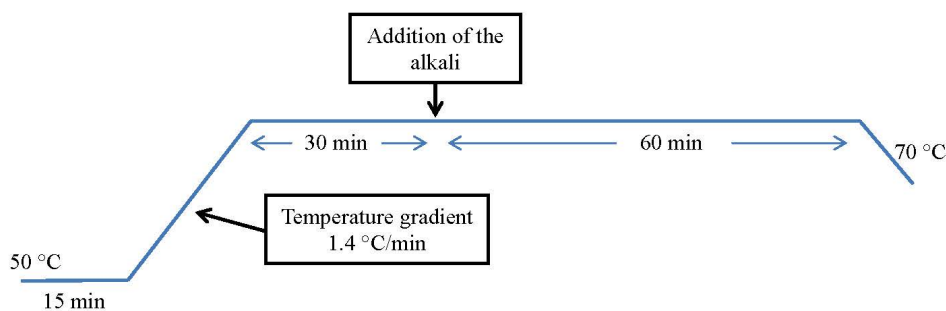
Samples of treated water were used for the dyeing of cotton fabrics (referred hereafter as reused dyeings) with the five selected dyes. Reference dyeings with decalcified tap water were also carried out. Dyeing tests were carried out at a liquor ratio (LR) 1/10 (fibre weight/water volume) [46] in a laboratory batch dyeing machine (Ti-Color OTX 200, Intex System, Prato, Italy) equipped with 12 stainless steel drums of 100 mL. Decolorated water was mixed and filtered with glass fiber to eliminate suspended solids. Cotton knitted fabric (Pique), scoured and prepared for dyeing, was selected.

Individual dyeing of 10 g of cotton samples was performed at standard depth with each dye at 3% o.w.f. (over weight fabric), which corresponds to 3 g/L at a LR of 1/10. A dyeing with a mixture of dyes (thricromie: Blue, Crimson and Orange) was also carried out, being the concentration of each dye 1% o.w.f. (1 g/L at LR 1/10). In the case of reference dyeings, 60 g/L NaCl was added as dyeing electrolyte. With the reused water, the addition of NaCl was not necessary. In both cases, 16 g/L Na<sub>2</sub>CO<sub>3</sub> was added as dyeing alkali.

According to the information supplied by dye supplier [47], a dyeing method “all in” was selected. The dye and the entire electrolyte were included in the initial dyeing bath and the alkali was added when the dyeing process was already started (see Figure 2). All the dyeing experiments were run in triplicate.

After the dyeing process, a washing process was applied to eliminate the unfixed dye. This process consists of nine successive washing steps. The first ones (1st–3rd washes) were at 50 °C with tap water during 10 min, then a soaping step (4th wash) took place with 2 g/L of COTEMOLL TLTR at 95 °C during 15 min. After, a tap water step (5th wash) and other soap step (6th wash) were carried out with the same conditions described above. Finally, another three washes at 50 °C were carried out during 10 min (7th–9th washes). All steps were performed at liquor ratio 1:10.

Figure 2. Dyeing method.



Color differences between reused and reference dyeing were measured to evaluate the viability of reusing the treated effluent. With this purpose, the final dyed fabric colour was measured by a spectrophotometer Macbeth Color Eye 7000, with illuminant D65 and 10° of standard observer. The instrument evaluates the chromatic coordinates of each dyed fabric. These coordinates are defined by three parameters (Lightness  $L_{cmc}$ ; Chroma  $C_{cmc}$ , and Hue  $H_{cmc}$ ). According to the standard UNE-EN ISO 105-J03: 1997 [48], the color difference between two samples is calculated with the formula  $DE_{CMC(2:1)}$ , represented in the Equation (1):

$$DE_{CMC(2:1)} = [(\Delta L^*/2S_L)^2 + (\Delta C^*_{ab}/S_C)^2 + (\Delta H^*_{ab}/S_H)^2]^{1/2} \quad (1)$$

where  $S_L$ ,  $S_C$  and  $S_H$  are calculated from the chromatic coordinates of the standard dyeings ( $L_R$ ,  $C_R$  and  $h_R$ ) as follows:

$$S_L = 0.040975L_R/(1 + 0.01765L_R) \quad (2)$$

$$\text{If } L_R < 16 \text{ } S_L = 0.511 \quad (3)$$

$$S_C = [0.0638C_R/(1 + 0.0131C_R)] + 0.638 \quad (4)$$

$$S_H = S_C(T_f + 1 - f) \quad (5)$$

$$f = \{(C_R)^4/[(C_R)^4 + 1900]\}^{1/2} \quad (6)$$

$$T = 0.36 + |0.4 \cdot \cos(35 + h_R)| \text{ if } h_R \geq 345^\circ \text{ or } h_R \leq 164^\circ \quad (7)$$

$$T = 0.56 + |0.2 \cdot \cos(168 + h_R)| \text{ if } 164^\circ < h_R < 345^\circ \quad (8)$$

In general, the acceptance limit for colour differences in the textile industry is one unit ( $DE_{CMC(2:1)} \leq 1$ ). This criterion, which is widely used in dyeing quality control to compare the colour differences between two fabric samples, is also applied in this work.

*TOC* measurements of decolorized water ready to reuse were carried out with a *TOC* analyzer (Shimadzu *TOC*-5050A, Shimadzu Corp., Kyoto, Japan) in order to evaluate the effect of organic matter content on quality dyeing.

### 3. Results and Discussion

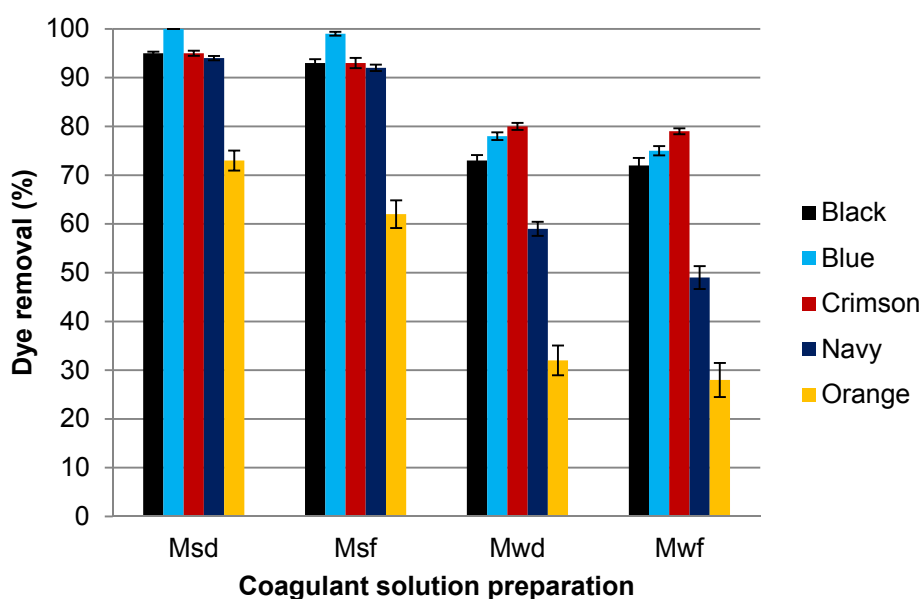
#### 3.1. Influence of the Coagulant Solution Preparation

Different ways to prepare the coagulant solution from *Moringa oleifera* suspensions were studied and their influence on dye removal efficiency was evaluated (Figure 3). These different conditions of

preparation were referred as Mwd, Mwf, Msd and Msf, which correspond to the Moringa seeds waste (M) stirred in water (w) or in salt solution (s) used either directly (d) or filtered (f), as it is indicated in Section 2.2 of the Experimental Section.

Figure 3 evidences that suspensions with salt (Msd and Msf) provided higher dye removal yields than without salt (Mwd and Mwf). Thus, Msd solutions reached more than 94% of dye removal for all dye solutions, except for Orange dye, whereas Mwd solutions reached 80% of dye removal in the best of cases. The presence of salt promotes the extraction of positive charged proteins, which cause the coagulant effect of *Moringa oleifera*.

**Figure 3.** Influence of the preparation conditions of coagulant solution on dye removal efficiency (Dye 0.1 g/L; *Moringa oleifera* 1000 mg/L and pH 5).



Also, when comparing the not filtered suspensions and the filtered solutions, it can be seen that the efficiency of the dye removal process is quite similar, although only a slight increase is shown with the not filtered suspensions.

The lower efficiency of *Moringa* to eliminate Orange dye with respect to the other dyes can be attributed to the smaller size of the dye molecule which only contains one reactive group. Also, the Orange MX-2R dye has three sulfonic groups whereas the new Procion H-EXL dyes have two reactive groups and 4, 6 or 8 sulfonic solubilizing groups (Table S1).

### 3.2. Influence of Dyeing Electrolyte

According to results of the previous section, Msf and Msd were selected to treat dye solutions prepared with distilled water (referred as Dye-w). However, the industrial reactive dyeing effluents are characterized by their high salt content. For this reason, in these cases the addition of salt may be unnecessary. To verify this, simulated industrial effluents were prepared with dye and 60 g/L NaCl (referred as Dye-s). Then, Dye-w solutions were treated with *Moringa* extracted with salt (Msf and Msd) whereas Dye-s solutions were treated with *Moringa* extracted in water (Mwf and Mwd). Results are displayed in Table 1.



**Table 1.** Influence of dyeing electrolyte on dye removal efficiency (Dye 0.1 g/L, Moringa oleifera 1000 mg/L, pH 5). Dye-s contains also 60 g/L NaCl.

| Dye solution | Extraction | Black           | Blue | Crimson | Navy | Orange |
|--------------|------------|-----------------|------|---------|------|--------|
|              |            | Dye removal (%) |      |         |      |        |
| Dye-w        | Msf        | 93              | 98   | 93      | 92   | 62     |
|              | Msd        | 95              | 100  | 95      | 94   | 73     |
| Dye-s        | Mwf        | 93              | 94   | 91      | 90   | 63     |
|              | Mwd        | 95              | 97   | 93      | 95   | 68     |

Dye removal results for salt containing simulated industrial effluents were similar to the ones of dye solutions treated with Moringa extracted with salt. This fact implies that in dye solutions which already contain salt (Dye-s), the extraction of Moringa oleifera waste can be performed only with water.

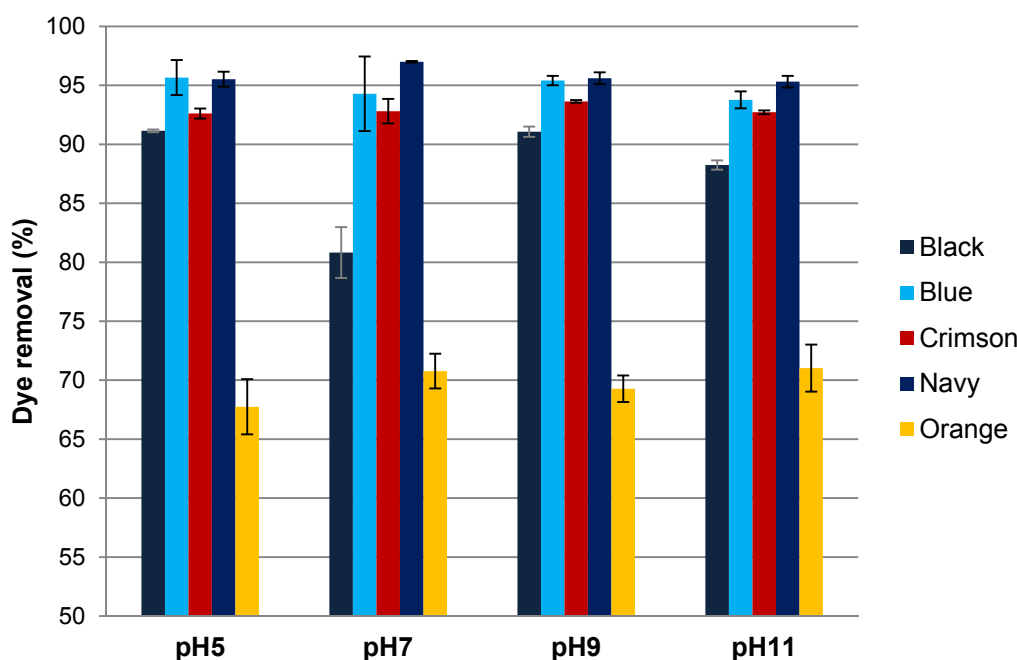
Dye removal yields higher than 90% were achieved for all dyes, except for Orange Procion dye, as expected. By another hand, not filtered suspensions of Moringa oleifera (Msd and Mwd) provided again slightly better results than filtered solutions (Msf and Mwf).

For this reason in the subsequent sections, Moringa oleifera suspensions were prepared only with water and were used directly without filtration (Mwd). Salt was added to the synthetic dye effluent to simulate industrial reactive dyebaths.

### 3.3. Influence of the pH

Different pH values ranging from pH 5–11 were tested in order to evaluate their influence on the dye removal efficiency (Figure 4).

**Figure 4.** Influence of pH on dye removal efficiency (0.1 g/L dye, 60 g/L NaC, Moringa oleifera 1000 mg/L).



As is shown in Figure 4, dye removal results were almost independent of pH, being slightly better at pH 9 for Black, Blue and Crimson. At this pH, dye removal values were higher than 90% for all dyes except for the Orange, which in all cases obtained lower results (closer to 70% of dye removal).

As reactive dyeing effluents and the subsequent washing baths are alkaline, this fact facilitates industrial application because pH adjustment is not required.

### 3.4. Influence of Coagulant Concentration

In order to optimize the addition of coagulant to the dye solutions, several *Moringa oleifera* suspensions were prepared in a range of 250 mg/L–1250 mg/L. Dye removal results obtained are shown in Figure 5.

**Figure 5.** Influence of *Moringa oleifera* concentration on dye removal (0.1 g/L dye, 60 g/L NaCl and pH 9).

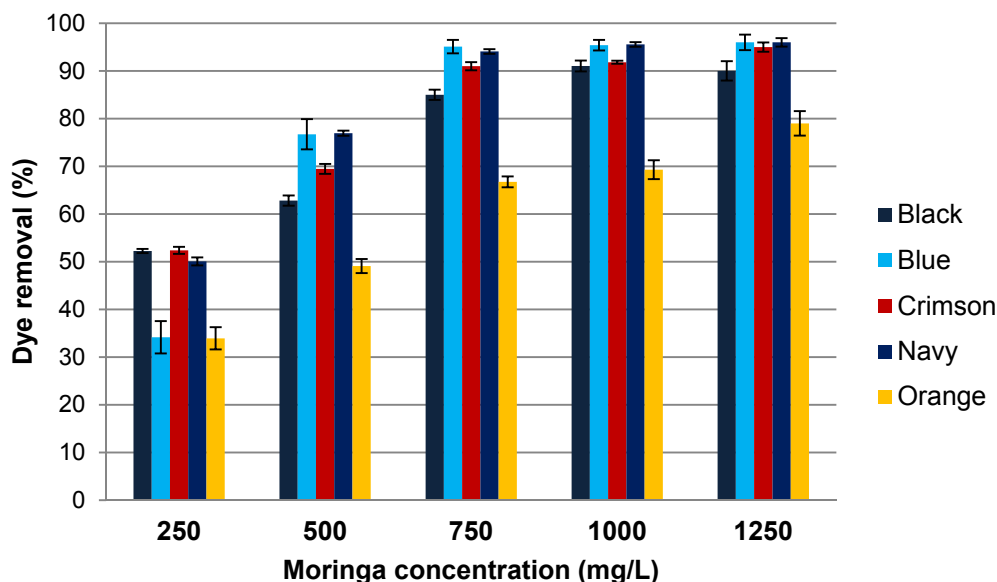


Figure 5 evidences the increase of dye removal when *Moringa oleifera* concentration was also increased up to 750 mg/L. More than 90% of dye removal was achieved with the 750 mg/L solutions for Blue, Crimson and Navy dye solutions and more than 85% for Black dye solution. The Black dye solution reached 90% of dye removal with the addition of 1000 mg/L *Moringa* solutions. Orange dye is the most difficult to be coagulated with *Moringa oleifera*. Nevertheless, the addition of 1250 mg/L *Moringa* solution enabled obtaining Orange dye removal close to 80%.

### 3.5. Efficiency of *Moringa oleifera* Waste versus Ferrous (III) Chloride

The dye removal efficiency of *Moringa oleifera* waste was compared with respect to the conventional wastewater coagulation-flocculation method with Ferrous (III) Chloride and a polyelectrolyte. In both cases, coagulant concentration was fixed at 750 mg/L. Jar Tests trials were carried out with 1 L samples which were subsequently allowed to settle in Imhoff cones. Dye removal and settled sludge volumes were determined after 30 min (V30 min) and 24 h (V24 h) decantation times.

As can be seen in Table 2, *Moringa oleifera* waste is much more efficient on dye removal than the conventional coagulation/flocculation treatment with  $\text{FeCl}_3$  and polyelectrolyte. *Moringa oleifera* reached 89%–96% removal yield for Blue, Crimson and Navy dyes after 30 min decantation and 96%–97% after 24 h. For the Black dye, the removal yield was 85% and for the Orange it decreased to 53%. In opposite, the dye removal obtained with 750 mg/L  $\text{FeCl}_3$  and 1 mg/L polyelectrolyte was very low, ranging from 0% to 56%. Only the Blue dye surpassed 50% removal yield.

**Table 2.** Jar Tests trials with *Moringa oleifera* waste (750 mg/L) and with  $\text{FeCl}_3$  (750 mg/L) + polyelectrolyte (1 mg/L). Dye 0.1 g/L, NaCl 60 g/L and pH 9. Decantation time: 30 min (V30 min) and 24 h (V24 h).

| Jar test                     |         | Black | Blue | Crimson | Navy | Orange |
|------------------------------|---------|-------|------|---------|------|--------|
| Dye removal (%)              |         |       |      |         |      |        |
| Moringa                      | V30 min | 83    | 90   | 89      | 96   | 54     |
|                              | V24 h   | 85    | 96   | 96      | 97   | 53     |
| $\text{FeCl}_3$ + poly       | V30 min | 9     | 56   | 24      | 30   | 3      |
|                              | V24 h   | 4     | 53   | 20      | 25   | 0      |
| Settled sludge volume (mL/L) |         |       |      |         |      |        |
| Moringa                      | V30 min | 38    | 150  | 100     | 130  | 33     |
|                              | V24 h   | 27    | 60   | 40      | 59   | 29     |

In this way, the promising results obtained with *Moringa oleifera* in the previous sections were corroborated by Jar Tests. Thus, whereas dye removal results with  $\text{FeCl}_3$  and polyelectrolyte were very poor, high dye removal rates were obtained with *Moringa oleifera* after 30 min decantation, which were even increased after 24 h decantation.

In addition, it should be highlighted that sludge generated by *Moringa oleifera* waste was easy to be decanted and settled. In fact, high settled sludge volumes (100–150 mL/L) were generated after 30 min of decantation in the three dye solutions with almost full dye removal (Blue, Crimson and Navy). These values were significantly decreased to 40–60 mL/L when decantation was extended to 24 h.

### 3.6. Reuse of the Decolorized Effluent for New Dyeing Process

Cotton fabrics were dyed with the five selected dyes with the decolorized water in order to evaluate the feasibility in reusing these high salt containing effluents. Dyeing was performed with a single dye and also with a trichromie of dyes (mixture of Blue, Crimson and Orange), as trichromies are very common in the textile dyeing process [49]. Color differences of each sample were evaluated with respect to the corresponding reference dyeing made with clean water (Table 3).

As can be seen in Table 3, color differences ( $DE_{\text{CMC}(2:1)}$ ) below 0.5 were obtained in dyeing with Blue, Crimson and Navy dyes, as well as for the trichromie, which is an excellent result. On the contrary, for Black and Orange dyes, color differences were slightly above the limit established in quality dyeing control ( $DE_{\text{CMC}(2:1)} \leq 1$ ).

The dyeing color differences, the dye removal rate and TOC content of the decolorized water reclaimed in the dyeing can be compared in Table 4. High quality dyeing with very low color differences were obtained when the residual dye was almost removed. On the other hand, color differences were

higher if the residual hydrolyzed dye was not properly removed. The residual hydrolyzed dye decreases the fixation of the new dye. Although the former cannot react with the cotton fiber, it can occupy the sites for the fixation of the new dye and in this way, the dye fixation rate is slowed down which implies an increase of new dye hydrolysis.

**Table 3.** Color differences of dyeing performed with decolorized water with respect to the corresponding reference dyeing.

| Dyeing     | DL    | DC    | DH    | SL   | SC   | SH   | DE <sub>CMC(2:1)</sub> |
|------------|-------|-------|-------|------|------|------|------------------------|
| Black      | −1.35 | −0.59 | 0.27  | 0.67 | 1.79 | 1.18 | 1.09                   |
| Blue       | 0.22  | 0.13  | −0.34 | 0.96 | 4.04 | 2.45 | 0.18                   |
| Crimson    | 0.54  | −0.11 | −0.66 | 0.89 | 6.65 | 4.52 | 0.33                   |
| Navy       | −0.72 | 0.10  | −0.01 | 0.73 | 2.02 | 1.30 | 0.49                   |
| Orange     | 2.28  | −5.40 | −1.49 | 1.15 | 9.04 | 3.90 | 1.22                   |
| Trichromie | 0.37  | −0.15 | 0.06  | 0.71 | 1.79 | 1.18 | 0.27                   |

An important fact to be highlighted is that the presence of organic matter in the reused water due to *Moringa oleifera* treatment did not cause any effect on the quality of dyeing. Very small color differences were obtained with reused water which contained 91–97 mg/L of *TOC*.

**Table 4.** Dyeing color differences and characteristics of the reused water (dye removal rate and *TOC* content).

| Parameter              | Black | Blue | Crimson | Navy | Orange |
|------------------------|-------|------|---------|------|--------|
| Dye Removal (%)        | 85    | 96   | 96      | 97   | 53     |
| <i>TOC</i> (mg/L)      | 101.1 | 95.9 | 91.4    | 97.4 | 108.0  |
| DE <sub>CMC(2:1)</sub> | 1.09  | 0.18 | 0.33    | 0.49 | 1.22   |

#### 4. Conclusions

The defatted *Moringa oleifera* wastes can be valorized as coagulant solutions for the removal of dyes from textile wastewater.

The optimal *Moringa oleifera* waste concentration was 750 mg/L. The coagulant effect of *Moringa* solutions/suspensions is enhanced in the presence of NaCl, which is used as dyeing electrolyte. Dye removal results were almost independent on pH, although they were slightly better at pH 9 (the usual pH of reactive dyeing and washing effluents). These conditions provided higher dye removal yield than with use of the conventional coagulation-flocculation with FeCl<sub>3</sub> and polyelectrolyte.

For a typical residual reactive dyebath, more than 95% Blue, Crimson and Navy dyes are removed with *Moringa oleifera* waste, 85% Black dye and almost 80% of Orange dye.

The different behavior of dyes with respect to the *Moringa oleifera* coagulant action can be attributed to their chemical structure, and specifically to the number of sulfonic groups. The Orange dye is the smallest one with only three sulfonic groups whereas the rest of dyes have four, six or eight sulfonic groups in their molecular structure.

Finally, the feasibility of reusing decolorized water in new dyeing processes with reactive dyes was demonstrated. The reuse of decolorized dye baths not only entails water saving but also NaCl saving and

the reduction of salinity in the discharged wastewater. Very good quality dyeing with  $DE_{CMC(2:1)}$  below 0.5 were obtained for Blue, Crimson and Navy dyes as well as for the trichromie. For Black and Orange dyes, color differences were slightly above the limit established in quality dyeing control ( $DE_{CMC(2:1)} \leq 1$ ).

## Supplementary Information

**Table S1.** Characteristics of the five reactive dyes studied.

| Commercial Name       | C.I. Name         | Chromophore/reactive group             | Number of sulfonic groups | $\lambda$ max (nm) | Chemical structure (Figure 1) |
|-----------------------|-------------------|--|---------------------------|--------------------|-------------------------------|
| Remazol Black B-133   | Reactive Black 5  | Bis-azo/bis-vinyl sulfone              | 4                         | 599                | a                             |
| Procion Blue H-EXL    | Reactive Blue 198 | Bis-oxazine/<br>bis-monochlorotriazine | 4                         | 625                | b                             |
| Procion Crimson H-EXL | Reactive Red 231  | Bis-azo/<br>bis-monochlorotriazine     | 8                         | 546                | c                             |
| Procion Navy H-EXL    | Not available     | Bis-azo/<br>bis-monochlorotriazine     | 8 or 6                    | 606                | c and d (mixture)             |
| Procion Orange MX-2R  | Reactive Orange 4 | Azo/dichlorotriazine                   | 3                         | 490                | e                             |

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## Author Contributions

Mercè Vilaseca performed the dye removal experiments, Jar tests and the dyeings of cotton fabrics; Víctor López-Grimau and Carmen Gutiérrez-Bouzán wrote and corrected the paper and they also coordinated the experimental work.

## Conflicts of Interest

The authors declare no conflict of interest.

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