

Reducing environmental impact of textile wastewater by natural coagulants and reuse of effluents

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ABSTRACT

Water scarcity is a global problem, therefore the reuse and recycling of water is promoted in all sectors and it is a real alternative for the conservation of water resources. The industrial sector is a key point in the reuse of water as it is a major consumer of this precious resource. The textile industry consumes more than one hundred liters of water per kilogram of finished fabric during the dyeing and finishing processes. The wastewater generated by this industry is generally coloured and can also contain other recalcitrant compounds. In addition, some textile effluents have high salinity and are highly alkaline. In this work, a new treatment using a natural coagulant, *Moringa Oleifera* extract, is presented. Coagulant solution was made from moringa seed ground degreased and was tested at variable concentration (1000–5000 mg/l) on different dyeing wastewater samples. Exhausted dyeing liquors and residual washing baths samples were efficiently treated. Up to 90% colour removal was achieved, preserving at the same time the alkaline and saline properties of the water. Consequently, the treated effluents could be reused in new dyeing processes with successful results. It was shown that the implementation of this practice would have considerable environmental and economic benefits.

Keywords: *Moringa oleifera*; Wastewater; Reuse; Recycling; Textile; Dyes

1. Introduction

Water is critical to sustain human life and nature. The industry has an important role in the global water use. In Europe, industrial activities have a relevant effect on the direct and indirect water usage (consumption, manufacture of products and/or services), which can be reflected as a large water footprint. In specific and worst future scenarios, blue water footprint (direct consumption) of the industrial production in the European Union could increase around

800% in Eastern Europe and around 30% in the western territory by 2050 compared to 2000 [1].

In the textile industry dyeing and finishing processes (including washing steps) consume a large quantity of water. The consumption of this resource varies in each company, which implies that this data varies depending on the reports generated by each author. Moreover, the water footprint of the textile sector could be considered even greater when the fibre production and domestic washes are taken into account [2].

The consumption of water and reagents depends on the dyeing process, the class of dye and the type of fabric [3]. The same happens with the volume of generated waste-

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water. Residual soluble dyes are more difficult to eliminate than the low solubility ones and they require a huge amount of water to be removed after dyeing [4]. In a typical dyeing and finishing plant, about 120–280 L of water can be consumed per kilogram of processed cotton fabric [5].

Fibres used in the textile processes can be classified by their natural or synthetic origin. One of the main natural fibres is cotton [6]. Two-thirds of dyes used for cellulose fibres are reactive dyes, and can also be used for dyeing wool, silk and nylon. Approximately 25% of the total global market corresponds to this class of colourants [7,8].

In addition, wastewater generated by the textile industry is one of the most polluting of the entire industrial sector. The main source of wastewater generated by the textile industry is the washing and bleaching of natural fibres, dyeing processes and finishing stages [9]. For this reason, pollution caused by residual dyes from dyeing and finishing processes is a major environmental problem. The treatment and dyeing of the textile products are responsible for about 20% of the industrial pollution in fresh waters, according to Carrera-Gallissà [2].

Wastewater effluents from the textile industry can be treated by biological and physical-chemical processes or by a combination of these. However, some contaminants such as synthetic dyes consist of highly complex and highly structured molecules, that make them very stable and therefore difficult to degrade. In this case, the biological processes are not very effective for this purpose [6].

Typically, textile effluents contain unreacted dyes, salts, dispersing agents, surfactants, wetting agents, fixatives, softeners and organic compounds from the dyed material [4,6,10]. These wastewaters could contain a variety of recalcitrant compounds, which come from various stages of the dyeing process and are different depending on fibres, dyes and additives used. Therefore, the wastewater composition and concentration varies considerably [3].

The high salinity of effluents due to the amount of residual electrolyte, generally NaCl, is also a real environmental problem associated with dyeing processes. The amount of electrolyte required depends of each dyeing process. After dyeing the salt is almost completely discharged into the wastewater. High salt concentration affects the aerobic and anaerobic biological wastewater treatments. It has been shown that high sodium concentration ($\text{Na}^+ > 3 \text{ g L}^{-1}$) can cause moderate inhibition of most bacterial activities and therefore low BOD removal performance [11]. These effluents, discharged directly to the environment, can be harmful for aquatic ecosystems [12]. Unfortunately, parameters such as conductivity or chloride ion concentration are not specifically regulated in some countries. In addition, the specific technologies for the removal of salt are rather expensive.

The amount of dye discharged into the environment is uncertain. Some authors mention that approximately 2,200 tons of hazardous dyes are discharged annually in the municipal wastewater treatment system [10]. In the case of reactive dyes, they usually have 60–90% fixation when dyeing cotton fibres, whereby the residual dye remains in the effluent [4].

Residual dyes (including non-toxic dyes) are easily detectable because they generate deep colour, which is unsightly and also can damage aquatic ecosystems because

they affect the transmission of light and alter the biological processes [6].

The large quantity of water consumed by the textile and clothing industry produces an important impact in the worldwide water footprint. For this reason, this work aims to provide a solution to some of the problems associated to the textile effluents such as the high environmental and visual impact of dyes, as well as their high salinity.

Reusing water after appropriate treatment extends its life cycle, but the reused water must fulfill some general conditions such as fit the quality for the particular purpose, do not lead to unacceptable environmental impacts and have an acceptable cost. As matter of fact, industrial water recycling has been implemented on a large scale since the seventies. Consequently, water reuse promotes the resource's symbiosis and the circular economy. An industry may reuse its own treated wastewater or reuse water from a different industry, from other sectors or even from urban water [13,14].

In Europe the limited awareness of potential benefits and the lack of a supportive framework are some of the barriers for extensive implementation of the water reuse. Nevertheless, actually there are many initiatives by the European Commission to support this practice [15].

The chemical treatments combined with a pretreatment (screening and homogenization of residual effluents) are widely used as industrial wastewater treatments for the further disposal of the sewage system. The process of coagulation-flocculation is one of the most extended chemical treatments [16].

Many impurities in water and wastewater are present in the form of colloidal solids that do not settle easily since they are finely dispersed and suspended. These particles, which cannot be efficiently removed by ordinary sedimentation, produce turbidity and water colour. The addition of a coagulant followed by the water stirring achieves the neutralization of the electrostatic surface potential in the particles. The resulting destabilized particles are bonded to each other upon contact to the formation of solids known as "flocs". Once these larger particles are generated and suspended, they are normally removed from the liquid by sedimentation [17].

A wide variety of coagulants are used in the industry. They can be classified in different ways: they are typically classified in inorganic and organic coagulant or they also can be classified as natural and synthetic coagulants. Sometimes the combination of coagulants can improve the process [6].

The most common inorganic coagulants in the treatment of textile effluents are usually alum, ferric chloride and ferrous sulphate. Generally, the procedure is economically viable with satisfactory disposal. A disadvantage of the inorganic coagulants is the increasing of salinity. However, the main drawback of the process is that the final product is a concentrated sludge produced in large quantities. Besides this, the elimination depends on the pH. Moreover, some troubles associated to health have also been reported such as the generation of diseases such as Alzheimer's, senile dementia and similar neurological problems [17,18].

The organic coagulants can be obtained from different sources. In comparison to inorganic coagulants, the management of generated sludge is much easier and less expensive. It is important to mention that the synthetic organic coagulants can be toxic and harmful to the man and the

environment [6], while the natural organic coagulants generally are not.

The efficiency of the *Moringa oleifera* to improve water quality has been demonstrated in several studies and it has been classified as one of the best coagulants applicable in water treatment plants. The seeds of this plant contain large amounts of coagulant proteins [19] that are efficient to treat water colour and turbidity. It has been widely used with the purpose of obtaining drinking water. Nevertheless, in our study we propose it to treat industrial wastewater.

The *Moringa oleifera* plant is easy to grow and is widespread in many tropical and subtropical areas of Africa and America, India, Malaysia, Australia, among others. Tropical tree of moringa is typically up to 10 m high. It belongs to the moringaceae family and 14 different species are known [18,19].

Moringa oleifera is a multipurpose plant. It is a fully edible plant (seed, leaf, flower and root). It is rich in nutrients and vitamins, and it is considered as nutraceutical food. It is also used as fertilizer, as a useful source of medicines and as a coagulant to clean water. Also, the moringa oil it is widely used in cosmetics and other areas. An important fact is that seed cake generated as a residue after oil extraction contains high levels of coagulant proteins. In addition, Vilaseca et al. [12] demonstrated that the *Moringa oleifera* can be used to treat simulated coloured wastewater and this discoloured effluent can be reused for new dyeing processes, which enables the reuse of water and salt. In this case, the coagulation efficiency increases at high NaCl concentration.

The main objective of this study is to apply the residual cake of *Moringa oleifera* seeds to the treatment of real industrial wastewater collected in a textile mill and also to verify the feasibility of reusing these effluents in the dyeing process. In this way, the industrial use of this waste as a natural coagulant will be validated.

2. Experimental

2.1. Coagulant preparation

Peeled *Moringa oleifera* seeds were ground and the oil fraction was separated by soxhlet extraction with ethanol. Around 25% oil was extracted and the remainder constituted the seed cake. This residual seed cake was dried at 60°C for 24 h and was used at room temperature to prepare coagulant stock solution at 5% w/v.

In order to evaluate and compare the moringa coagulant performance, ferric chloride (FeCl₃) at 10% w/v was prepared, as well as Hyfloc SS polyelectrolyte 0.1% w/v as a auxiliary flocculant. This is the one of the most conventional commercial coagulants widely used at industrial level.

2.2. Samples characterization

Different textile wastewater samples were obtained from a textile mill specialized in dyeing and finishing processes (Table 1):

- Samples taken from residual dye liquors; these samples contain high dye concentration, have high salinity and exhibit highly alkaline pH.
- Samples taken from washing baths; these samples also exhibit highly alkaline pH. Contain high dye concentration, high salinity but lower than dye liquors samples.

“Standard Methods” [20] were employed for characterization. Platinum-Cobalt colour units (Pt-Co) were evaluated by visual and instrumental techniques using Shimadzu UV-2401PC spectrophotometer. pH, conductivity (Cond.) and salt concentration were analysed by Crison GLP 21 pH meter, Crison GLP 31 conductivity meter and Dionex ion chromatograph, respectively. By the same methods Total Suspended Solids (TSS) were evaluated. By other hand Spanish Standard UNE-EN 1484:1998 [21] was employed for Total Organic Carbon (TOC) determination by Shimadzu TOC analyser.

2.3. Treatment

Tests were performed at different moringa coagulant concentrations without pH adjustment: 1000, 2000 and 5000 ppm. The efficiency of *Moringa Oleifera* coagulant was compared with FeCl₃ performance at 1000 ppm with 0.4% polyelectrolyte. FeCl₃ coagulation-flocculation test was performed and samples adjusted to pH 9.5.

A jar test system was used to carry out the experiments. The efficiency of the colour removal was evaluated by both visual and instrumental methods mentioned above. Also, the supernatant at 30 min and 24 h was evaluated for each sample.

Table 1
Industrial textile wastewater samples characterization

Sample	pH	TSS (mg/L)	Cond. (mS/cm)	TOC (mg/L)	NaCl (g/L)	Colour (Pt-Co Hazen units)
Dye liquor Purple	10.75	47	100	473	75	4,650
Dye liquor Purple 2	10.41	476	87	358	–	3,609
Dye liquor Black	11.61	99	108	1,187	86	228,880
Washing bath Purple	10.75	35	35	698	21	1,839
Washing bath Purple 2	10.65	5220	27	261	20	1,386
Washing bath Black	11.35	69	44	727	31	79,850

2.4. Reuse of treated water

Supernatant was collected by decanting process after samples treatment. The reuse feasibility was evaluated using the treated effluents to perform dyeing tests with cotton fabrics. Purple wastewater samples were used for this test. For reuse purpose, 3 reactive dyes were selected: Yellow, Navy blue and Crimson Procion H-EXL. The dyeing method was “all in” [4]. That is to say, the initial dyeing bath contains dyes, electrolyte and alkali at programmed temperature (50–95°C). The liquor ratio was 1/10 (fibre weight/water volume) and the dyeing equipment was a Ti-Color. The dyeing step was followed by multiple subsequent washes.

The colour of the dyed fabrics was measured by means of a spectrophotometer CM-3600d, Konica Minolta that evaluates the chromatic coordinates. Results were expressed in $DE_{CMC(2:1)}$ which refers to colour differences between reused and reference dyeings, according to the UNE-EN ISO 105-J03:1997 [22].

3. Results

The coagulant prepared from the cake of *Moringa oleifera* seeds demonstrated to be efficient as coagulant for all of the collected samples. As an example, Fig. 1 shows the dye removal efficiency in dye liquor and washing effluent.

As expected, the colour removal depends on the coagulant concentration of *Moringa oleifera* as well as the amount of reactive dye in the wastewater. In the experiments carried out, results of colour removal up to 90% were achieved (Fig. 2).

The results obtained with 1000 ppm moringa coagulant were very variable. The best results were obtained in samples with low concentration of dye. It should be noted that with 2000 ppm moringa the colour of the samples is considerably removed. Ferric chloride coagulant was not effective to eliminate colour from samples, since it was only possible to remove up to 10% of colour.

High coloured samples required higher concentration of coagulant. In general, the higher concentration of moringa coagulant, the greater dye removal. An important fact is that pH is not a relevant parameter for coagulant efficiency, which is a clear advantage with regard to the most commercial coagulants that are affected by high alkalinity.

Concerning to the reuse step, all the dyes tested provided good dyeing results with colour difference $DE_{CMC(2:1)} \leq 1.0$. The general textile industry practice considers that results equal to or less than one unit are very good and fits clearly the acceptance limit. Depending on the fabric applications, $DE_{CMC(2:1)} \leq 1.5$ are also good and can be accepted.

As expected, the reuse of the treated washing sample exhibited better dyeing results than the ones obtained with dye liquor, probably due to the interference of the residual dye, as well as the remainder of moringa coagulant. This effect is variable depending on the dye used for the dyeing. The navy dye was more affected compared to those made with yellow and crimson (Fig. 3). Clean water was used as a control sample to evaluate the effect of moringa coagulant in the dyeing quality.

Moreover, moringa coagulant did not significantly affect dyeing quality in clean water samples. In general, excellent results were obtained with yellow and crimson dye. Some of the results were above one but less than 1.3 about $DE_{CMC(2:1)}$, meaning also a good dyeing quality.

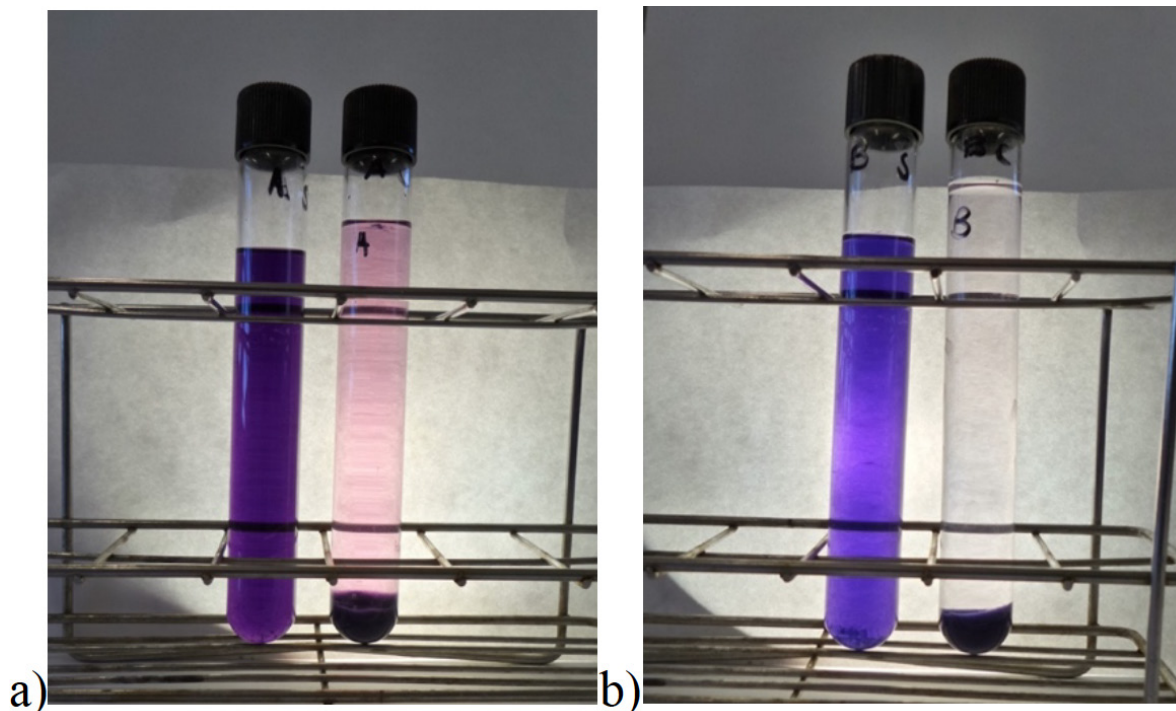


Fig. 1. Colour removal with *Moringa oleifera* coagulant in a sample of dye liquor (a) and a sample of washing (b).

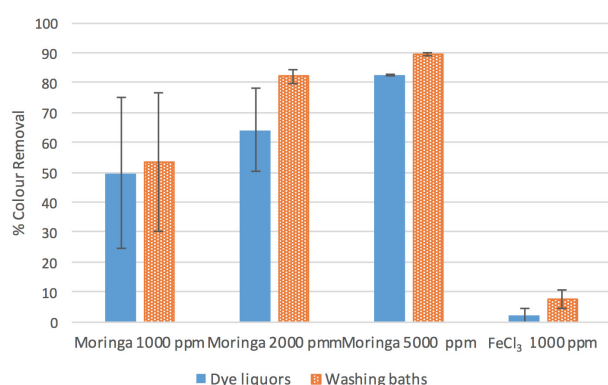


Fig. 2. *Moringa oleifera* colour removal efficient at different concentrations compared with FeCl₃.

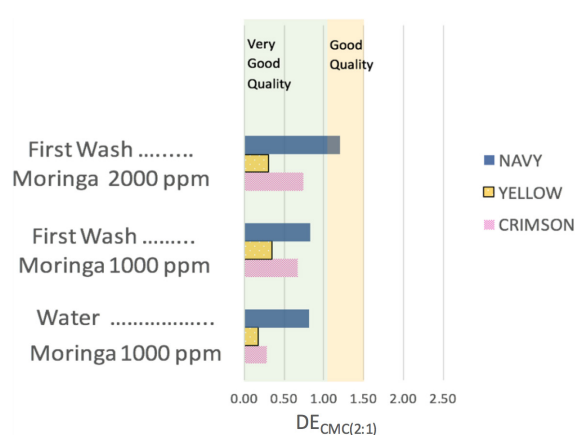


Fig. 3. Quality of dyeings performed with *Moringa*-treated water.

One of the clear advantages of using *Moringa oleifera* is the low-cost process and implementation compared to other treatment alternatives. It is economically viable and promotes the valorization of natural waste. It is based on the idea that moringa seeds are inexpensive, easy to store and available in large quantities in specific regions [23]. Even in the not endemic regions, the moringa seed cake can be acquired after oil extraction at a very low cost.

4. Conclusions

The use of *Moringa oleifera* waste as coagulant shows important benefits. It is safe and easy to use. Besides, it provides good colour removal rate and exhibits low influence of alkaline pH. In addition, the treated effluent can be reused in new dyeing processes. Good quality dyes can be obtained, thus taking advantage of salt contained in the effluents.

The environmental advantages are first, the conservation of the fresh water sources; second, the increase in water life cycle which reduces the 'water stress' and the water footprint of the industrial sector; and third, to avoid the use of toxic or dangerous chemical and synthetic coagulants and the use of chemicals for pH adjustment. Finally, an additional advantage

is the reduction of salinity impact on the environment or on biological wastewater treatment plants.

Moringa oleifera coagulant is a very inexpensive alternative in regions where this plant is endemic. Also, the coagulant could be considered zero cost since it is a waste from the extraction process of the oil obtained from the seed.

For its adequate implementation it is suggested to make an optimal dosage study for each specific case because the colour concentration in textile wastewater is variable.

The reuse of textile wastewater and specifically the effluents from the reactive dyeing process is a feasible alternative to address the problem of water scarcity.

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