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Electro-flocculation associated with the extract of *Moringa oleifera* Lam as natural coagulant for the removal of reactive blue 5G dye

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ABSTRACT. Although an important significant sector in world economy, the textile industry is known for its large volumes of wastewater generated in production processes. In the search for cleaner technologies, the application of electrochemical processes, such as electro-flocculation, or natural coagulants, such as *Moringa oleifera Lam* extract, have become recurrent in literature. Since the required operating conditions for alternative technologies are such that they hamper effective application, current paper presents results obtained with the use of a hybrid system of treatment which combines electro-flocculation and the aqueous extract of *Moringa oleifera lam* to evaluate the removal of reactive blue 5G dye from aqueous solutions. Milder conditions of electric current intensity (0.10 – 1.50 A) and natural coagulant concentration (250-2000 mg L^{-1}) were tested. Through a Central Composite Rotatable Design, it was possible to obtain a quadratic model which subsidized the optimization of operating conditions. Applying an electric current of 0.97 A to sacrificial electrodes of iron and a concentration of 2000 mg L^{-1} for the extract of *Moringa oleifera Lam*, an average 86.79% color removal was obtained, considered a satisfactory rate.

Keywords: textile effluent, electrochemical treatment, optimization.

Aplicação da eletrofloculação associada ao extrato de *Moringa oleifera* Lam como coagulante natural para remoção do corante reativo azul 5G

RESUMO. A indústria têxtil, apesar de representar um importante setor para a economia mundial, também é conhecida pelos grandes volumes de águas residuárias geradas no seu processo produtivo. Na busca por tecnologias mais limpas de tratamento, aplicações de processos eletroquímicos, como a eletrofloculação, ou ainda de coagulantes naturais, como o extrato de *Moringa Oleifera Lam*, têm se tornado recorrente na literatura. Entretanto, por vezes as condições operacionais exigidas por estas tecnologias alternativas inviabilizam sua aplicação efetiva. Neste contexto, o presente trabalho apresenta os resultados obtidos com o emprego de um sistema híbrido de tratamento, conciliando a eletrofloculação à adição de extrato aquoso de *Moringa Oleifera Lam*, avaliando-se a remoção do corante reativo Azul 5G de soluções aquosas. Foram testadas condições mais brandas de intensidade de corrente elétrica (0,10 – 1,50 A) e concentração de coagulante natural (250 – 2000 mg L^{-1}). Por meio de um Delineamento Composto Central Rotacional foi possível obter um modelo quadrático, que subsidiou a otimização das condições operacionais. Aplicando-se a corrente elétrica de 0,97 A aos eletrodos de sacrifício de ferro e uma concentração de 2000 mg L^{-1} para o extrato aquoso de *Moringa Oleifera Lam* foi observada a remoção média de 86,79% da cor, valor considerado satisfatório.

Palavras-chave: efluente têxtil, tratamento eletroquímico, otimização.

Introduction

Society´s development and, consequently, progress in technologies caused a growing concern with the environment (Brito, Ferreira, & Silva, 2012). In such a scenario, textile industries are characterized as activity responsible for part of industrial development, or rather, while it brings benefits, it is also a causative agent of environmental degradation (Brito et al., 2012; Baêta, Aquino, Silva, & Rabelo, 2012).

Among all forms of pollution, one of the most worrisome is the pollution of water resources. In fact, the textile sector is one which most contributes towards this problem since it is a generator of significant amounts of wastes. Further, its effluents contain dyes which, even at low concentrations, may be highly toxic to living organisms. In fact, they are one of the main sources of water contamination (Aquino Neto, Magri, Silva, & Andrade, 2011).

Textile effluents containing dyes are usually treated by chemical or physical methods. A combination of different methods may be employed to obtain the desired quality of water on a costs-effects basis. Such methods include flocculation, flotation, electro-flocculation, membrane filtration, coagulation, electrochemistry, ion exchange, precipitation, radiation, ozonisation, among others (Srinivasan & Viraraghavan, 2010). In addition, there is also the biological treatment, or rather, the use of microorganisms for the degradation of different pollutants (Özcan, Öncü, & Özcan, 2006). However, special emphasis has been given recently to the use of electrochemical processes for the treatment of potentially polluting effluents, such as electro-flocculation technique (Cerqueira & Marques, 2011).

Electro-flocculation is an electrochemical process with four stages: generation of small gas bubbles; contact between the bubbles and suspended particles; adsorption of small gas bubbles on the surface of the particles and rise of particle bubbles set to a surface. All suspended matter is floated, causing bleaching of the liquid. On the surface, a layer of foam is formed containing floated particles that are easily removed (Aquino Neto et al., 2011). Unlike conventional processes in which the coagulants are added to the effluent in the form of salts, the coagulators (iron or aluminum) in the electro-flocculation process are added to the suspension by the dissolution of the anode, which is oxidized due a potential difference application, which causes the aggregation of particles later removed by sedimentation or filtration (Sasson & Adin, 2010).

In the search for alternative technologies in the treatment of textile effluents, some initiatives are worth mentioning. One of the products which have been largely studied in coagulation/electro-flocculation is the *Moringa oleifera Lam* seed, either in natura or as extract. Early scientific studies on the plant as a coagulant were developed in Germany and the UK in the 1980s (Arantes, Ribeiro, & Paterniani, 2012). Surveys conducted in the 1990s demonstrated that high molecular weight proteins in *Moringa oleifera Lam* seeds are responsible for the coagulation process (Ndabigengesere, Narasiah, & Talbot, 1995; Okuda, Baes, Nishijima, & Okada, 1999).

The use of the coagulant agent of *Moringa oleifera Lam* presented significant results as a natural coagulant and may be considered an alternative technique for the treatment of water (Santos, Pereira, Santana, & Silva, 2011). The success of the coagulant solution based on seeds of *Moringa oleifera Lam* is reported in the literature, but with no standardization for the procedure (Arantes et al., 2012).

Therefore, it is believed that the combination of the above techniques, specifically electro-flocculation and the addition of *Moringa oleifera Lam* as natural coagulant, may demonstrate an efficiency of the treatment system higher than the use of these technologies employed alone. Further, when applied individually, the conditions normally employed for the two techniques are more intense than when employed within a hybrid treatment system which aims at milder operating conditions.

Current assay proposes to contribute to cleaner technologies since it aims at efficiency in the removal of pollutants from textile effluents (specifically Reactive Blue 5G dye) by techniques which are less aggressive to the environment due to reduction in chemical agents. The assay´s goal is the application of a hybrid system, or rather, the combination of electro-flocculation and the addition of the natural coagulant from *Moringa oleifera Lam* in a batch operating system.

Material and methods

Analytical methodology

The solutions of dyes used have been prepared from the commercial reactive blue 5G dye. Color evaluation of the samples was carried out by Molecular Absorption Spectrophotometer UV-Vis double beam scanning, PerkinElmer, Lambda 45 model.

Wavelength at which the compound to be quantified absorbs maximum radiation was determined by scanning along the spectral range of interest.

Preparation of solution of reactive blue 5G dye

Solutions for the experiments were prepared with reactive blue 5G dye at a concentration of 50 mg L^{-1}, obtained from the dissolution in distilled water.

Electro-flocculation treatment

The electro-flocculation system comprised 1 L beaker, magnetic stirrer, direct current source and the sacrificial electrodes of iron, measuring 100 long, 50 wide and thickness 0.6 mm. Further, 500 mL of reactive blue 5G dye solution at 50 mg L^{-1} concentration were used for each test. The pair of electrodes was separated at a distance of approximately 1 cm and the area actually used for electro-flocculation measured 2.5×10^{-3} m^2. Further, 1 g of sodium chloride was added to the dye solution, which provided an average electrical conductivity of 4.23±0.45 mS cm^{-1}. Figure 1 shows the scheme of the electro-flocculation batch system.

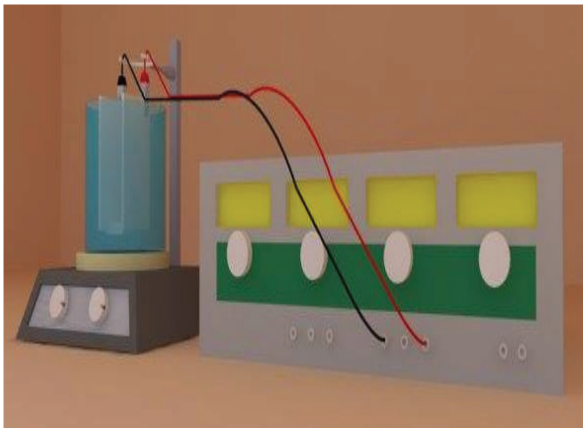

Figure 1. Experimental module for the treatment of textile effluent by electro-flocculation (batch system).

Preparation of aqueous extract of *Moringa oleifera Lam* seed

Moringa oleifera Lam (MO) seeds were obtained in Medianeira, Paraná State, Brazil, at 25° 17' 43" S and 54° 05' 38" W, and in Marechal Cândido Rondon, Paraná State, Brazil, at 24° 33' 22" S and 54° 03' 24" W. Seeds were selected according to uniformity, size and coloring.

First, the husks were removed from MO seeds which were macerated manually with a pestle and a homogeneous material was obtained. A pie was produced for the preparation of the coagulant solution at a proportion of 5 g of MO for 100 mL of solution using 20% NaCl. The solution was then agitated for 20 s in an ultrasound device at a frequency of 80 kHz to extract the coagulant proteins from MO seeds. After the extraction stage, the solution was vacuum-filtered by 3-micron pore filter paper. Solution was thus ready for the coagulation/flocculation tests at a ratio of 50,000 mg L^{-1} (matrix solution of the coagulant).

Experimental design

A Central Composite Rotatable Design (CCRD) assessed the influence of the variables: electric current intensity (I) applied to the sacrificial electrodes and concentration of coagulant added to reactive blue 5G dye solution. Response was the percentage removal of color.

Experimental design techniques, such as CCRD, are very useful for bench scale experiments since the external influences are generally controlled. Furthermore, CCRD provides the experimental error (calculated from replications on the central point), and a possibility of adjusting a mathematical model. If this model is statistically validated, the surface response may be generated and sometimes the process optimization is possible (Rodrigues & Iemma, 2009).

According to the CCRD experimental design, 2^2 factorial runs were executed, coupled to the four replications on the central point and four runs on the axial points, totaling 12 runs, in duplicate. Table 1 shows real values, corresponding to the study of the variables. The variable codification followed Equations 1 and 2. The reaction time was settled for the tests in 5 min.

$$I_{coded} = (2.0143)\, I_{real} - 1.6114 \quad (1)$$
$$MO_{coded} = (1.6113E-03)\, MO_{real} - 1.8129 \quad (2)$$

Table 1. Real and coded rates corresponding to factors studied.

	-1.41	-1	0	+1	+1.41
I (A)	0.10	0.30	0.80	1.30	1.50
MO (mg L^{-1})	250.0	504.4	1125.0	1745.6	2000.0

Five tests, as control (they evaluated the removal of color without the addition of the coagulant), were carried out to verify the actual removal of color by the natural coagulant of *Moringa oleifera Lam*.

For a better analysis of CCRD, a correction of color removal had to be performed since the dilution could mask the color removal results when a significant volume of coagulant extract was added. Correction was done with Equation 3.

$$RCcorrected = (RC)\left(\frac{Veffluent}{Veffluent + Vextract}\right) \quad (3)$$

where:
$RC_{corrected}$ = Removal of corrected color.
RC = Color removal.
$V_{effluent}$ = Volume of dye solution used in the test.
$V_{extract}$ = Volume of coagulant (aqueous extract of *Moringa oleifera Lam*) added.

Results and discussion

The wavelength at which absorption of reactive blue 5G dye was highest corresponded to 618 nm, as seen in Figure 2. From these results, the other trials were based on the biggest absorption wavelength.

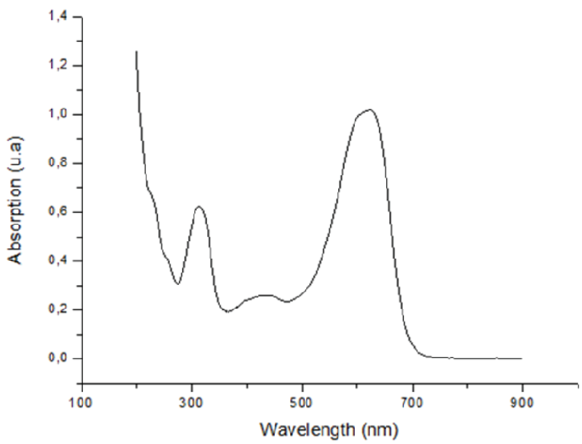

Figure 2. Spectrum scanning of reactive blue 5G dye.

Table 2 shows the coded values of 12 runs, with the respective values of the response variable color removal after treatment of dye solution by the hybrid system. Removal percentage of color was determined by comparing post-treatment samples and pre-treatment aqueous dye solutions, at 618 nm absorbance. The data are mean values, since runs were performed in duplicate.

Table 2. Results for color removal by hybrid treatment system.

Run	I	MO	Color Removal (%)	Standard Deviation (%)
1	-1	+1	41.56	0.86
2	+1	+1	77.92	0.05
3	-1	-1	4.84	0.04
4	+1	-1	80.81	1.09
5	0	0	64.26	0.05
6	0	0	67.19	0.36
7	0	0	66.89	0.25
8	0	0	68.28	0.19
9	+1.41	0	69.39	1.07
10	-1.41	0	13.45	0.18
11	0	+1.41	67.25	0.17
12	0	-1.41	68.73	0.44

Table 2 demonstrates the removal of the final color, ranging between 13.45 and 80.81%. Since the mean rate of color removal for control tests was 4.79% (Table 3), the efficiency of the coagulant and electro-flocculation of samples analyzed must be underscored. It should be pointed out that, for the analysis of results, the removal of the final color has been corrected for the volume of the coagulant used.

Table 4 and Figure 3 show regression coefficients calculated for a quadratic model. It may be observed that the linear and quadratic term of electric current intensity and the interaction of *Moringa oleifera Lam* extract and electric current intensity were statistically significant at 5% ($p < 0.05$).

Table 3. Color removal (%) for control tests.

Run	Color Removal (%)	Mean (%)	Standard Deviation (%)
1	9.73		
2	7.55		
3	1.66	4.79	3.69
4	1.44		
5	3.58		

Table 4. Regression coefficients for color removal (%).

	Effects	Coefficients	Standard Error	p value
Mean		66.6654	3.6946	1.9E-06
I(I^2)	-27.0834	-13.5417	2.9331	0.0036
I	47.9441	23.9721	2.6164	9.5E-05
I(MO^2)	-0.3516	-0.1758	2.9331	0.9541
MO	7.9573	3.9787	2.6164	0.1792
I:MO	-19.8038	-9.9019	3.6947	0.0365

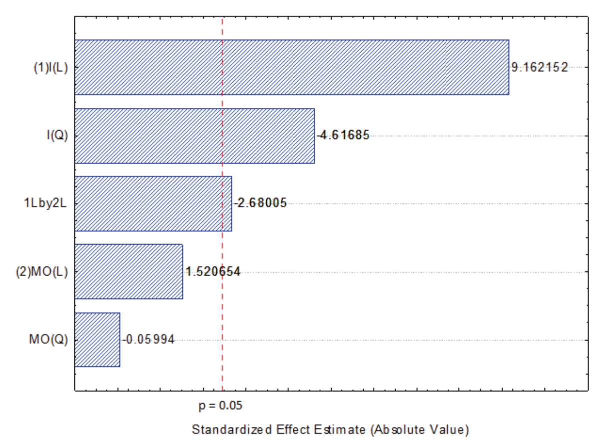

Figure 3. Pareto Chart for color removal process, with 5% significance.

Analyzed for the Color Removal response, Table 5 revealed that regression was highly significant ($p < 0.05$). Moreover, the coefficient of determination showed a good adjustment to experimental data, with a rate of 0.9506. Equation 4 shows the mathematic mode for Color Removal. The response surface may be seen in Figure 4.

$$RC = 66.6654 - 13.5417\,I^2 + 23.9721\,I - 0.1758\,MO^2 + 3.9787\,MO - 9.9019\,I.MO \quad (4)$$

Table 5. Analysis of variance for color removal response.

Source of Variation	Sum of Squares	Degrees of freedom	Mean squares	$F_{calculated}$	$F_{tabulated}$ $F_{0.05;5;6}$	p value
Regression	6307.0	5	1261.4	23.1	4.39	0.0007
Residual	327.6	6	54.6			
Total	6634.6	11				

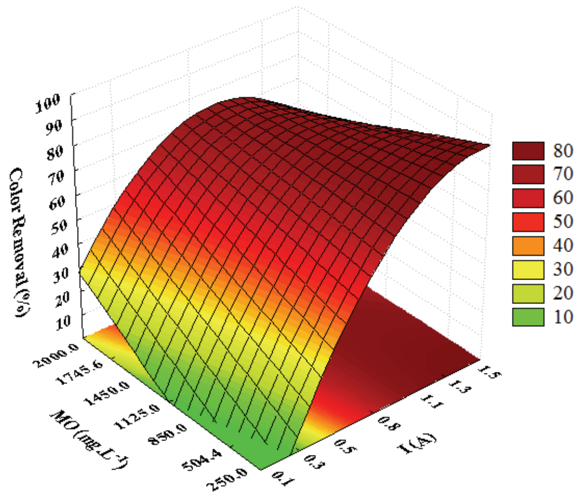

Figure 4. Graph of response surface for color removal.

Validation model tests of color removal from reactive blue 5G dye solution treated by a hybrid system

Analysis of response surface determined the optimal process conditions that provided the maximum color removal of reactive blue 5G solution dye, when the hybrid treatment system comprising electro-flocculation and natural coagulant *Moringa oleifera Lam* extract was applied. These conditions were determined by solving the partial derivatives of the model, whose Equations were equated to zero, resulting in coded values of 0.35 for I and 1.46 for MO. However, since optimal value of MO extrapolated the range of study, the nearest value at 1.41 was employed. Therefore, the model confirming experimentally the removal of the color in a wider range, taking into account the optimal region obtained, was validated.

Table 6 shows the operational conditions of the validation model test and its results. The average removal of color obtained reached 86.79%, albeit a high error rate (15%). The experimentally removal of the color was higher than the one predicted by the model.

Several studies may be currently found in the literature related to the implementation of electro-flocculation. These experiments employed the technique under different conditions of treatment to evaluate the efficiency process of the parameters (Harif & Adin, 2007).

Although in the case of *Moringa oleifera Lam*, several authors have investigated the potential use of its seeds, obtaining a coagulant solution has been reported in a great number of ways (Arantes et al., 2012).

Some studies of these techniques are mentioned in Table 7 so that results could be compared.

Based on these studies, treatment by electro-flocculation associated with the coagulant potential of *Moringa oleifera Lam* is an alternative from the technical-economic-environmental viability point of view. Two promising technologies of textile effluent treatment may be employed based on the hybrid system, using milder operating conditions, i.e. to enhance the level of treatment that would be achieved with the techniques when used alone. The percentage removals achieved in current study were similar to those found by other researchers (see Table 7).

Table 6. Results of validation model tests.

Run	I	MO	Color Removal [Experimental (%)]	Color Removal [Predicted (%)]	Error (%)
1			87.48		
2	+0.5 (0.97 A)	+1.41 (2000 mg L^{-1})	80.91	73.77	15.00
3			91.99		
Mean			86.79		

Table 7. Methods for the treatment of textile effluents.

Treatment	Effluent/ Coagulant	Operational Conditions	Removal (%)	Ref.
Electro-flocculation	Textile Industrial laundry	Electrolysis time: 15-45 min Initial pH: 3-11 Electric current density: 28.6-142.9 A m^{-2}	COD (88.3%) Color (100%)	(Palácio et al., 2009)
Electro-flocculation	Textile industrial effluent	Electric current intensity: 0.4-5 (A) Iron and Aluminum Electrodes	Color (95%) Turbidity (100%) COD (87%)	(Cerqueira, Russo, & Marques, 2009)
Coagulation/ Flocculation	- Supply water and wastewater; - Coagulant from *Moringa oleifera lam*	Coagulant concentration: 0,02-1.2 g L^{-1}	Turbidity – 2 hours sedimentation (22.3%) Turbidity – 24 hours sedimentation (35.3%)	(Lo Monaco, Matos, Ribeiro, Nascimento, & Sarmento, 2010)
Coagulation/ Flocculation	- Effluent from jeans industrial laundry - Coagulant from *Moringa oleifera lam*	Coagulant concentration: 1400-2600 mg L^{-1}	Color (80.33%) Turbidity (91.10%)	(Ströher, Couto Junior, Menezes, Bergamasco, & Pereira, 2012)
Electro-flocculation associated to Coagulation/Flocculation	- Reactive Blue 5G Dye solution; - Coagulant from *Moringa oleifera lam.*	Electric current intensity: 0.97 A Iron Electrodes Coagulant concentration: 2000 mg L^{-1}	Color (86.79%)	Current paper

Conclusion

Effluents generated by the textile industry have large amounts of non-biodegradable organic compounds, resulting from the incomplete fixation of dyes to the fibers. Cleaner treatment technologies may be an alternative to conventional methods used, such as electro-flocculation associated with natural coagulant *Moringa oleifera Lam* extract. To enhance treatment level, the two techniques were associated in a batch system and an average 86.79% efficiency of color removal was obtained for the optimum conditions evaluated.

The hybrid treatment system, under milder operation conditions, showed a broad region of excellent color removal, subsidizing the implementation of such techniques in a continuous operation regime.

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