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Treatment of acidic dyes solutions by adsorption in soybean meal

Luana Marcele Chiarello, Ivonete Oliveira Barcellos*, Gabriela Spengler and Davi Eduardo Roza

Departamento de Química, Universidade Regional de Blumenau, R. Antônio da Veiga, 140, 89012-900, Blumenau, Santa Catarina, Brazil.

*Author for correspondence. E-mail: iob@furb.br

ABSTRACT. In this study, we tested the potential use of a natural sorbent based on soybean meal from oil extraction in the treatment of solutions containing the acid dyes: yellow Erionyl RXL, navy blue Erionyl R and red Erionyl A-3B, used to dye polyamide fibers. To that end, adsorption studies were performed under different conditions of temperature, adsorbent concentrations, pH values, and color mixes (two- and three-color) on dye solutions produced in laboratory. Soybean meal showed great ability to remove color, especially in solutions with pH 4 and 6 at 60°C and containing 10 g L\(^{-1}\) of adsorbent. Considering that values of adsorption efficiency ranged between 74 and 99%, depending on the dye and treatment conditions, soybean meal proved to be an alternative material for the adsorption of acidic dyes.

Keywords: wastewater treatment, acid textile dyes, soybean meal.

Introduction

Water is used in the textile industry as a vehicle for the chemical products in fiber processing, as well as to remove excess levels of products deemed undesirable for thread or fabric (TOLEDO, 2004). Contamination of natural waters is one of the main social problems causing constant concern and leading to the creation of new norms and rules establishing limits for contaminant discharge, in order to minimize environmental impacts (PINHEIRO; LOCATELLI, 2006).

In that context, the presence of dyes is easily noticeable in textile industry effluents if not treated in a timely manner even at low concentrations, especially those generated during the dyeing process, and are capable of increasing the contamination level of natural waters, affecting aquatic equilibrium (ZANONI; GUARATINI, 2000).

The variety of processes and products used in textile factories make effluents more complex, hindering treatment. Dyes are included among the different products used in that industry, with annual worldwide production of 700,000 tons. Of that total, 50% are compounds featuring the azo group in their makeup, and 2 to 20% of the dye applied in the dyeing process can be discharged in effluent, depending on tonality, characteristics of the dye and nature of the fiber (BELTRAME et al., 2004).

The textile industry in the State of Santa Catarina is one of the most advanced in Latin America, standing out in Brazil for textile production. It is concentrated in the region of the Itajaí-Açu river Valley, with 75 factories, 36 of which are textile. It is responsible for approximately 10% of total revenue generated by textiles nationwide and 30% of all products exported by Brazil's textile sector. The importance of this industrial sector to the state draws attention to the environmental aspects regarding this activity. It can be observed that businesses have increased their concern with the possibility of reusing discharge baths, directly or indirectly, in order to use the least possible treatment, so as to make reuse feasible without
affecting final product quality or excessively increasing the cost of the process, as water is already regarded as an additional component in the cost spreadsheets of textile industries and not only a vehicle in the dyeing process (TWARDOKUS; SOUZA, 2005).

Thus, studies evaluating the possibility of reusing treated water from dye baths are of significant importance (CHIARELLO et al., 2008, 2009).

According to Vončina and Majeen-Le-Marechal (2003), the processes employed in textile plants to treat liquid effluents, dye removal and other chemical products present in effluent can generally be classified as physical, biological and physical-chemical. Within that classification these are included: extraction, coagulation, flocculation, precipitation, filtration, adsorption, reverse osmosis, oxidation, (by chlorine, with ozone or hydrogen peroxide), reduction, complexometric methods, ion exchange, photoelectrochemical methods and membrane technologies. However, solid/liquid adsorption is one of the most effective techniques to remove molecularly stable water-soluble liquid dyes, as in the case of reactive dyes (JUANG et al., 2001; OTERO et al., 2003). Several of the studies involving advanced oxidative processes have also been applied in the breakdown of aqueous solutions (LIU et al., 2006; SUNDRARAJAN et al., 2007).

As adsorption is essentially a surface phenomenon, an adsorbant must have a large specific surface area in order to have significant adsorptive capacity, which implies a highly porous structure. Adsorptive properties depend on pore size, on the distribution of pore size and the nature of the solid surface. Therefore, activated charcoal is a great potential adsorbant, but its cost is not attractive. Moreover, its efficiency is limited for certain dyes – basic dyes, for instance – due to the issue of surface load. (CHAO et al., 2004).

Dye adsorption is highly dependent on concentration, and this adsorption capacity is reduced for mixtures. Gomes et al. (2007) studied the adsorption of three acid dyes: Acid Red 97, Acid Orange 61, and Acid Brown 425, with activated charcoal to remove the acid dye from aqueous solutions at room temperature (25°C). The results indicate that activated charcoal can be employed to remove acid dyes from wastewater, both in individual solutions and mixtures of dyes from this class (three-color).

Adsorption techniques have consisted of removing the dye by passing the sample through activated charcoal, bauxite, silica gel, vermiculite, cellulose derivatives, ion-exchange resins and membranes etc. (CHIRON et al., 2003).

The diversification of methods is related to the varied characteristics of textile industry effluents, resulting from the use of different raw materials and production technologies. Park et al. (2005) studied the adsorption of acid dyes (Acid Violet 17, Acid Red 44 and Acid Blue 45) in a cationic polyelectrolyte adsorbant saturated with silicone mesopores and in regular silicone supports. The results of that study showed that the adsorbant had rapid adsorption due to the cylindrical structure of the mesopores.

Papić et al. (2004) analyzed the removal of certain reactive dyes from wastewaters, by combining Al(III) coagulation with adsorption in activated carbon. In that study, the effect of pH, coagulant dose, contact time and pulverized activated carbon dose were evaluated for dye removal. The process was optimized using an amount of flocculant, generating a significant volume of slush. Coagulation is the main part of the process followed by adsorption, resulting in almost total elimination of both dyes (C.I. Reactive Red 45 and C.I. Reactive Green 8) from wastewater, with significant reduction (90%) in chemical oxygen demand (COD) of total organic carbon (TOC) and adsorbable organic halogens (AOX). According to the authors, in addition to high dye removal efficiency, the combined treatment process offers several advantages, such as: less flocculant use, reduced slush formation, and greater savings in chemical products and equipment.

Kimura et al. (2000) determined adsorption isotherms by varying pH and final concentration of dyes. Adsorption experiments were analyzed using the Langmuir isotherm, and the results indicated increased adsorption capacity with pH reduction.

Certain factors alter adsorption capacity, such as: temperature, adsorbate and adsorbant concentration, pH, contact surface, among others. Besinella Júnior et al. (2009) studied adsorption with two variables: temperature (30 and 40 °C) and particle size (1.70 ± 0.30 mm and 3.00 ± 0.40 mm). The results showed that temperature increase or diameter reduction lead to higher adsorption.

The main objective of this work was to evaluate the ability to remove acid dyes using soybean meal as adsorbant, by determining efficiency using spectroscopy in the visible spectrum.

Material and methods

In order to optimize treatment conditions of the dye solutions, the following parameters were varied: temperature, adsorbant concentration, pH, and combinations of two or three dyes in the solutions (two- and three-color).
Adsorbant

One sample containing 20 grams of soybean meal (provided by Bunge Alimentos S.A.) was used to determine adsorbant particle size. This analysis was carried out using sieves with particle size ranging between 0.044 mm and 2 mm in a sieve shaker (BERTEL 10.02), during 5 min. Table 1 shows the range of adsorbant particle size used in this study, in which it could be observed that soybean meal particle size were predominantly (96.24%) between 2 – 0.25 mm.

Table 1. Range of particle size in 20 grams of soybean meal used as adsorbant.

<table>
<thead>
<tr>
<th>Quantity present (%)</th>
<th>Particle size (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>66.36</td>
<td>0.84 – 2.0</td>
</tr>
<tr>
<td>29.88</td>
<td>0.25 – 0.71</td>
</tr>
<tr>
<td>3.22</td>
<td>0.08 – 0.17</td>
</tr>
<tr>
<td>0.53</td>
<td>0.04 – 0.07</td>
</tr>
</tbody>
</table>

Adsorbates

The adsorbates used were the following acid dyes: yellow Erionyl RXL, navy blue Erionyl R and red Erionyl A-3B, provided by Huntsman (formerly Ciba Segmento Têxtil). Figures 1a and b show the molecular structures of the acid dyes employed in this study (Colour Index (CI), 1987). Only the dye Red Erionyl A-3B is not registered in CI, and the manufacturer did not make that information available.

Adsorption Study

The adsorption study was carried out using pure one-color acid dye solutions, varying adsorbant concentration by 10, 20, 40, 70 and 100 g L⁻¹, and also in mixtures of these dyes in two- and three-color solutions, keeping adsorbant concentration at 10 g L⁻¹ in that case.

The two-color solution was prepared by mixing 50% acid dye navy blue Erionyl R and 50% acid dye red Erionyl A-3B, and the three-color solution was prepared using 1/3 of each acid dye in this study, totaling a concentration of 0.1 g L⁻¹ in all cases.

First, the influence of concentration of the adsorbant (soybean meal) was evaluated in removing the dye. To that end, the solutions were kept under constant agitation in a Dubnoff metabolic water bath at 60°C. Aliquots of 5 mL were taken at fixed intervals until adsorption equilibrium was reached, and centrifuged when necessary. The absorbance values to calculate the concentration of the solution, after adsorption, were obtained using UV visible spectrophotometer (Shimadzu UV-1601 PC), in the $\lambda_{\text{max}}$ of each dye: yellow 435.5 nm, navy blue 565.5 nm and red 521.5 nm. Each removed aliquot was returned to the experimental solution, to avoid volume variation.

Based on the results of the influence of adsorbant concentration (single-color), adsorption was monitored by fixing adsorbant concentration and dye, varying the parameters of temperature (40, 50, 60 and 70°C) and pH (4 and 6). All experiments were performed in triplicate.

Results and discussion

Influence of adsorbant concentration in the adsorption of acid dyes

Adsorption rate depends on driving power per area unit. In this case, that is true as long as the initial concentration of the solution and other variables of the system remain constant.
Several adsorbant concentrations were used to determine the efficiency of color removal and choice of the best adsorbant concentration in the adsorption process of the acid dyes yellow Erionyl RXL, acid navy blue Erionyl R and acid red Erionyl A-3B, at 60ºC. Absorbance values at infinite time (adsorption equilibrium) were obtained from the maximum absorption wavelength spectrums for each dye (λm). Considering absorbance values at the starting time (0 hour) and at infinite time (24 hours), the efficiency percentage for color removal is given in Equation 1.

\[
\text{Removal}(\%) = \frac{\text{Abs}_s - \text{Abs}_i}{\text{Abs}_s} \times 100
\]

(1)

Figure 2 shows the absorbance spectrum (visible) of the dyes studied at the start of the experiment at 60ºC (t = 0) and at the infinite contact time (constant absorbance) employing 10 g L\(^{-1}\) of adsorbant. An almost total decrease was observed in absorbance intensity for all three studied dyes.

In the performed experiments, it was observed that the reduction in adsorbant concentration in relation to adsorbate (treated at 60ºC for 24 hours) caused a slight increase in adsorbed quantity. This was observed for all dyes, although acid dye yellow Erionyl RXL was the most influenced. That dye showed the greatest variation in efficiency percentage for color removal, although the affinity by that adsorbant was the lowest among all three dyes (Figure 3), as the lowest efficiency values were observed for that dye.

In Figure 3, it was observed that efficiencies are greater than 95.96% with 10 g L\(^{-1}\) of adsorbant, reaching up to 98.83%, for dye acid red Erionyl A-3B in a 60ºC isotherm, in a 24-hour period.

The literature generally contemplates that the effectiveness of color removal can be evaluated by using a spectrophotometrically permissible standard. Comparing our results with other works published in the literature employing natural adsorbants, the treatment of reactive dye solutions using rice husk ash proved efficient, with a color removal ability over 87% in times ranging from 24 to 148 hours, depending on the experimental conditions of treatment (CHIARELLO et al., 2008).

In another study, performed by Chiarello et al. (2009), the treatment of red dye solutions red from different classes (reactive, disperse and acid) by the method of adsorption using rice husk ash, obtained efficiency above 89% (24 to 96 hours) for all three dye classes studied. In that case, the acid dye is the same as that used in our study.

**Influence of temperature in the adsorption of acid dyes**

The influence of temperature was analyzed, keeping constant the concentration of adsorbant (10 g L\(^{-1}\)), dye (0.1 g L\(^{-1}\)) and pH (6).

The experiments were carried out varying temperatures between 40 and 70ºC. Figure 4 shows that temperature increase favors dye adsorption, with 60ºC showing greater color removal efficiency compared to the other temperatures. A temperature increase can lead to a rise in kinetic energy and mobility of dye molecules, and can also cause an increase in the intra-particle diffusion rate of the adsorbate (ROBINSON et al., 2002). This increase also affects the solubility and chemical potential of the adsorbate, possibly becoming a factor that controls adsorption (KHATTRI; SINGH, 2000). However, an extremely high temperature may favor the desorption process (NETPRADIT et al., 2004), as can be observed in the figure below: above 60ºC, efficiency is reduced. Therefore, it is believed that desorption is favored at that temperature.

**Influence of pH in the adsorption of acid dyes**

pH is one the most important factors in the adsorption process (MOHAN et al., 2002). Alterations in environment pH can lead to changes in adsorbant surface load and affect the degree of
The adsorption of dyes is influenced by the surface load of the adsorbant and by the degree of ionization of the dye, which in turn are influenced by pH.

The pH value of the dye solution exerts influence on the overall adsorption process, possibly affecting adsorption capacity.

![Figure 4](image1.png)  
**Figure 4.** Efficiency percentage of soybean meal adsorbant, at 40, 50, 60 and 70°C.

Considering that the pHs of waste from dyeing processes using acid dyes are below neutral, the treatments were carried out at pH 4 and 6, with the objective of optimizing conditions and treatment in terms of pH. The study was also performed at 60°C, with 10 g L⁻¹ of adsorbant, in a 24-hour period, which were the best conditions observed in the previous experiments.

As shown in Figure 5, the different pHs showed similar behaviors for color removal efficiency: yellow, navy blue and red dyes at pH 4 and pH 6 obtained 98.11, 98.32, 99.32 and 95.96, 98.49, 98.83% efficiency, respectively. Those give evidences that an acid or slightly acid pH does not alter the adsorption capacity of the adsorbant, which indicates no change occurs in the surface load of the adsorbant at that pH range.

![Figure 5](image2.png)  
**Figure 5.** Efficiency percentage of color removal for soybean meal adsorbant at different pHs, at 60°C during 24 hours.

Comparing these values with the literature, it is possible to find similar values. For example, the efficiency values of color removal using the adsorption comb 80/20 nylon 6.6/chitosan blend (in flake form) also showed high affinity with these same three-color acid dyes, reaching values of 97-98% over a period of 180 minutes (BARCELLOS et al., 2008).

![Figure 6](image3.png)  
**Figure 6.** Efficiency percentage of soybean meal adsorbant, in two- and three-color solutions of acid dyes yellow, red and navy blue Erionyl.

The only remaining question is what to do with this treatment residue. Perhaps the solution would be to perform biodegradability studies for this adsorbant saturated with dye. Thus, meals could be tested as nutrients for fungal growth. For instance, in a study using fungus *A. casiellus*, conventional soybean meal was used as substrate and nutrient source for the optimization of the fermentative medium (PARIS et al., 2010). Likewise, as observed in some citations, certain fungal species are capable of degrading textile dyes. Fungi such as *Phanerochaete chrysosporium*, *Pleurotus ostreatus*, *Trametes versicolor*, *Pleurotus sajor-caju*, *Phellinus gilvus* and *Picnoporus sanguineus* proved efficient in biodegradation and discoloration of textile effluents (SOUZA; ROSADO, 2009).
Conclusion

The proposed use of natural adsorbant (soybean meal) in the adsorption process of acid dyes: yellow Erionyl RXL, navy blue Erionyl R and red Erionyl A-3B reached its objective, considering the obtained results. The removal efficiency of yellow dye ranged from 78 and 95%, and 92 to 98% for navy blue and red dyes; yellow proved more dependent on adsorbant concentration than the others. Color removal efficiency, in both two- and three-color solutions, was also greater than 95%.

With regard to the influence of temperature on the adsorption of these acid dyes, it can be observed that the rise in temperature provides dye adsorption up to 60ºC; above that temperature, the desorption phenomenon is favored.

In this study, it was confirmed that a solution in acid or slightly acid pH does not alter the adsorption capacity of the adsorbant, as the efficiencies were 95%, meaning there is no need to adjust the pH of dyeing residues for treatment.

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References


Adsorption of textile dyes in soybean meal


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