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Application of chitin and chitosan extracted from silkworm chrysalides in the treatment of textile effluents contaminated with remazol dyes

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ABSTRACT. Chitin extracted from silkworm chrysalides was used to prepare chitosan applied in this investigation. Adsorption studies were carried out in column and in aqueous suspension with two dyes, blue remazol (RN) and black remazol 5 (RB). The study showed that adsorption is better in the chitosan-packed column than in the chitin-packed one. However, the comparison of the adsorption in column and in suspension revealed better results for the latter. The plotted Langmuir isotherm did not indicate significant difference in the theoretical capacity of saturation of the monolayer (Q_o) for either dye. The application of the adsorption process to actual conditions was evaluated by adsorption assays of actual textile effluents. In acid pH, chitosan adsorbed the dyes responsible for the effluent coloration completely. This study showed that the use of chitosan obtained from silkworm chrysalides is a viable alternative for the immobilization of dyes in textile industry effluents.

Keywords: chitin, chitosan, silkworm, adsorption, dyes.

Aplicação de quitina e quitosana extraídas de crisálidas do bicho-da-seda no tratamento de efluentes têxteis contaminados com corantes remazol

RESUMO. Quitina extraída de crisálidas do bicho-da-seda foram utilizadas para preparar a quitosana utilizada neste estudo. Os experimentos de adsorção foram feitos em fluxo continuo de soluções de corantes: azul remazol (RN) e preto remazol 5 (RB) através de uma coluna recheada de quitina ou quitosana, ou em suspensão. Os resultados mostraram que a adsorção foi mais eficiente nas colunas de quitosana do que nas colunas de quitina e os experimentos em suspensão foram superiores em relação aos feitos em coluna. As isotermas de Langmuir não indicam diferença significativa na capacidade teórica de saturação da monocamada (Q_o) para ambos os corantes. A aplicação do processo de adsorção em condições reais foi avaliada através de experimentos realizados com efluentes têxteis reais. Em pH ácido a quitosana adsorveu completamente os corantes responsáveis pela coloração dos efluentes têxteis. Esse estudo revelou que a quitosana obtida de crisálidas do bicho-da-seda é uma alternativa viável de imobilização de corantes para a indústria têxtil.

Palavras-chave: quitina, quitosana, bicho-da-seda, adsorção, corantes.

Introduction

Surface water constantly receives a large amount of industrial and domestic wastes, which brings about a major environmental impact. The textile industry stands out for its environmental impact, given the complexity and difficulty of treating its effluents. Textile effluents are densely pigmented due to the presence of azo dyes not fixed to fibers during the dying process. This results in visual pollution, changes in biological cycles, particularly of aquatic photosynthesis. This has driven the constant search for new methodologies to treat these wastes (GARCIA et al., 2009, 2012; KUNZ et al., 2002).

This study proposes the development of alternative processes to immobilize dyes in textile industry effluents. Conventional treatments use aluminum salts and auxiliary polyelectrolytes for the agglutination and flocculation of polluting compounds. These treatments are a low cost and effective alternative for the removal of particulate materials and reducing the turbidity of these effluents. However, the residual aluminum may contaminate the treated water, thus causing a secondary contamination problem. Furthermore, studies indicate an association between diseases like Alzheimer's and aluminum compounds

(DIVAKARAN; PILLAI, 2002; HUANG et al., 2000; SIMIONATO et al., 2006).

Chitosan, a deacetylated biodegradable cationic polyelectrolyte derived from chitin (β-(1→4)-N-acetyl-D-glucosamine), has been investigated in the treatment of industrial effluents. Due to its efficient electrostatic action, it may act in the agglutination of colloidal particles. Besides acting as an auxiliary agglutinating polyelectrolyte, chitin and chitosan are good adsorbents capable of removing azo dyes efficiently from textile effluents (DUARTE et al., 2002; SZYGUŁA et al., 2008).

It has been reported the efficient use of chitin and chitosan obtained from silkworm chrysalides in the adsorption of residual aluminum from treated effluents (SIMIONATO et al., 2006). We have investigated their applicability and efficacy in the direct adsorption of dyes in textile effluents.

Material and methods

Extraction of Chitin and Chitosan

Chitin was extracted by two procedures previously reported in literature (PAULINO et al., 2006). In the first, an open reactor was placed on a heating plate under constant agitation. In the second, it was used a closed Teflon® reactor in oven. The two procedures involved acid and base steps with two objectives. The acid step aimed to remove proteins, and the base step, to remove fat. Chitosan was obtained by deacetylation of chitin with NaOH 40% (m v^{-1}) and $NaBH_4$ (0.850 g L^{-1}). The products were characterized by infrared spectroscopy (FTIR), nuclear magnetic resonance (^{13}C NMR/CPMAS) differential thermal analysis (DTG), and scan electronic microscopy (SEM).

Adsorption columns

Pyrex glass columns with 8.00 cm i.d. were filled with 300.0 mg of either chitin or chitosan and used in the adsorption experiments. The flow of 2.00 mL min^{-1} was obtained by gravity force and controlled through the equipment. Solutions of 50.00 mg L^{-1} of blue remazol RN (RN) and black remazol 5 (RB) were run through the columns. The structures of the dyes are given in Figure 1. Samples were collected at regular intervals of 25 min. of adsorption. All the analyses were performed in triplicate.

Adsorption of textile dyes in chitosan suspension

Chitosan (300.0 mg) suspensions and 100.0 mL standard dye solutions of RN and RB (50.00 mg L^{-1} each) were vigorously agitated for 430 min. Samples were collected at 5, 10, and 15 min. The samples were placed back into the reactor after each absorbance measurement. Measurements were done at 590 nm for RN and 596 nm for RB. The analyses were performed in triplicate.

RN and RB solutions with concentrations of 10.00, 50.00, and 10.00 mg L^{-1} were prepared for the study of the adsorption equilibrium of chitosan. The solutions were left in thermostated bath at 25.5°C with 300.0 mg chitosan. At regular intervals, samples collected taken and returned to the reactor after absorbance measurements. Up to 200 min. absorption measurements were carried out.

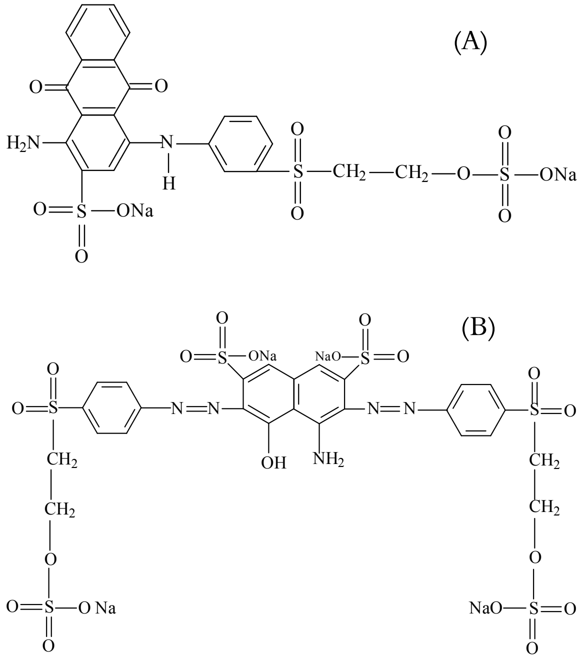

Figure 1. Dyes structures: (A) (RN); (B) (RB).

Quantification of the residual concentration of dyes after adsorption on chitin and chitosan

The residual dyes after adsorption on chitin and chitosan were evaluated with the help of an analytical curve. The analytical curve is given by equation $Y = A + BX$, for dye RN, where was found the parameters $A = 0.00824$, $B = -0.01042$, $R^2 = 0.9998$ and $SD = 0.0122$. To dye RB the equation $Y = A+BX$ give $A = 0.0132$, $B = 0.02967$, $R^2 = 0.9998$ and $SD = 0.0217$. These curves were plotted from mean absorbance values obtained at different concentrations.

Langmuir isotherms plots

Solutions of both dyes were prepared with concentrations ranging from 100.0 to 1000 mg L^{-1}. The solutions were agitated in thermostated bath at 25.5°C for four days. The amount of dye adsorbed per mass unit of adsorbent, q_e, was calculated with equation $qe = [(C_i - C_e)/m_a] V$, where, C_i is the initial concentration of the dye in solution, C_e is the concentration of the dye not adsorbed in solution in equilibrium, V is the solution volume, and m_a is the mass of adsorbent used in the experiment. Based on the model proposed by Langmuir and the values of qe and C_e, it was possible to study the adsorption equilibrium of the dye in chitosan and plot the isotherm given by equation $C_e/q_e = (1/K_L) + (\alpha_L / K_L) C_e$, where K_L and α_L are Langmuir isotherm constants and α_L/K_L give the theoretical capacity of saturation of the monolayer, Q_o.

Characterization of the Real Effluent

The real effluent was collected at MR Malharia in Maringá City. It was made up of a mixture of the dyes studied and others. Its characteristics are: $N_{NH4}^+ = 5.90$ mg L^{-1}; $N_{org} = 7.10$ mg L^{-1}; pH = 7.90 and DQO = 382.72 mg $O_2 L^{-1}$.

Study of dye adsorption

A preliminary study of the capacity of adsorption of the mixture of dyes by chitosan in aqueous suspension was done. It was used a mixture with solutions of 25.00 mg L^{-1} of dyes RN and RB. The mixture was vigorously agitated for 133 min. at room temperature, after which the residual concentration of the dyes was determined by spectrophotometry. An FTIR (FT–GOmax Bomem Easy MB-100, Nichelson) spectrogram of chitosan after adsorption was also recorded. After verifying the applicability of the method, tests of capacity of adsorption of chitosan were done with real effluents at two pH values, pH 7.90 (the natural pH of the effluent) and pH 3.00. Spectrophotometry provided information on adsorption.

Adsorption Measurements

Color removal from the dyes and the effluent was monitored by UV-Vis spectrophotometry (Hitachi U2000) adsorption measurements at the maximum peaks of the respective spectra.

Results and discussion

Quantification of the dyes after adsorption in chitin and chitosan columns

The results showed that the capacity of adsorption of dyes RN and RB of chitosan is higher than that of chitin due to the larger amount of amino groups dispersed on the surface of chitosan when compared to chitin (PAULINO et al., 2006; SIMIONATO et al., 2006). These groups have the ability to absorb contaminant due to their Lewis base character. Studies show that the adsorption of dyes by chitosan has favorable Gibbs free energy, while for chitin, this process has positive Gibbs energy (PRADO et al., 2004).

As the Gibbs energy is unfavorable for the adsorption of the dyes by chitin, it is expected very little or nearly no adsorption. However, as observed in Figure 2, adsorption occurs for chitin. In the first 25 min., adsorption reaches approximately 40% for RB and 60% for RN. However, this value does not remain stable for very long. After 100 min., both dyes are minimally adsorbed.

The adsorption of the dyes by chitin may be explained by favorable Van der Waals-type interactions, which afford suitable enthalpy to the system (PRADO et al., 2004).

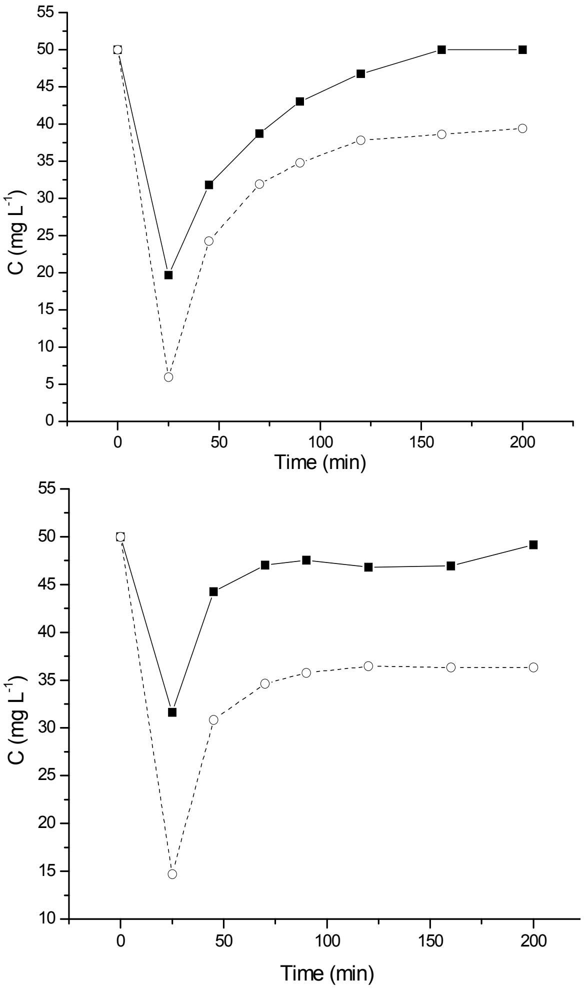

Figure 2. Concentrations of RN (a) and RB (b) after adsorption in chitin (■) and chitosan-packed column (○).

As the best conditions found for the adsorption of the dyes studied were those of chitosan, the aqueous suspension study was performed only for these conditions.

The adsorption of the RN and RB, 50.00 mg L^{-1} each, was measured in solution. The results in

Figure 3 show that it is possible to observe the complete adsorption of both dyes in solution after 300 min. agitation.

When compared to the adsorption of the dyes on chitosan in suspension with that in packed columns, it is clear the difference between them. Thus, the adsorption of dyes on chitosan in aqueous solution with agitation retains many more pollutant particles. This results from the much larger contact time between the adsorbent and the adsorbate in the aqueous solution.

As shown in Figure 3, when the RN and RB dyes, 50.00 mg L^{-1} each, were left in contact with 300.0 mg chitosan under vigorous magnetic agitation, the adsorption of RB was much more efficient than that of RN. This indicates that the amount of chitosan added was not sufficient for the adsorption of all the RN dye.

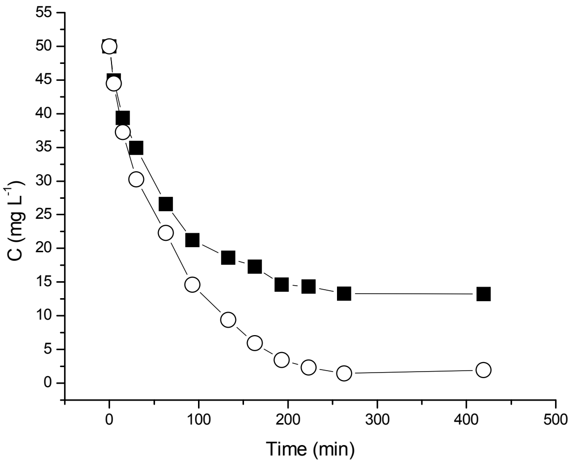

Figure 3. Variation of dye concentration as a function of the time of adsorption in chitosan aqueous solution of RN (■) and RB (○), 50.00 mg L^{-1}.

It is worth noting that the dye molecule in case has intramolecular interactions with the sulfonic (SO_3^-) and (NH_2), groups, both located in the same benzene ring. These interactions prevail over the intermolecular chitosan/dye interactions, making adsorption difficult. Additionally, the diffusion of the RN dye into the chitosan pores is more difficult, as its organic chain is branched (CESTARI et al., 2004; CHATTERJEE et al., 2007).

The study that investigated the point of equilibrium of the RN and RB dye solutions in the concentrations of 10.00, 50.00, and 100.0 mg L^{-1} (Figure 4) showed that the added mass of chitosan of 300.0 mg was sufficient to adsorb 10.00 mg L^{-1} RN and 10.00 and 50.00 mg L^{-1} RB completely.

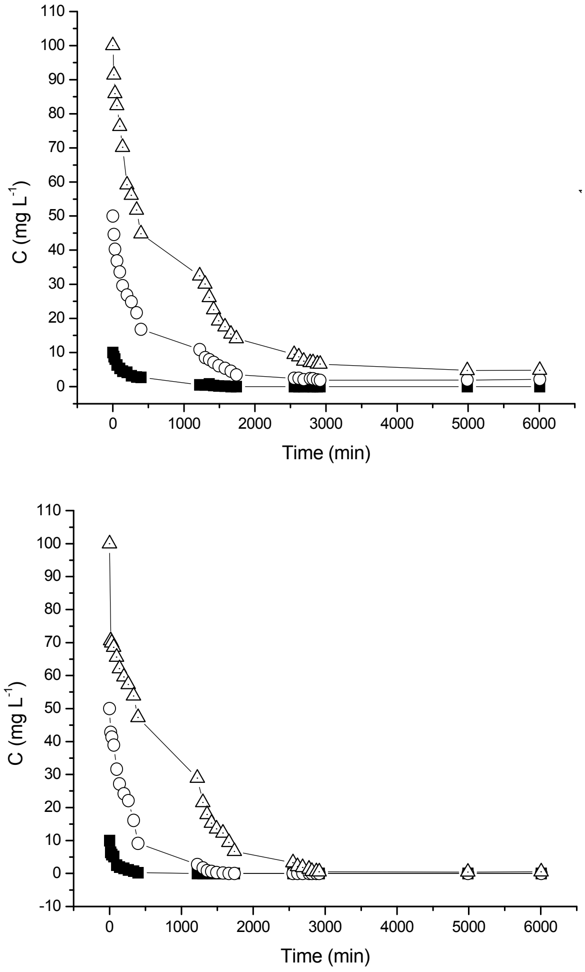

Figure 4. Concentration of dyes (a) RN and (b) RB after adsorption on chitosan under slow agitation and constant temperature for initial concentrations of 10.00 mg L^{-1} (■), 50.00 mg L^{-1} (●), and 100.0 mg L^{-1} (▲).

Equilibrium was reached for the RN 50.00 mg L^{-1} solution after 42.5h of agitation and for 100.0 mg L^{-1} after 44.8h of agitation, remaining only 2.000 mg L^{-1} and 5.000 mg L^{-1} of the respective dyes. For dye RB 100.0 mg L^{-1}, it was left only 0.5000 mg L^{-1} in solution after approximately 47h of agitation. It was also noticed difficulty in the adsorption of dye RN by chitosan when compared to RB, which is explained by the molecular interactions of this dye and by its number of branches, factors that make the chitosan/dye interaction difficult.

The FTIR spectra in Figure 5a and b show chitin and chitosan before and after RN adsorption. These spectra are useful to confirm the physical adsorption process that occurs between chitin/dye and chitosan/dye. Adsorption is determined by electrostatic forces that transfer the dye from the solution to the surface of the adsorbent, and also by diffusion of the dye molecules into the material pores (CESTARI et al., 2004).

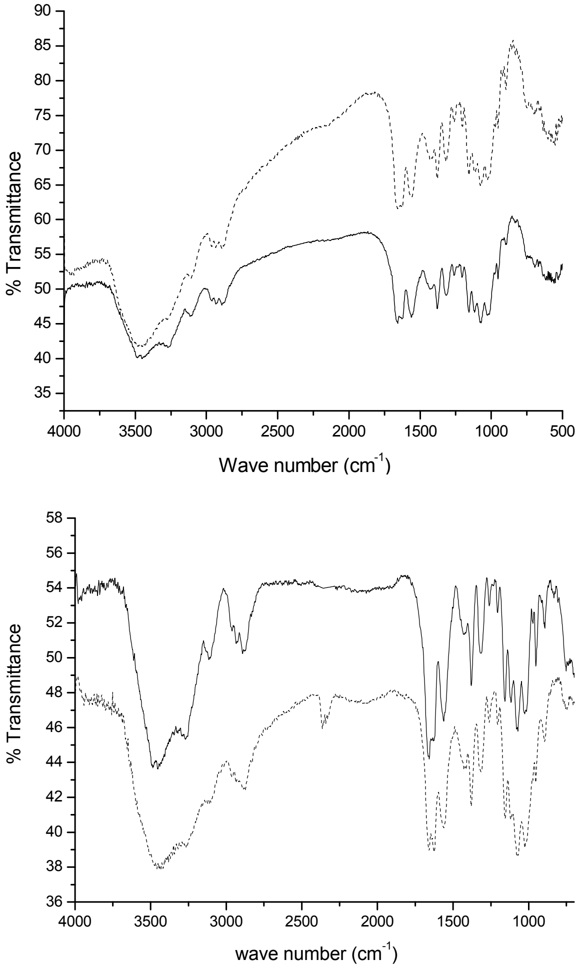

Figure 5. FTIR (a) chitin before (---) and after (—) adsorption of blue remazol and (b) chitosan before (---) and after (—) adsorption of blue remazol.

Study of the adsorption equilibrium

The adsorption equilibrium was studied with a fixed amount of chitosan (300.0 mg) and 100.0 mL of RN and RB aqueous solutions in a controlled temperature bath at 25.5°C. Preliminary studies showed that the RN solutions in concentrations of 50.00 and 100.0 mg L^{-1} reached equilibrium after approximately three days. The same study indicated nearly complete adsorption of 100.0 mg L^{-1} RB after this time.

For this reason, concentrations ranging from 100.0 to 1000 mg L^{-1} were chosen for both dyes under agitation at controlled temperature for 96h.

After this time, it was possible to plot the isotherms. Isotherms are important tools to describe the amount of adsorbate that interacts with a certain amount of adsorbent; thus, being an important criterion for the optimization of the use of the adsorbent. The amount of adsorbed dye per mass unit of adsorbent, q_e, was calculated with equation 3.

The values of q_e and Ce were used in the study of the adsorption equilibrium of the dye in chitosan based on the model proposed by Langmuir. The results in Table 1 show that the theoretical capacity of saturation of the monolayer per gram of chitosan is equal to 143.0 mg for RN and 130.6 mg for RB.

Table 1. Saturation capacity of the monolayer according to the Langmuir isotherm.

Dye	K_L (L g^{-1})	α (L mg^{-1})	Q_0(mg g^{-1})	R^2
RN	9.033	0.063	143.38	0.9950
RB	31.35	0.240	130.63	0.9949

The results indicate that the Q_0 of RN was larger than that of RB, but the difference was not significant. However, the slightly larger result for RN may be explained by its molecule size, which is significantly smaller than that of RN. Therefore, the amount of RN adsorbed per gram of the same mass of adsorbent, is much larger.

Application to real textile effluent

The real textile effluent was investigated at two pH values, pH 7.90 (the natural effluent pH) and pH 3.00, to verify the best condition of adsorption. The adsorption was less effective at the pH 7.90, it was observed a very small reduction of the bands, as seen in Figure 6. At modified pH of 3.00, the adsorption was complete. It can also be observed an overall decrease in the bands in relation to those of the effluent at natural pH.

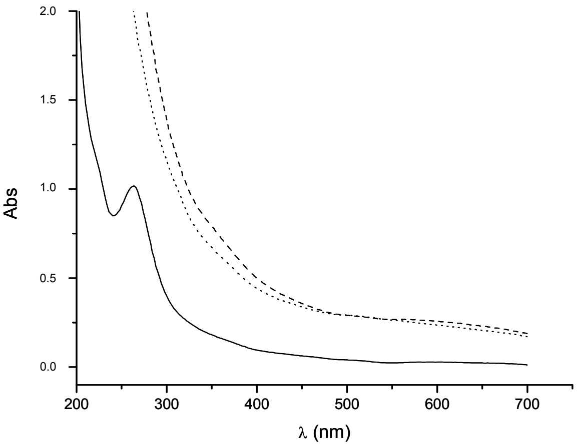

Figure 6. UV/Vis spectra of actual effluent before (-----) and after adsorption at (—) pH 3.00 and (....) pH 7.90.

The chitosan amino groups strongly adsorb anionic dyes by electrostatic attraction. This justifies the better adsorption in acidic medium of this effluent, as it had anionic substance. In this condition, chitosan is protonated (BENAISSA; BENGUELLA, 2004). Adsorption did not modify the structure of chitosan; thus, it was a physical.

Conclusion

The study showed that the adsorption of the dyes is better in columns packed with chitosan than with chitin. However, when compared to the adsorption of the dyes on column and in aqueous suspension, the latter gave far better results. The plotted Langmuir isotherm did not show any significant difference in the theoretical capacity of saturation of the monolayer (Q_o) for either of the dyes. In acidic pH, chitosan completely adsorbed the dyes responsible for the actual textile effluent coloration. The experiments described above showed that the use of chitosan obtained from silkworm chrysalides is a viable alternative for the immobilization of dyes in textile industry effluents.

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