Application of polyurethane foam chitosan-coated as a low-cost adsorbent in the effluent treatment

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Giselle S.N. Machado Centenaro, Bruno Ricardo Facin, Alexsandra Valério,
Antonio Augusto Ulson de Souza, Adriano da Silva, José Vladimir de Oliveira,
Débora de Oliveira*

Department of Chemical and Food Engineering, Federal University of Santa Catarina, 88040-900, P.O. Box: 476, Florianópolis-SC, Brazil

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Synthetic dyes are an important class of organic pollutants, and a part of the total amount of dye used in dyeing processes are discarded as effluent, which is discharged into the environment with harmful effects on aquatic life. Dyes removal by adsorption is an attractive method due to the effectiveness and economic viability. Thus, in the present work, a low-cost adsorbent, obtained by using polyurethane foam coated with chitosan film (0.51 wt %), was developed for textile reactive dyes removal in aqueous solutions. Polyurethane foam chitosan-coated (PU chitosan-coated) was characterized by zeta potential, Fourier transformed infrared and scanning electronic microscopy. For the isotherms adjustment, as well as, the determination of the influence of the temperature, adsorption kinetics, and adsorbent reuse capacity, batch experiments were carried out using reactive blue dye RB198. The experimental data were evaluated by Langmuir and Freundlich isotherm, and the data showed a better correlation with Langmuir isotherm with a maximum adsorption capacity of 86.43 mg g^{-1}. In addition, in this work, it was verified that even after seven reuse cycles of adsorption, the PU chitosan-coated was efficiently in the RB198 dye remove, confirming the advantage of the proposed PU chitosan-coated as a low-cost adsorbent.

1. Introduction

Industrially, dyes are used for coloring a wide range of products such as rubber, plastics, paper, cosmetics, medicines, food, and textiles products [20]. About 700,000 tons of synthetic dyes are annually produced [2], and two-thirds of this production is consumed by the textile industry [3,53,49].

It is estimated that 15% of the dyes used in textile processes are discarded as effluent without treatment [17]. The presence of dyes in the effluents involves serious environmental problems such as water coloration, decreasing the sunlight penetration required by aquatic life, increased biochemical oxygen demand (BOD), chemical oxygen demand (COD), toxicity and potential carcinogenicity [2,42].

Due to the aromatic structure and synthetic characteristic, most of the dye molecules are stable to light and heat, as well as non-biodegradable [48]. The physicochemical and biological methods, traditionally used in the wastewater treatment, showed low efficiency in the treatment of the most colored textile effluents, with the necessity of association of consecutive treatments including electro-oxidation, biological treatment, photochemical processing, ion-exchange, and also membrane techniques [6,26].

In the literature, are reported as alternative treatments for dye removal in aqueous solution, enzymatic degradation [13,31], photoelectrocatalytic degradation [38], combined techniques of biological degradation and photochemical oxidation [52], as well as membrane separation [36]. From the related techniques, the dye removal from aqueous solutions by adsorption is the most used methodology, due to the easier operation process, economic viability, and range of adsorbent materials [25,48,49].

In this way, adsorbent material as turf [27], bentonite clay [11,8], wastes from steel industry [5], coal ash [57], cellulose [37], polyethylene glycol and polyvinyl alcohol [46], and wood sawdust [47] are related in the literature. In addition, the natural biopolymers as chitosan is extensile reported and used due to the biodegradable, non-toxic characteristics [33,21,12,44], high adsorption capacity, cationic characteristics, and macromolecular structure [55,4].

The association of adsorbents material is also reported in the literature. The synthesis of composites based on chitosan and polyurethane foams was reported by Lee et al. [34] for adsorption of acid dye in aqueous solution. The authors reported good color removal ability of the system, using higher chitosan concentrations (20 wt%) and maximum dye adsorption capacity of 30 mg g^{-1}. In addition, for

the dye removal, the adsorbents should be replaced or desorbed to be continued use, in order to reduce the process and adsorbent material cost, as well as, improve the adsorbent performance [10,14]. Thus, in each new treatment, a high content of solvents or water are required to recover the adsorbent, increasing once again, the effluent production.

Although the research focused on the development of clean technologies for the dye removal have been used and reported in several areas of the science, it was verified a lack of information in the literature for the use of a low-cost absorbent in several reuses cycles, spatially, with no necessity of a desorption or treatment process before a new cycle. Thus, the novelty of this work was to use a chitosan film to coat a polyurethane foam, rather than using pure chitosan in the support matrix. Another important point of this work was the reduction in the chitosan content, as for example, compared to Lee et al. [34]. The authors used 20 wt% of chitosan, while in this work, it was used a film with 0.51 wt% of chitosan, with similar absorptive capacity as reported by Lee et al. [34], reducing the absorbent cost associated to the chitosan.

In front of this scenario, the main goal of this work, was the synthesis of polyurethane chitosan-coated as a low-cost adsorbent for the reactive blue 198 dye removal, and the evaluation of reuse cycles capacity, without PU chitosan-coated treatment before a new reuse cycle, aiming water saving.

2. Materials and methods

2.1. Materials

Reactive blue dye 198 (RB198, λ_{max} = 625 nm) was kindly donated by Malwee textile industry (Blumenau-SC-Brazil). Polyol polyether and toluene diisocyanate (TDI 80/20, mixture of 2,4 and 2,6 isomers in the proportions of 80/20) used in the flexible polyurethane foam synthesis was kindly provided by Mannes Ltda. (Guaramirim-SC-Brazil). For the PU foam modification, chitosan (190.000–310.000 Da, Sigma Aldrich) and acetic acid solution (99.5%, LAFAN) was used.

2.2. Synthesis and modification of flexible polyurethane foam

Flexible polyurethane foam (PU) was synthesized according to the methodology described by Silva et al. [50], by using 3 mL of toluene diisocyanate (TDI) and 5 mL of polyol polyether. The mixture was mechanically stirred for 5 min to completely homogenization, after EPU expansion, it was kept at room temperature to dry and cure for 48 h. After this period, the foams were cut into cubes of uniform size (5 × 5 × 5 mm) [16].

To EPU surface modification, based on preliminary results (data not shown), a chitosan acid solution (0.51 wt%) was prepared by the dissolution of chitosan in 0.5% (v/v) acetic acid solution (pH 3), kept under magnetic stirring for 24 h at 25 °C. The EPU cubes were immersed in the chitosan solution until completely cover, then the cubes were removed by filtration and dried at 40 °C for 24 h. The dried PU chitosan-coated cubes were stored at room temperature (25 °C).

2.3. PU chitosan-coated characterization

FTIR analyses in ATR (attenuated total reflectance, Zn Se) mode was performed on Cary 660 Series FTIR Spectrometer (Agilent Technologies) with 20 scans in the range from 4000 to 650 cm^{-1} at a resolution of 4 cm^{-1}. The samples morphological evaluation was determined by Scanning Electron Microscopy (SEM, TM3030), with acceleration voltage of 5 kV and a magnification of 20 and 50 ×.

2.4. RB198 dye adsorption assay and adsorption isotherm

Based on the preliminary assays (data not shown), for the study of RB198 dye adsorption in the PU chitosan-coated, a calibration curve in

a range from 1 to 50 mg L^{-1} of RB198 dye concentrations was prepared at pH of 5 and 7 (50 mM citric acid/citrate buffer solution), and pH 11 (sodium carbonate/sodium bicarbonate buffer solution 50 mM). All dye solution was prepared with distilled water. To obtain adsorption isotherms, RB198 dye solutions with initial concentrations in a range from 20 to 500 mg L^{-1} prepared in 50 mM sodium citrate/sodium citrate buffer (pH 5 and 7) and carbonate/bicarbonate buffer sodium 50 mM (pH 11) was used. The assays were carried out in triplicate (n = 3) in an orbital shaker (Excella® E25) 150 rpm, at 27 °C, for 24 h, and analyzed using a UV–vis spectrophotometer (Shimadzu UV-mini 1240) at room temperature. The obtained experimental data was fitted to the Langmuir isotherm (Eq. (1)) [7,19]. The Langmuir constant (K_L, L mg^{-1}) is used in the characterization of the adsorption process according to the separation factor (R_L, Eq. (2)) [9].

$$\frac{C_e}{q_e} = \frac{1}{K_L * q_{max}} + \frac{1}{q_{max}} * C_e \qquad (1)$$

$$R_L = \frac{1}{1 + K_L * C_0} \qquad (2)$$

Where q_e is the adsorption capacity in the equilibrium (mg g^{-1}), Ce is the liquid-phase of dye concentration at equilibrium (mg L^{-1}), C_0 is the initial dye concentration in the solution (mg L^{-1}), and q_{max} is the maximum dye uptake in the monolayer (mg g^{-1}).

The temperature influence on the PU chitosan-coated adsorption process (255 mg) was carried out by using a RB198 dye solutions in 50 mM sodium citrate/sodium citrate buffer (pH 5) at initial concentrations of 20–400 mg L^{-1}. The experiments were carried out in an orbital shaker (Excella® E25) for 24 h at 150 rpm in a temperature range from 15 to 45 °C.

2.5. Influence of RB198 dye initial concentration in the adsorption kinetic

The equilibrium adsorption capacity of the PU chitosan-coated was obtained with a mass balance, where the adsorbate content in the PU chitosan-coated adsorbent is equal to the amount of dye removed from the solution (Eq. (3)) [11,12]. RB198 dye solutions with initial concentrations from 20 to 500 mg L^{-1} (pH 5, 50 mM sodium citrate/sodium citrate buffer) was used. All dye solution was prepared with distilled water. For the kinetic evaluation, the reduction in the dye absorbance was evaluated periodically using a spectrophotometer (Shimadzu UV mini-1240) at 625 nm. The adsorbed dye in the PU chitosan-coated at equilibrium, qe (mg g^{-1}), was calculated by Eq. (3).

$$q_e = \frac{C_0 - C_e}{w} * V \qquad (3)$$

Where, C_0 and C_e are the initial and equilibrium dye concentrations (mg L^{-1}), respectively, V is the volume of solution (L), and w is the mass of the PU chitosan-coated adsorbent (g). The amount of adsorption at time t, q_t (mg g^{-1}) was calculated by Eq. (4) [29].

$$q_t = \frac{C_0 - C_t}{w} * V \qquad (4)$$

The experimental data was fitted to the kinetic models of pseudo-first order (Eq. (5)) and pseudo-second order (Eq. (6)), according to the equations described by Zhang et al. [59].

$$\ln(q_e - q_t) = \ln q_e - k_1 * t \qquad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 * q_e^2} + \frac{t}{q_e} \qquad (6)$$

Where k_1 is the is the pseudo-first-order rate constant (min^{-1}), k_2 is the is the pseudo-second-order rate constant (g mg^{-1} min^{-1}), and t is the time (min).