RED 2 DYE ADSORPTION BY CHITOSAN-BASED BIOADSORBENT: A KINETIC STUDY

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Abstract

In this paper the synthesis of a chitosan-based bioadsorbent is presented, their characterization was completed by FTIR spectroscopy, scanning electron microscopy and surface area measurement; furthermore determination of the water content and adsorption kinetic at three temperatures were studied. Prior to the kinetic study, optimum conditions were determined: ratio of hydrogel mass-dye concentration also pH of adsorption. It was concluded that the bioadsorbent is capable of removing Red 2 dye from aqueous solutions at an acidic pH, and can be used for environmental remediation.

Introduction

Water pollution is caused by many chemical products, some of them are dyes [2], which are discharged into the atmosphere by industries that require to produce higher volumes for the sustenance of daily life, e.g.: pulp industry, paper, textile, food, wine, oil, metallurgy, tanning, metal finishing, pharmaceutical industry, etc. [1].

Effluents with high concentrations of azo dyes in water bodies has triggered a significant negative effect on human health, and a serious hazard for aquatic living organisms furthermore during the decomposition of dyes may occur amines, which are toxic compounds even more harmful than the dye itself. An application that is currently gaining importance has been the use of hydrogels as polishing treatment of wastewater by removing contaminants that have not removed on conventional treatments [3].

Hydrogels as being relatively new materials, still under investigation and characterization, lack of a precise definition of hydrogel, but it can be described as a polymeric material shaped three-dimensional cross-linked network of natural or synthetic origin, which swells in contact with the water giving rise to a soft, resilient material and that retains a significant fraction thereof in their structure without dissolving [4]. So that they have become very important due to their applications in the fields of biomedicine, optics, agriculture, engineering, food, agroforestry, environmental, and even more in recent years in the removal of synthetic dyes type azo which are generally toxic and carcinogenic, one such example is the dye Red 2.

Experimental

Experiments were carried out using the following reagents: commercial dye Red 2 was supplied by Sensient Co.; polyvinyl alcohol (PVA) USP grade high viscosity was purchased from Golden Bell; ethyleneglycol diglycidylether (EGDE) was acquired from Tokyo Chemical Industry Co. and used without further purification; chitosan (Q) was supplied by Alimentos America; all other utilized reagents were analytical-reagent grade. Distilled water was used to prepare all solutions.

Chitosan was dissolved in 0.4 M acetic acid and PVA in deionized (DI) water to obtain solutions at 3.1 wt% and 10.17, respectively. Subsequently both solutions were mixed, and then the resulting mixture was dropped into a 0.1 M NaOH solution and formed hydrogel beads (Q-PVA). Q-PVA beads in DI water at
basic pH; nitrogen atmosphere and chemical cross-linking reagent EGDE were mixed and shaken for 6 h at 70 °C in a water bath. Finally cross-linked Q-EGDE-PVA beads were washed with DI water until the wash water pH was equal to the DI water.

Hydrogel wetness content was determined by drying them to constant weight in an oven at 40 °C. Functional groups identification of Q and PVA was made by a spectrometer 640-IR Varian FTIR using 16 scans with a 4 cm⁻¹ resolution and a 4000-500 cm⁻¹ range. FTIR spectra have been recorded using ground and dried samples. Morphology of Q-EGDE-PVA beads was observed by scanning electron microscope JEOL JSM-6610LV using acceleration voltage of 10 KV and backscattered electrons. Samples were previously lyophilized (17 h, -50 °C and 1.5 mbar). Surface area and pore volume on beads previously freeze-drying have been measured operating a Brand Bel Model Sorp Max device and using nitrogen gas at 100 °C for 3 h. The isotherm adsorption/desorption was adjusted to BET method.

Experiments for determining dye concentration-hydrogel mass were carried out on several 15 mL capacity vials, which contained dye solutions of 100, 200 and 300 mg/L at pH 2 and 40 to 80 mg Q-PVA-EGDE hydrogel. All solutions were taken into contact to two different masses in triplicate under the following experimental conditions: 10 mL of dye solution were added to the hydrogel mass in corresponding vials, and were stirred using an orbital thermo-shaker at 30 °C and 150 rpm during 72 h. Once the contact time was completed, solutions were decanted and pH of supernatants was measured. Dye concentration was quantified by UV-vis spectrophotometry.

R2 dye 200 mg/L solutions were prepared and adjusted at pH to 2, 3, 4, 5, 6 and 7 respectively, each of the solutions were put contacted in triplicate using an orbital shaker in vials with 40 mg of the hydrogel; under the following experimental conditions: 10 mL of dye solution, 30 °C and 150 rpm for 72 h. At end of contact time proceeded in a manner analogous to that described above.

Kinetic studies have been performed after preliminary of pH optimum testing using those conditions and three temperatures, 30, 40 and 50 °C in order to determine the best percentage of R2 dye removal; therefore, from a concentration of 200 mg/L of dye solution R2 was adjusted to pH 3 and vials were prepared with 40 mg of Q-EGDE-PVA beads by triplicate which were put in contact to 10 ml of solution and stirring speed was 200 rpm in an orbital shaker for 72 h at 18 different sampling times. Results are presented in Figure 4.

**Results and Discussion**

Percentage of water retained in the areas analyzed was 97.8%, so that Q-EGDE-PVA hydrogel can be classified as a high-swelling hydrogel. This high water content allows high permeability and good surface properties for the adsorption of the Red 2 dye.

Figure 1 shows the FTIR spectrogram of synthesized material and chemically cross-linked Q-EGDE-PVA. It is observed that the characteristic bands of chitosan are kept at 3460 and 3417 cm⁻¹ belonging a stretching vibration of a primary and deformation amine belonging to the group NH2 to 1593 cm⁻¹ and 1026 cm⁻¹, band corresponding to the characteristic bond of COC polysaccharides such as is observed at the chitosan.
Figure 1. FTIR spectra of Q-EGDE-PVA beads.

Micrographs in Figure 2 show morphology of Q-EGDE-PVA beads, were taken by SEM at a magnification of 500X and 33X, both with an accelerating voltage of 10KV using backscattered electron; where is evident the material porosity, all pore have different diameters and some cracks (Figure 2b) on the bead surface were formed possibly either the freeze drying process previously carried out during the preparation of the sample or by vacuum which they were subjected in the SEM at the time of taking the micrographs.

Figure 2. Micrograph of hydrogel Q-PVA EGDE amplified, a) at 500X and b) at 33X.

The surface area of the hydrogel Q-EDGE-PVA was determined by fitting the curve of isotherm adsorption-desorption obtained as measurement result by BET method, thereby obtaining a value of 65.85 m²/g of total surface area.

Results for determining dye concentration-hydrogel mass are presented in Table 1, which highlights the best adsorption conditions for Red 2 dye.

Table 1 Percentage removal at different concentrations of the dye Red 2 using different amounts of hydrogel.

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<tr>
<th>Hydrogel mass (mg)</th>
<th>Percentage of removal at different concentrations of dye Red 2</th>
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<td></td>
<td>100 mg/L</td>
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<td>40</td>
<td>99.95</td>
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<td>80</td>
<td>99.92</td>
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In Figure 3 shows results of the study of the behavior of the adsorption phenomenon of beads Q-EGDE-PVA varying the pH of the solutions containing Red 2 during a contact time of 72 hours, 150 rpm and 30 °C. The greater amount of dye adsorbed per gram of adsorbent material is in the range of pH 2 - 3, due to the high concentration of H⁺ the active sites of the adsorbent were protonated so that the dye were negatively charged in aqueous media was attracted to the material being attached to it.

Figure 3 Effect of pH on the percentage of removal of dye R2 at 200 mg/L and 40 mg hydrogel.

Adsorption kinetics experimental data are presented in Figure 4, it is observed that the equilibrium was reached at 28 hours and kinetics behavior very similar for the three temperatures, which indicates that there are not an important dependence of temperature.

Figure 4. Percent dye removal R2 with respect to time at 30, 40 and 50 ° C

Conclusions

It is possible to perform the synthesis of hydrogel beads chitosan-based polyvinyl alcohol cross-linked with EGDE capable of adsorbing Red 2 dye at a pH between 2 and 3. The high percentage of water retained by the hydrogel synthesized favors the adsorptive capacity of Red 2. Using FTIR analysis it is possible to observe the major functional groups of each polymers. Characterization by SEM allowed knowing that hydrogel Q-EGDE-PVA is a porous material. Surface area was 65.85 m²/g. Adsorption tests showed that the best conditions to quantify the percentage of removal of dye were 200 mg/L of solution R2 at pH of 3 and 40 mg hydrogel. According to the results obtained the greatest percentage removal was 66.23%, achieving it at 30 ° C and 28 h.
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References


