Colloids and Surfaces A 556 (2018) 43–50

Contents lists available at ScienceDirect

Colloids and Surfaces A

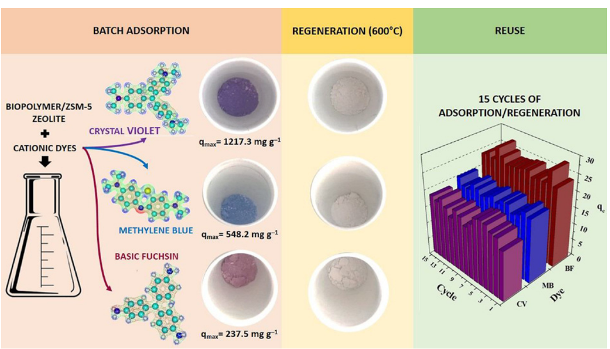
journal homepage: www.elsevier.com/locate/colsurfa

Highly efficient and reusable mesoporous zeolite synthetized from a biopolymer for cationic dyes adsorption

Giani V. Brião, Sérgio L. Jahn, Edson L. Foletto, Guilherme L. Dotto*

Chemical Engineering Department, Federal University of Santa Maria–UFSM, 1000 Roraima Avenue, 97105–900, Santa Maria, RS, Brazil

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Dyes
Mesoporous
Simulated effluents
Regeneration
Zeolite

ABSTRACT

A highly efficient and reusablezeolite was prepared using the biopolymer chitin as mesoporosity agent and applied to adsorb three cationic dyes. The zeolite was synthetized by the hydrothermal method and characterized. The potential of zeolite to adsorb crystal violet (CV), methylene blue (MB) and basic fuchsin (BF) was evaluated conducting kinetic, equilibrium, thermodynamic and regeneration studies. The treatment of simulated effluents was also performed. The modification with chitin biopolymer provided attractive adsorptive characteristics for the zeolite structure. The adsorption was attractive with adsorbent dosage of 2.0 g L^{-1} and pH of 7.5, 8.0 and 9.0, for CV, MB and BF, respectively. The adsorption kinetic was well described by the Homogeneous Surface Diffusion Model (HSDM). The equilibrium was adequately adjusted with the Langmuir (CV) and Sips models (MB and BF). Maximum adsorption capacities predicted by the isotherm models were 1217.3, 548.2 and 237.5 mg g^{-1} for CV, MB and BF, respectively. The modified zeolite can be used for fifteen adsorption cycles maintaining the same adsorption capacity. Also, the adsorbent was able to treat a simulated textile effluent providing 85% of color removal. These results demonstrated that the synthetized zeolite is a highly efficient and reusable material to adsorb cationic dyes.

1. Introduction

Dye removal from aqueous media is a motive of several studies, since the water pollution from textiles activities is a persistent problem. Dyeing is the main step responsible to color the textile wastewaters, once the water is a direct participant in the essential dye–fiber interaction mechanism [1]. To color acrylic fibers, cationic dyes are applied. In this class of dyes, the chromophore is present as a cation. Basic

* Corresponding author at: UFSM, 1000, Roraima Avenue, 97105-900, Santa Maria, RS, Brazil.
E-mail addresses: giani.eq@gmail.com (G.V. Brião), sergiojahn@gmail.com (S.L. Jahn), efoletto@gmail.com (E.L. Foletto), guilhermeldotto@ufsm.br (G.L. Dotto).

https://doi.org/10.1016/j.colsurfa.2018.08.019
Received 10 July 2018; Received in revised form 7 August 2018; Accepted 8 August 2018
Available online 10 August 2018
0927-7757/

Fuchsin (BF), Methylene Blue (MB) and Crystal Violet (CV) are examples of cationic dyes. Crystal violet and Basic fuchsin are triphenylmethanes and Methylene blue is a phenothiazine. These dyes are extensively used in textile industries. The cited dyes present some undesirable proprieties like: genotoxicity, mutagenicity, neurotoxicity, hematotoxicity, acute oral toxicity, cytotoxicity and carcinogenicity [2]. These proprieties give to the effluents a toxic and dangerous character, which indicates the necessity of an adequate treatment before discharge.

Adsorption can be a good option to treat textile effluents since the adsorbent (solid matrix) have many favorable characteristics like good chemical, thermal and mechanical stability, and high specific surface area. Zeolites have these properties and more, they have ion–exchange capacity, a negatively charged lattice and selectivity [3,4]. Even with their advantages, zeolites also show diffusion restrictions to the transport of large molecules inside the material [5]. However, recent researches obtained hierarchical zeolites with secondary porosity maintaining the properties of zeolites [6]. The hierarchical zeolites have been extensively studied in catalysis, but few researches exist in relation to the potential of this material to adsorb dye molecules [7–9].

The micropores display diffusion restriction of dye molecules because the pore diameter of the zeolites can be lower than the molecular size of dyes [10]. Therefore, in order to employ zeolites for dye adsorption, is necessary a change in the porosity of this material. An alternative to overcome the limits regarding dye adsorption is the introduction of chitin, a natural, low cost and available biopolymer [11–13] as modifying porosity agent. In a previous report [9], it was demonstrated that chitin can be a promising mesoporosity agent to produce a zeolite. Here, the potential of a biopolymer/ZSM–5 zeolite was extended for three cationic dyes. Furthermore, fundamental aspects like regeneration/reuse and treatment of simulated effluents are demonstrated.

This work aimed to verify the adsorption potential of a ZSM–5 zeolite, modified by the biopolymer chitin in the synthesis route, to adsorb cationic dyes. For this purpose, ZSM–5 zeolite was synthetized with the addition of chitin biopolymer (biopolymer/ZSM–5 zeolite) and characterized. Biopolymer/ZSM–5 zeolite was evaluated as adsorbent to remove CV, BF and MB dyes from aqueous solutions. The dye molecules were modeled by PM3 method and the electrostatic potential was mapped. In the adsorption study, the effects of adsorbent dosage and pH were evaluated. The mass transfer mechanism was studied using a diffusional mass transfer model. Isotherms were constructed at different temperatures (298–328 K) and the curves were fitted with Freundlich, Langmuir and Sips models. Thermodynamic was evaluated by enthalpy (ΔH°), Gibbs free energy (ΔG°) and entropy (ΔS°) changes. A regeneration study was done to estimate the adsorbent reuse potential. The proposed adsorbent was tested to treat simulated textile effluents.

2. Materials and methods

2.1. Chemicals

Chitin (particle size of 75 µm, crystallinity index of 86 ± 1%, deacetylation degree of 44 ± 1%) was produced from shrimp (*Penaeus brasiliensis*) wastes [11]. NaOH (99.0%), SiO_2 (Aerosil) (0.2–0.3 µm), H_2SO_4 (95.0%), tetrapropylammonium hydroxide (TPAOH (20% v/v)) and $Al_2(SO_4)_3$ were purchased from VETEC (Brazil) and Sigma Aldrich (United States). Crystal Violet dye (CV) (color index 42555, molar weight of 407.98 g mol^{-1}, λ_{max} = 590 nm, purity of 99.0%), Basic Fuchsin (BF) (color index 42500, molar weight of 337.85 g mol^{-1}, λ_{max} = 540 nm, purity of 99.0%) and Methylene Blue (MB) (color index 52015, molar weight of 319.85 g mol^{-1}, λ_{max} = 640 nm, purity of 99.0%) were purchased from INLAB Ltda. (Brazil). Deionized water was used to prepare all solutions. All other reagents utilized were of analytical grade.

2.2. Dye molecular modeling

Dyes properties and characteristics are very important to compare the different adsorption capacities of the biopolymer/ZSM–5 zeolite. Therefore, geometry optimization and dipole moment were calculated for each dye by Hyperchem 8.0 software using the semi empirical method PM3 (Parametric Method 3) [14]. The geometry optimization was done by Polak–Ribiere algorithm with terminal conditions of RMS gradient of 0.01 kcal Å^{-1} mol^{-1} or 570 cycles.

2.3. Preparation and characterization of biopolymer/ZSM–5 zeolite

Biopolymer/ZSM–5 was synthetized by the procedure developed in a previous work [15], employing a nucleating gel as structure–directing agent. 1% wt of the nucleating gel was placed into a precursor gel under magnetic agitation, resulting in a mixture with TPAOH/SiO_2 molar ratio of 0.001. The proportions of chemical compounds were used in order to obtain a ZSM–5 zeolite containing SiO_2/Al_2O_3 ratio of 30 [16].

The biopolymer/ZSM–5 characterization was carried out by several techniques. The functional groups were identified; the crystallinity index was obtained; textural characteristics were acquired and surface images were recorded. More details about the synthesis procedure and characterization can be found in supplementary material (Fig. 1S) and literature [9].

2.4. Batch adsorption experiments

Typical adsorption experiments were realized in discontinuous batch system to verify the potential of biopolymer/ZSM–5 zeolite as adsorbent. Detailed procedure is presented in supplementary material.

2.5. Mass transfer and equilibrium models

When mass transfer resistance is internal, intraparticle diffusion controls the process. In this case, considering some simplifications like amorphous and homogeneous particles, constant diffusivity, negligible external resistance, the adsorption operation can be represented by the HSDM model, Eq. (1) [17–23]:

$$\frac{\partial q}{\partial t} = \left(D_p \frac{\partial^2 q}{\partial r^2} + \frac{2}{r}\frac{\partial q}{\partial t}\right) \tag{1}$$

Using appropriate boundary and initial conditions, for a finite volume process [24], a solution can be obtained and then approximated to the first term of series when the Fourier number is higher than 0.2, Eq. (2):

$$\frac{q}{q_e} = 1 - \left[\frac{6\alpha(\alpha+1)\exp\left(-\frac{q_n^2 D_p t}{R_p^2}\right)}{9 + 9\alpha + q_n^2\alpha^2}\right] \tag{2}$$

where D_p is the intraparticle diffusivity ($m^2\,min^{-1}$), α is the effective volume ratio, expressed as a function of the equilibrium partition coefficient (solid/liquid concentration ratio) and is obtained by the ratio ($C_e/C_0 - C_e$) and q_n represents the non–zero solutions of Eq. (3):

$$\tan q_n = \frac{3q_n}{3 + \alpha q_n^2} \tag{3}$$

Freundlich, Langmuir and Sips isotherms were used to fit the equilibrium data, according the Eqs. (4–6). The choice of these models was based on the shape of equilibrium curves [25–27].

$$q_e = k_F C_e^{1/nF} \tag{4}$$

$$q_e = \frac{q_m k_L C_e}{1 + (k_L C_e)} \tag{5}$$