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Comparative analysis of tropaeolin adsorption onto raw and acid-treated kaolinite: Optimization by Response Surface Methodology

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ABSTRACT

The comparative adsorption of Tropaeolin (TP) onto raw kaolinite (RK) and kaolinite submitted to acid treatment (AK) was studied. RK and AK were characterized by zeta potential and energy dispersive X-ray spectroscopy (EDS). The adsorption was investigated using Composite Central Design (CCD) and the parameters evaluated were initial TP solution concentration, quantity of adsorbent and the pH of the solution. The optimized parameters were: initial TP solution concentration of 75 mg L^{-1}, pH 4 and 0.12 g adsorbent. Kinetic data were evaluated by pseudo-first order, pseudo-second order and Avrami models. The equilibrium adsorption was analyzed by Langmuir, Freundlich and Sips isotherms. The kinetic data were best fitted to the pseudo-second order model. The Sips isotherm model gives the better correlation to predict the adsorption equilibrium. The maximum adsorption capacities were 18.3 mg g^{-1} and 23.2 mg g^{-1} for RK and AK, respectively. The calculated thermodynamic parameters showed that the process was spontaneous, endothermic and involving the disorganization of the adsorption system for both adsorbents. The desorption step showed that the AK sample was more suitable as an adsorbent.

1. Introduction

Due to their negative effects on many life forms, dyes in effluents are considered one of the most important pollution problems nowadays (Ravikumar et al., 2005). Azo dyes are one of the most extensive synthetic dye groups used in the textile industry, constituting 60–70% of the whole production. They are substances characterized by the presence of one or more azo groups (R1-N=N-R2) substituted by aromatic groups containing sulfonate groups and/or hydroxyl groups, which are considered toxic and non-biodegradable (Riaz et al., 2012). Among the dyes belonging to this class, tropaeolin stands out as being a model dye molecule present in more than 15% of the worldwide textile production. Although it has high applicability, results indicate that the dye molecule is resistant to degradation by light, the action of O_2 and common acids and bases (Riaz et al., 2012). Due to this fact, its use can be damaging, with high leaching potential in soils and possible contamination of groundwater (Sarkar et al., 2011).

In this context, research has been carried out with the objective to contribute to an optimal removal, associated with safe disposal (Ravikumar et al., 2005). Biological degradation and techniques such as Fenton, photo-Fenton and photo catalysis employing TiO_2 have been used in attempts to minimize the environmental impacts of the use of this acid dye (Morrison et al., 1996). However, these methods are unable to remove it completely, making it necessary to find other techniques of low cost and high efficiency. Among the possible alternatives identified, adsorption is indicated for having ideal characteristics: easy operation, high efficiency and low cost (Liu et al., 2012).

In this process, the use of clay minerals as adsorbent materials has been validated by research, since they present high ion exchange, low cost, wide availability and are not considered toxic (Karaoglu et al., 2010; Magriotis et al., 2010). Kaolinite, focus of the present study, is a phyllosilicate constituted by the stacking of one silicon tetrahedral sheet and one aluminum octahedral sheet, forming a type 1:1clay mineral, and it is used for adsorption, since it is chemically inert at pH values between 4 and 9 (Magriotis et al., 2012).

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Although clay minerals are used for the removal of different contaminants, it has been shown that this removal can be efficiently increased by treatments employed to produce materials competitive with those available in the market (Teixeira-Neto and Teixeira-Neto, 2009). Acid treatment has been reported as ideal to produce adsorbents with higher surface areas as a result of particle deagglomeration, elimination of impurities and dissolution of octahedral cations (Panda et al., 2010). Clay minerals submitted to acid treatments have a wide application, which emphasizes their use in adsorption optimized by the use of a response surface. The Response Surface Methodology can be defined as a method applicable in the study of the effect of the variables that influence on responses by their simultaneous variation in a limited number of experiments (Singh et al., 2011).

In this context, the aim of this study was to evaluate the influence of acid treatment on kaolinite, employing the response surface in order to optimize the parameters in the adsorption of tropaeolin well as analyze the reuse of adsorbents studied.

2. Materials and methods

2.1. Adsorbate

The adsorption tests were carried out using the dye Tropaeolin 000 (VETEC) as an adsorbate, whose characteristics and properties are shown in Table 1. The three-dimensional structure, optimized using the base functions B3-LYP and 6-31G, delineated in the Gaussian 09 program is shown in Fig. 1. The solutions used in the experiments were diluted from a dye solution at a concentration of 1 g L^{-1}.

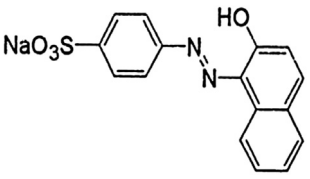
2.2. Adsorbents

The raw kaolinite (RK) was supplied by Mineradora Química e Minérios from the city of Ijaci, Minas Gerais, Brazil. The acid treatment was performed on the clay mineral using a sulphuric acid solution at 2 mol L^{-1}, for 3 h, at a temperature of 25 °C, under agitation. For this purpose, the solid/liquid ratio used was 1:20 (1 g kaolinite: 20 mL acid solution). After the treatment, the sample was submitted to vacuum filtration with type II water to neutral pH and dried in an oven at 100 °C, for 24 h. Then, the samples were macerated and sieved in a 0.42 mm mesh sieve (35 Tyler). The sample derived from the acid treatment of the RK sample was called AK.

2.3. Characterization of the adsorbents

The zeta potential of the kaolinites was measured using a Zeta Meter 3.0+, model ZM3-D-G (Zeta Meter Inc). Kaolinite suspensions (particle size <37 μm) were adjusted to an appropriate pH (in the range 2–12) and sedimented/conditioned for 2 h at 22 °C in 250 mL conical flasks containing 2 mmol L^{-1} sodium nitrate solution used as a supporting electrolyte. The applied tension ranged in an interval of 75–200 mV. Twenty measurements were made to achieve the average representative potential. The chemical composition was identified through Energy Dispersive X-ray Spectroscopy (EDS) in Quantax X Flash 5010 Bruker apparatus.

Table 1
Properties and characteristics of Tropaeolin (TP).

Generic name	Tropaeolin 000 n°2
Chemical name (IUPAC)	sodium 4-[(2E)-2-(2-oxonaphthalen-1-ylidene) hydrazinyl]benzenesulfonate
C.I.	15,510
Chemical formula	$C_{16}H_{11}N_2NaO_4S$
Molecular weight (g mol^{-1})	350.33
$\lambda_{máx}$ (nm)	481
Chemical structure	

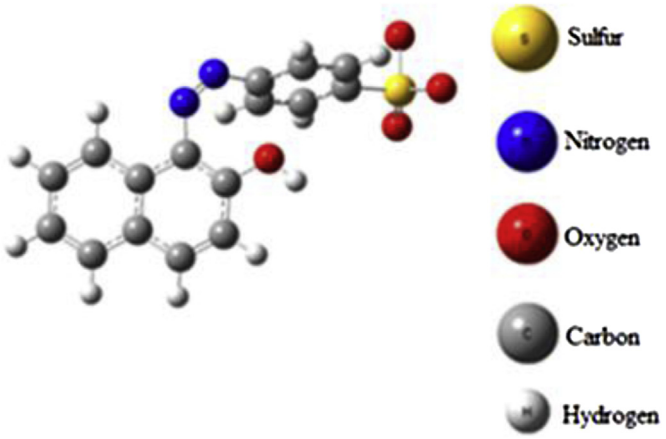


Fig. 1. Optimized three-dimensional structure of TP.

2.4. Experimental design

In order to study the effect of the parameters initial concentration, adsorbent mass and pH of the solution on the removal of TP from RK and AK samples, experiments were carried out using Central Composite Design (CCD). Therefore, N is defined as the number of experiments, and consists of 2^n factorial points with $2n$ axial points and n_c central points, where n is the number of independent variables. For the three variables studied, the design involved eight factorial points, six axial points and three central points used to estimate experimental error and the reproducibility of the data. Thus, the total number of experiments with the three variables was 17.

The responses obtained for the adsorption of TP on RK and AK samples were correlated, using the most appropriate model developed from the second degree polynomial equation, as follows: (Myers and Montgomery, 1995).

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_1^2 + \sum_{i=1}^{k-1} \sum_{j=1}^{k} \beta_{ij} x_i x_j + \varepsilon \quad (1)$$

In the equation, y is the predicted response; β_0, a constant; β_i, the linear coefficient; β_{ii}, the quadratic coefficient; β_{ij}, the interaction coefficient; and ε, the error associated with the model. All the statistical tests were applied at 95% confidence.

The Chemoface program, version 1.4 (Nunes et al., 2012), was used in order to delineate the experimental design, as well as to optimize the systems through the estimation of the statistical parameters.

2.5. Adsorption experiments

The adsorption of the dye TP was carried out in batches and according to the factorial design described. For each 5 mL dye solution at known concentrations and pH adjusted with 0.1 mol L^{-1} KOH solution or concentrated hydrochloric acid, predetermined quantities were put in 10 mL bottles. The mixture was kept under