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Research paper

Experimental design investigation for vermiculite modification: Intercalation reaction and application for dye removal

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ABSTRACT

With the aim to improve the anionic dye sorption capacity of vermiculite, ethylenediamine was employed to modify vermiculite under different conditions. In this study, a 2^4 factorial design was used for organovermiculite preparation to assess the influence of the temperature (303 and 323 K), ethylenediamine concentration (0.1 and 0.2 mol L^{-1}), reaction time (24 and 48 h) and acid activation of the clay mineral (leached and non-leached samples). The pristine and modified solids were characterized by CHN elemental analysis, infrared spectroscopy and X-ray diffraction. Principal component analysis and hierarchical cluster analysis were performed on the IR spectra to investigate the effect of parameter variation on the vermiculite modification. The reaction temperature and the acid activation of the vermiculite significantly influenced the vermiculite structural features. The optimized sample presented good adsorption capacity for Remazol Brilliant Blue RN, 11.02 mg g^{-1}. This study concluded that vermiculite modified with ethylenediamine behaved as a good sorbent to anionic dye.

1. Introduction

Clay minerals have great versatility regarding surface chemistry (Gómez-Romero and Sanchez, 2004). The physical and chemical properties of clay minerals depend on their structure, resulting in a specific surface area, ion exchange capacity and reactivity of the surface. The use of clay minerals in various fields, including ceramic industry, paper fabrication, catalytic supports (Chmielarz et al., 2012), adsorbents and ion exchangers (Zhang et al., 2010). Most of these applications involve natural products, without chemical alteration of the surface. However, the possibility of chemical modification is important for the improvement of the special properties and novel applications (Liang et al., 2013).

The growing interest in these inorganic backbones is because they are chemically active, low-cost and from abundant sources. Chemical modification has been used in a large variety of systems, most commonly for environmental remediation purposes, such as heavy metals adsorbents (Do Nascimento and Masini, 2014; Liang et al., 2013).

Vermiculite is formed by the hydrothermal alteration of mica, such as biotite and phlogopite (Mouzdahir et al., 2009). Vermiculite is widely used in agriculture and environmental applications (Duman and Tunç, 2008). The 2:1 layered structure consists of one octahedral sheet sandwiched between two opposing tetrahedral sheets. (Duman et al., 2015; Bailey et al., 1980). However, the isomorphic substitutions, either in the tetrahedral or octahedral sites for cations of comparable radii, cause residual negative charges that are neutralized by alkaline and alkaline earth cations (typically sodium, calcium and magnesium). Thus, the ions present in the interlayer space of vermiculite can be exchanged by other cationic ions. An important characteristic is the hydration of the cations of vermiculite resulting in ordering of water molecule layers (Folorunso et al., 2012).

Vermiculite is very abundant and much cheaper compared with other clays. This mineral clay has typical features, such as lamellar structure, high ion exchange capacity and known chemical composition, allowing interactions with organic substances (Carrado, 2004). In addition, vermiculite, having a porous structure, is a potential candidate as an adsorbent material for the removal of dyes from aqueous solutions (Duman et al., 2015). Although vermiculite is used as adsorbent, few studies have focused on vermiculite-reinforced polymer composites (Qian et al., 2011, Wang et al., 2013). To improve the compatibility between the clay mineral and polymer, the clay mineral surface can be made more organophilic by the exchange of the original interlayer cations by suitable organic ions, e.g., alkyl ammonium. Organically modified clay minerals with different properties can be prepared by varying the nature and quantity of alkyl ammonium. Most of these investigations have been done with smectites (Paiva et al., 2008).

Vermiculite can be modified in many ways, resulting in multifunctional materials in the class of inorganic-organic hybrid materials (Hashem et al., 2015; Jaber and Miehé-Brendlé, 2008; Oliveira et al., 2013; Wu et al., 2015). In this context, acid activation of vermiculite is an effective route to prepare porous solids with layered structures. In

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the acid attack, firstly the original exchangeable cations are exchanged by H_3O^+. The second step is the exit of ions from the octahedral and tetrahedral sheets without the leaching of silicon from the tetrahedral sheet (Steudel et al., 2009). These treatments lead to a permanent reduction of the global negative charge of the clay mineral layers (Rey-Perez-Caballero and Poncelet, 2000). Therefore, acid-activated solids have altered structural properties, and their applications can be improved. Acid-activated vermiculites were applied as precursors for clay-polymer nanocomposites, adsorbents (Hashem et al., 2015), catalysts (Chmielarz et al., 2012), catalytic supports (Jin and Dai, 2012) and luminescent species (Silva et al., 2014).

Modification of vermiculite depends on the application, and there are several factors, such as temperature, concentration, adsorbent dosage, pH, solvent and particle size, that have an influence and can be controlled to improve the material properties (Jiménez de Haro et al., 2004, 2005; Maqueda et al., 2007). In conventional methods to determine the influence of each of these factors, experiments are performed by systematically varying the studied factor while keeping the others constant. A suitable technique should be selected to reveal the possible interactions among variables with a minimum number of experiments. Factorial designs (Barros Neto et al., 2006) include the concept of sustainability, avoiding material waste and long reaction times, and they can be applied for simultaneously studying the effect of each process variable as well as interaction effects to find an optimal experimental condition. Furthermore, some of the results can be analyzed by multivariate methods (Massart et al., 1988) to find patterns, clusters and similarities among the samples. These statistical tools are rarely applied to materials science and are a promising way to optimize experimental conditions, providing enhanced properties, which increases the performance for the application.

No studies have been performed with modified vermiculite using a factorial design and chemometric tools. The present study investigates the influence of four variables on the incorporation of ethylenediamine in vermiculite in acid medium using an experimental design technique. A complete 2^4 factorial design was applied to investigate the most important factors affecting the intercalation reaction, i.e., temperature, ethylenediamine concentration, stirring time and vermiculite leaching. The infrared (IR) spectra obtained for the characterization of the modified solids were also evaluated by principal component analysis and hierarchical cluster analysis.

One of the requirements for enhanced designed materials is to demonstrate the solid performance concerning some viable application. Usually, these chemically modified surfaces are employed in adsorption processes for pollutant species, such as heavy metal ions, dyes and drugs (Zaitseva et al., 2013; Jing et al., 2013; Kamarudin et al., 2013).

Because the dye contamination of wastewater has dramatically increased and has become an environmental remediation issue, new adsorbents to remove toxic pollutants, such as dyes, has become an important topic. Considering that the adsorption capacity of natural vermiculite for anionic dyes is limited, in this study, the synthesis of modified vermiculite was optimized, and the modified sample was applied to the removal of the Remazol Brilliant Blue RN from aqueous solution.

2. Materials and methods

2.1. Starting material and chemicals

Vermiculite from Santa Luzia (Paraíba, Brazil) was used as the precursor material. Ethylenediamine was purchased from Aldrich, and nitric and hydrochloric acid were purchased from Vetec. For adsorption experiments, Remazol Brilliant Blue RN (RBB) dye was supplied by Dystar Company. Deionized water was used as the solvent and was obtained from an ultra-pure Milli-Q 18 MΩ cm^{-1} system. All chemicals and dye were used as received without further purification.

2.2. Vermiculite treatment

Acid activation was performed on pristine samples by adding 20.0 mL of 1.0 mol L^{-1} HNO_3 per gram of vermiculite. The solution was refluxed under mechanical stirring at 353 K for 2 h. After decantation the solid was washed with deionized water and dried at 333 K for 72 h.

2.3. Experimental design and multivariate analysis

Factorial designs are often used to optimize experimental conditions for a series of applications while performing a minimum number of experiments. In a two-level, full-factorial design with four factors, at least $2^4 = 16$ experiments must be executed (Barros Neto et al., 2006). The factors studied in this work are presented in Table 1; levels of each experimental factor are stated as plus and minus signs for high and low levels, respectively.

All possible combinations of the levels of the four factors are in Table 2 in columns two to five, the evaluated response for investigating the vermiculite intercalation reaction with protonated ethylenediamine (en^+) was the percentage of nitrogen (% N), shown in column seven. Table 2 also presents the percentages of carbon (% C), the C/N ratio and the calculated degree of functionalization (F).

The principal and interaction effects were calculated using

$$Effect = \overline{R}_+ - \overline{R}_- \quad (1)$$

where $\overline{R}_+$ and $\overline{R}_-$ represent the averages of the results with high (+) and low (−) levels, respectively (Ruiz et al., 2004). For the interaction effects, the signs were determined by multiplying the sign columns for the involved factors. Because replicates were not performed, the experimental error could not be directly calculated. The significance of the effects can be statistically tested using a cumulative normal probability plot (Bortoloti et al., 2005) or by considering the third and fourth interaction effects to be noise. In this last case, the standard error of one effect was calculated by the square root of the average of the sum of squares of the third and fourth interaction effects (Barros Neto et al., 2006).

Principal component analysis (PCA) and hierarchical cluster analysis (HCA) are the most common multivariate chemometric techniques used for data (Beebe et al., 1998). PCA reduces the dimensionality of large data sets by producing new linear combinations of the original variables while retaining the most significant information. PCA decomposes the matrix **X** (n samples and p variables) into a product of two matrices

$$\boldsymbol{X}_{nxp} = \boldsymbol{T}_{nxq}\boldsymbol{P}^t_{qxp} + \boldsymbol{E}_{nxp} \quad (2)$$

where $\boldsymbol{T}$ is the score matrix, $\boldsymbol{P}$ is a loading matrix and $\boldsymbol{E}$ is the residuals matrix. The number of principal components (PC) describing the major part of the variance is represented by q, and $\boldsymbol{P^t}$ is the transpose of matrix **P** (Soares et al., 2007).

In general, the results of PCA and HCA are complementary. The goal of HCA is to group similar objects into a single group, where objects in different groups are somewhat different from one another. HCA decomposes the dataset into several levels of nested clusters represented by a

Table 1
High and low levels of experimental factors of the 2^4 factorial design: concentration of ethylenediamine (C_{en}/mol L^{-1}), temperature (T/K), time (t/h) and leaching (L).

Factors	Levels	
	Low (−)	High (+)
C_{en} (mol L^{-1})	0.10	0.20
T (K)	303	323
t (h)	24	48
L	No	Yes