



Adsorption studies of etherdiamine onto modified sugarcane bagasses in aqueous solution



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ARTICLE INFO

Article history:

Received 12 February 2013
Received in revised form
13 November 2013
Accepted 20 November 2013
Available online 9 January 2014

Keywords:

Adsorption
Etherdiamine Flotigam 2835
Modified sugarcane bagasse
Iron ore flotation

ABSTRACT

In this study sugarcane bagasse was modified with succinic anhydride and EDTA dianhydride to obtain SCB 2 and EB adsorbents, respectively. These adsorbents were used to remove etherdiamine, which is used for iron ore flotation from single aqueous solutions. The removal and recovery of etherdiamine is important for environmental and economic reasons due to its toxicity and high cost. The results demonstrated that adsorption of etherdiamine by SCB 2 and EB was better fitted by a pseudo-second-order kinetic model than pseudo-first-order and Elovich models. Adsorption isotherms were better fitted by the Langmuir model rather than the Freundlich, Sips, and Temkin models. The maximum adsorption capacities (Q_{\max}) of SCB 2 and EB for etherdiamine adsorption were found to be 869.6 and 1203.5 mg/g, respectively. The calculated ΔG° values for adsorption of etherdiamine on SCB 2 (-22.70 kJ/mol) and EB (-19.10 kJ/mol) suggested that chemisorption is the main mechanism by which etherdiamine is removed from the aqueous solution for both adsorbents. The high Q_{\max} values showed that SCB 2 and EB are potential adsorbents for recovering the etherdiamine and treating effluents produced from iron ore flotation.

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1. Introduction

Brazil has the fifth largest reserve of iron ore in the world. With a high percentage of iron in iron ores, Brazil is among the largest producers and exporters of iron in the world (Alves, 2006). With the reduction in reserves of high-grade iron ore, concentration processes have become indispensable for mining companies that commercialize iron ore as a raw material to make steel (Filippov et al., 2010; Magriotis et al., 2010). Froth flotation is the most effective method from both the technological and economical points of view for iron ore beneficiation (Lima et al., 2005) and to upgrade the iron concentration (Filippov et al., 2010; Pearse, 2005). Although different flotation methods are available, reverse cationic flotation of quartz is by far the most widely used method to separate this major contaminant from iron ore (Araujo et al., 2005). Reverse cationic flotation of quartz is accomplished using fatty primary alkylamines partially neutralized with acetic acid, and basically consists of the selective separation of quartz particles from

iron oxides (Lima et al., 2005). For this purpose, commercial organic amine salts, known as etheramines, are commonly used (Araujo et al., 2005). These compounds may have one or two amine groups and the overall chemical structure of such organic compounds is: $[R-O-(CH_2)_3-NH-(CH_2)_3-NH_3]^+CH_3COO^-$ for etherdiamine and $[R-O-(CH_2)_3-NH_3]^+CH_3COO^-$ for etheramine (R = alkyl group with carbon number >10), respectively (Araujo et al., 2010).

The presence of an ether group in the etheramine chain also increases its solubility in water (Lima et al., 2005). In the flotation process, the fatty amine is added to the system and is adsorbed on the quartz surface, and both are removed from the system as an aqueous pulp. However, at the pH at which this process occurs (close to 10), both quartz (SiO_2) and hematite (Fe_2O_3) surfaces are positively charged, and therefore they can adsorb the amine despite its preferential attraction for quartz. In order to avoid competitive iron oxide flotation, starch is used as a depressing agent (Araujo et al., 2010).

Globally, iron ore processing consumes 15,000–20,000 tons of etheramine, representing approximately 85 million US dollars (Magriotis et al., 2010). Due to its toxicity to aquatic organisms, high chemical oxygen demand (COD) value, corrosive properties and

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high cost, the removal and the possible reuse of this compound is important. The adsorption of etheramine onto efficient and low cost supports enables water recycling and the recovery of amines from the effluent, which could result in a considerable reduction in operating costs (Magriotis et al., 2010). In addition, the adsorption process could also help to decrease the amount of toxic etheramines discharged without any treatment into the environment (Magriotis et al., 2010).

Among the various methods available for water treatment, adsorption has received much attention since it not only reduces environmental contamination but also allows for water recycling and chemical recovery, which increases the feasibility of the process. At the present moment, few studies in the literature have investigated the adsorption of etheramines (Magriotis et al., 2010; Safa and Bhatti, 2011; Teodoro and Leão, 2004), and in both studies, clays were used as the solid support. No study of etheramine recovery has been performed yet.

Sugarcane bagasse is a residue from the sugarcane crushing process. It is composed of lignin (20–25%), polyoses (25–30%), cellulose (40–50%); the minor components are extractives and ash (Caraschi et al., 1996). In the Brazilian scenario, the use of agricultural residues for novel applications is particularly attractive and a promising source of new materials, given that the investments made by local industries in recent years for the production of renewable fuels continue to grow. According to the Brazilian Ministry of Agriculture, the sugarcane harvest in the 2011/2012 season is expected to reach 571.4 million tons, which will generate about 142.9 million tons of bagasse and 116.6 million tons of straw (CONAB, 2011). The macromolecules present in sugarcane bagasse, through their hydroxyl groups, are able to chemically react to produce new materials with new properties (Navarro et al., 1996; Xiao et al., 2001). Various studies on the use of bagasse as adsorbent for the removal of various pollutants can be found in the literature (Crini, 2006; Gupta and Suhas, 2009; Gurgel and Gil, 2009; Ho et al., 2005; Karnitz et al., 2007; Kumar, 2006; Ngah and Hanafiah, 2008; Xing and Deng, 2009); however, at the present moment, none have investigated etheramine adsorption.

In our previous studies (Gurgel et al., 2008; Gusmao et al., 2012; Karnitz et al., 2009, 2010; Pereira et al., 2009; Pereira et al., 2010), sugarcane bagasse modified with succinic anhydride (SCB 2) and with EDTAD (EB) were used as adsorbent materials for heavy metal and cationic dye adsorption. Both adsorbent materials (SCB 2 and EB) present a negatively charged surface due to the presence of carboxylate groups that are released after modification with succinic and EDTAD anhydrides and treatment with sodium bicarbonate solution. These charges are able to interact with cationic species such as dyes and heavy metals among others. At pH 10, about 50% of etheramine is in the ionized form and 50% is in the non-ionized form (Leja, 1982). Thus, at pH levels lower than 10, etheramines are positively charged (protonated) and can interact with negatively charged solid supports as SCB 2 and EB.

In the present study, the removal of the etherdiamine Flotigam 2835 by adsorption from aqueous solution using SCB 2 and EB was extensively investigated with the aim of evaluating the possibility of applying SCB 2 and EB to the treatment of effluents containing etheramines from iron ore mining. SCB 2 and EB were chosen as the adsorbents due to their vast range of possible industrial applications including the treatment of effluents from textile and plating industries and from acid mine drainage. The adsorption studies were carried out using different contact times, pH values, and initial etherdiamine concentrations. The results were evaluated by different kinetic and adsorption models.

2. Materials and methods

2.1. Materials

Sugarcane bagasse was collected from a local alcohol and sugar plant in the city of Ouro Preto, Minas Gerais, Brazil. Succinic anhydride and pyridine were purchased from Vetec (Brazil). Pyridine was left under reflux overnight with NaOH and then distilled. *N,N*-Dimethylformamide (DMF) was purchased from Synth (Brazil) and distilled under reduced pressure before use. EDTA (disodium salt) and acetic anhydride were purchased from Synth (Brazil) and used without further purification. Etherdiamine Flotigam 2835 ($[R-O-(CH_2)_3-NH-(CH_2)_3-NH_3]^+CH_3COO^-$ with R = alkyl chain with carbon numbers of 12 (20%) and 13 (80%), respectively) was produced and distributed by the Clariant® company (São Paulo, SP, Brazil).

2.2. Sugarcane bagasse preparation

First, sugarcane bagasse was dried in sunlight. The bagasse stalks were manually broken to reduce their length and then dried in an oven at 90 °C for 24 h. After that, it was pulverized in a vibratory disc mill equipped with tungsten carbide. The powder was sifted in a four-sieve system composed of screens of 10 (1.68 mm), 60 (0.251 mm), 100 (0.152 mm) and 200 (0.075 mm) mesh. The fraction between 100 and 200 mesh was collected and washed at first with hot distilled water at 60–70 °C for 1 h to eliminate the residual sugars and then washed with 95% EtOH and dried at 90 °C in an oven. Finally, this fraction was washed in a Soxhlet apparatus with hexane-ethanol (1:1, v:v) for 4 h and then dried at 90 °C in an oven to remove the organic solvents and stored in a desiccator prior to use.

2.3. Preparation of SCB 2

SCB 2 was prepared and characterized according to the methodology described by Gurgel et al. (2008). Sugarcane bagasse (5 g), succinic anhydride (15 g), and anhydrous pyridine (50 mL) were added to a round-bottom flask equipped with a reflux condenser. The mixture was heated under pyridine reflux for 24 h. At the end of the succinylation reaction, modified bagasse was separated by filtration using a sintered glass funnel (porosity 3), washed with a solution of acetic acid in methylene chloride (1 mol/L), ethanol (95%), distilled water, saturated sodium bicarbonate solution, distilled water, and finally with acetone. SCB 2 was dried in an oven at 90 °C for 1 h.

2.4. Preparation of EB

EDTA dianhydride was prepared using the methodology described by Karnitz et al. (2009) using EDTA disodium salt and acetic anhydride. EDTA disodium (50.0 g) was dissolved in a 1000 mL beaker containing 500 mL of distilled water. Concentrated HCl was added drop by drop until the precipitation of H₄EDTA occurred. The precipitate was vacuum filtered and rinsed in 95% EtOH, diethyl ether and subsequently dried in an oven for 2 h at 105 °C and cooled in a desiccator prior to use. For the preparation of EDTA dianhydride, 18.0 g of H₄EDTA was suspended in 31 mL of anhydrous pyridine in a 250 mL round-bottom flask and 24 mL of acetic anhydride were added to the suspension. A reflux condenser was attached to the flask and the mixture was heated at 65 °C and kept under constant magnetic stirring for 24 h. After the reaction time, the solid (EDTA dianhydride) was vacuum filtered, rinsed in diethyl ether and stored in a desiccator under reduced pressure prior to use.

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