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Cadmium sorption by sodium and thiourea-modified zeolite-rich tuffs

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ABSTRACT

In the present investigation, two zeolite-rich tuffs from Guaymas and El Cajon (State of Sonora), which were conditioned with a sodium chloride solution and subsequently modified with a thiourea solution, were chosen to evaluate the removal of Cd from aqueous systems. The zeolitic materials were characterized by scanning electron microscopy and X-ray diffraction. The surface area was also determined. The experiments were performed in a batch system, and the influences of pH, contact time between phases, and the concentration of Cd in the solution on the adsorption by sodium or thiourea-modified zeolite-rich tuff were investigated. It was found that the efficiency of Cd ion removal from aqueous solutions is influenced by the pH of the aqueous systems. The Cd adsorption kinetic data were well fitted to a pseudo-second-order model in all cases. The Langmuir and Langmuir-Freundlich isotherms adequately described the Cd sorption behavior by the zeolite from El Cajon pretreated with NaCl and the zeolite from Guaymas modified with thiourea, respectively.

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Introduction

Wastewater streams represent a source of water that can certainly contribute to the supply for the growing demand of water worldwide. The pollutants discharged in wastewater affect human health and the environment (Papageorgiou et al., 2007). The maximum concentration of heavy metals that can be present to consider wastewater streams risk free to living organisms is established in different standards around the world. For Cd, the limit permitted is 0.5 mg/L according to EPA recommendations for wastewater, while WHO guidelines states 0.003 mg/L is the limit in drinking water. Mexican regulations established 1 mg/L as the limit of Cd in wastewater for instant

samples (NMX-002-SEMARNAT-, 1996). Different technologies are applied to treat wastewater to meet the necessary properties for reuse (Datta and Mishra, 2014). The type of wastewater treatment technology will depend on the type of pollutant in the water, the previous treatment the water has been through, if any, and in addition, the budget. Furthermore, it has been stated in the literature that the performance, sludge production, life period and operation of wastewater treatment technology will be taking into account (Gupta et al., 2012).

Sorption is an operation applicable to wastewater as a tertiary treatment. It is preferred over other treatments due to its relatively low cost and simple technique (Wang and Peng, 2010). To select an appropriate material for sorption processes,

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the porosity, specific surface area and number of available sites are compulsory parameters, because the sorption process involves either physical or chemical bonds (Rao et al., 2013).

Sorbents of common use can be expensive, such as activated carbon, chitosan derivatives, and synthetic polymers, among others (Zhao et al., 2011; Shemshadi et al., 2012). Materials naturally occurring in the landscape are preferred to synthetic materials, especially when they have high selectivity, good sorption capacity, and chemical stability (Jal et al., 2004).

Zeolites are very valuable microporous materials to sorption processes, not only for acting as molecular sieves but for their cationic exchange capacities, which let them take up heavy metal ions in aqueous systems (Motsi et al., 2009). To improve the external capacity of zeolites to remove anions or neutral chemical species from aqueous systems, some compounds have been used to modify them, such as hexadecyltrimethylammonium bromide (Salgado-Gómez et al., 2014) and cystamine dihydrochloride (Gebremedhin-Haile et al., 2003), to name a few. A common gap is to look for those chemical groups present in a compound that can bind with the chemical species of interest.

Some researches have been made related to the removal of Cd ions from aqueous media by natural zeolites (Cortés et al., 2009). However, these zeolitic materials were not modified to increase the heavy metal sorption capacity. Thiourea is an organic compound that has sulfide in its molecule and can participate in a chemical reaction upon chelating. An increase in the cadmium uptake by natural zeolites can be expected after being modified with thiourea. Therefore, the aim of the present work was to describe the Cd²⁺ adsorption behavior by a thiourea-modified natural zeolite while considering the effect of pH, the sorption kinetic and the sorption isotherms. The unmodified natural zeolite was also considered for comparison purposes.

1. Materials and methods

1.1. Materials

Two samples of zeolite-rich tuff were obtained from Sonora, México (denoted in the present work as ZSC for Cajon zeolite-rich tuff and ZSG for Guaymas zeolite-rich tuff). The zeolites were ground in an agate mortar and sieved, and the grain size chosen for the experiments was between 0.600 and 0.71 mm particle size (20 mesh).

1.2. Treatment with NaCl and thiourea

All chemicals used in this work were analytical grade reagents. Water type 1 (conductivity 0.06 μ S/cm, sartorius deionizer, model Arium 611 UF; SARTORIUS, Germany) was used for preparing all solutions and standards. To have the homoionic form of the zeolites, 100 g of zeolite-rich tuffs was in contact with 1200 mL of 0.3 mol NaCl solution for 24 hr under reflux. The zeolite-rich tuffs were separated by decantation. The material was washed with distilled water until Cl⁻ free, and a silver nitrate solution was used as the indicator. Finally, the zeolite-rich tuffs were dried in the oven at 40°C for 12 hr (Macedo-Miranda and Olguín, 2007). These natural zeolites were labeled as ZSCNa and ZSGNa (sodium-modified zeolite-rich tuff from Cajon and sodium-modified zeolite-rich

tuff from Guaymas, respectively). This pretreatment enables the zeolitic material to optimize its cation exchange since zeolites naturally provide an intra-crystalline environment to cations that have different exchange properties. The pretreatment improves their effective exchange capacities and consequently, it enhances their performance in ion exchange applications (Díaz-Nava et al., 2005). Pabalan and Bertetti (2001) reported that the selectivity in clinoptilolite is higher for potassium than for sodium. Therefore, the Na⁺ will exchange for other cations more easily.

ZSCNa and ZSGNa (50 g) were modified with a 1.8 mol solution of thiourea (700 mL) in a bath with oscillation at a constant temperature of 60°C for 16 days (Baker and Ghanem, 2009). After the contact time, the samples were dried in the oven at 40°C for 12 hr. These samples were labeled ZSCThio and ZSGThio (thiourea-modified zeolite-rich tuff from Cajon and thiourea-modified zeolite-rich tuff from Guaymas, respectively). Heavy metals have been proved to show high affinity for sulfur (Lagadic et al., 2001). Therefore, modification of zeolite-tuffs with thiourea could improve the removal of Cd²⁺ from aqueous media.

1.3. Characterization

1.3.1. Scanning electron microscopy

The equipment used to characterize the natural and modified zeolite-rich tuffs for scanning electron microscopy (SEM) analysis was a JSM-5900LV. The images were collected at 20 keV and 1500 magnified times using a JEOL JSM 5900 electron microscope (SEMTECH Solutions, USA), and the chemical compositions were determined with an OXFORD® electron dispersive spectroscopy (EDS) system (OXFORD, UK.). The samples were mounted directly on holders and fixed with graphite bands.

1.3.2. X-ray diffraction

The different zeolite-rich tuffs, natural and modified with thiourea, were characterized with X-ray diffraction (DRX) to verify the crystallinity of each sample and its mineral composition. Powder diffractograms of the zeolite samples were obtained with a SIEMENS D5000 diffractometer (SIEMENS, Germany) coupled to a copper-anode X-ray tube. The setup was established at 4° and 60° for angle 2 θ and step size of 0.05 sec, using a copper cathode for calibration.

1.3.3. Fourier transform infrared spectroscopy

FT-IR spectra of the material were obtained with a Varian 640-IR (Varian, USA) from 4000 to 500 cm⁻¹ to identify specific chemical groups in the natural and thiourea-modified zeolite-rich tuffs. Samples for analysis were prepared using the standard KBr pellets method.

1.3.4. Textural parameters

A BELSORP-28SA specific surface area analyzer (BELSORP, Japan) was used to determine the specific areas and total pore volume of the samples. The samples were pre-treated at 200°C for 4 hr. The model BJH was applied to the results.

1.3.5. Nitrogen, carbon, hydrogen and sulfur elemental analysis

Carbon, hydrogen, nitrogen and sulfur determinations were performed in an Organic Elemental Analyzer Flash 2000, which has a FPD1112 flame detector (Thermo Electron

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