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Competitive adsorption of dyes and heavy metals on zeolitic structures

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ABSTRACT

The adsorption of Acid blue 25, basic blue 9, basic violet 3, Pb^{2+}, Ni^{2+}, Zn^{2+} and Cd^{2+} ions has been studied in single and dye–metal binary solutions using two mineral materials: Clinoptilolite (CL) and ER (Erionite). These zeolites were characterized by FT-IR spectroscopy; potentiometric titration and nitrogen adsorption isotherms at 77 K to obtain their textural parameters. Results indicated that ER has an acidic character and a high specific surface (401 $m^2\ g^{-1}$) in contrast with the zeolite CL (21 $m^2\ g^{-1}$). Surprisingly, the removal of dyes was very similar for the two zeolites and they showed a considerable selectivity by the basic dyes in comparison with the acid dyes. In the case of heavy metals, ER was more effective in the adsorption process showing a selectivity of: $Pb^{2+} > Ni^{2+} > Zn^{2+} > Cd^{2+}$. In the multicomponent adsorption experiments an antagonistic effect was observed in the removal of basic dyes and heavy metals. Particularly, the adsorbed amount of basic violet 3 decreased more significantly when the heavy metals are presents in contrast with the basic blue 9.

1. Introduction

The water pollution caused by organic and inorganic compounds is a world problem originated by natural or anthropogenic sources. Particularly, the wastewaters produced by metal plating facilities, production of paints and pigments, ammunition, ceramic and glass industries contain heavy metals. According to the list of priority pollutants of the US Environmental Protection Agency (EPA), arsenic, chromium, cobalt, nickel, copper, zinc, silver, cadmium, mercury, titanium, selenium and lead represent a serious problem for the human health because they are not biodegradable and tend to accumulate in living organisms causing several diseases that affect the kidney, nervous, hematopoietic and gastrointestinal systems of humans (Hsu and Guo, 2002; Argun and Dursum, 2008). Additionally, in the wastewater of paints and pigments industries, heavy metals are also present with dyes and, considering that some dyes are toxic, no degradable, stable and even carcinogenic (Jain et al., 2010), the treatment of these wastewaters is very difficult and mostly ineffective when using traditional purification processes.

Nowadays, some treatment processes are used in the removal of dyes and heavy metals from water including ion exchange, precipitation, phytoextraction, ultrafiltration, reverse osmosis and electrodialysis. However, adsorption is preferred for the removal of these pollutants due to easy handling and removal performance. On the other hand, the economy and efficacy of the adsorption process are limited by the physicochemical characteristics and the cost of the adsorbent. In this context, several works have reported the adsorption of dyes and heavy metals in monocomponent solutions using low-cost adsorbents of inorganic origin such as: clays (Gupta and Bhattacharyya, 2005), sepiolite (Bingol et al., 2010), egg shell (Arami et al., 2006), fly ash (Lin et al., 2008), sandstone (Atun et al., 2009), rice husk ash (Mane et al., 2007), zeolites (Turan et al., 2005), shells of lentil, wheat and rice (Aydin et al., 2008), among others. Zeolites are highly porous aluminosilicates with different cavity structures that make them attractive adsorbents. Their structures consist of a three dimensional framework, having a negatively charged lattice. The negative charge is balanced by cations which would be eventually exchangeable with certain type of cations present in solution (Qiu et al., 2009). More than 40 natural species of zeolites have been reported and particularly in Mexico the following minerals have been already identified: analcime, clinoptilolite, chabazite, scolecite, stilbite, erionite, heulandite and mordenite (Teutli-Sequeira et al., 2009). Specifically, clinoptilolite is the most abundant natural zeolite and its tubular morphology shows an open reticular structure that would ease the access of different molecules, including pollutants, to the inner pore structure. This property has been exploited for wastewater treatment and some studies have

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already reported the application of clinoptilolite as adsorbent of several dyes, such as Amino Black 10B, Safranin T, Everzol Black, Everzol Red, Everzol Yellow, Methylene Blue, Rhodamine B and Toluidine Blue O (Qiu et al., 2009; Armağan et al., 2004; Wang and Zhu, 2006; Alpat et al., 2008). Also, clinoptilolite or chitosan/clinoptilolite composites have been used as adsorbent of heavy metals including Pb^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Cr^{3+}, Mn^{2+} and Zn^{2+} ions (Qiu et al., 2009; Dinu and Dragan, 2010; Wang and Ariyanto, 2007; Kosobucki et al., 2008; Inglezakis and Loizidou, 2007; Motsi et al., 2009; Kocaoba et al., 2007). However, the simultaneous adsorption of dyes and heavy metals in mixtures using zeolites as adsorbents has been scarcely studied and, to the best of our knowledge, only one work has reported the competitive adsorption of malachite green and Pb^{2+} ions on a natural zeolite (Wang and Ariyanto, 2007). Herein, it is convenient to remark that both heavy metals and dyes may be present simultaneously in real effluents of industrial activities such as paper manufacturing and automobile production. In addition, the improper handling and management of effluents of different industries can generate multicomponent solutions of these priority water pollutants due to the mixture of several effluents containing these types of pollutants (Körbahti et al., 2011). For this reason the purpose of this work is to study the adsorption of dyes and heavy metals in single and binary solutions (i.e., competitive conditions) using two species of Mexican zeolites. Results obtained have been related to the physicochemical characteristics of these zeolites, specifically their composition and textural parameters.

2. Materials and methods

2.1. Zeolites

Two Mexican natural zeolites obtained from the states of San Luis Potosí and Sonora were used in the present work. The zeolite from the specie Clinoptilolite was denominated CL and the Erionite as ER. These zeolites were crushed, grounded and passed through 30 and 40 mesh sieves. The two materials were thoroughly washed with deionized water until constant pH was attained. These adsorbents were dried in an oven at 110 °C for 24 h. The zeolites were characterized and the presence of bulk functional groups was determined at room temperature using a Nicolet-8700 FT-IR spectrometer (Thermo Electron Co.), while the acidity and basicity were determined by potentiometric titration according to the methodology reported in (Faria et al., 2004). A pH meter Oakton was employed during continuous deaeration with nitrogen. The textural parameters were calculated from the adsorption isotherms of nitrogen at 77 K measured in an automated adsorption apparatus (Quantachrome/Autosorb-1). Also the zeolites were analyzed by X-ray diffraction. Diffraction patterns of zeolites were recorded in a Bruker D8 Advance diffractometer equipped with a Cu K_{α} X-ray source operated at 40 kV and 40 mA. A single Göbel mirror configuration was used to monochromatise and focus the x-rays on the sample, attaining highly efficient parallel beam geometry. Diffraction data were collected by step scanning with a step size of 0.02° 2θ and a scan step time of 5 s.

2.2. Reagents

The dyes selected for this study were commercial products from Aldrich with the following name and color index (C.I.) number: acid blue 25 (C.I. 62055), methylene blue or basic blue 9 (C.I. 52015) and basic violet 3 (C.I. 42555); they were used without any additional purification and their structure, code and dimensions are shown in Table 1. The following nomenclature will be used henceforth: AB25 for acid blue 25, BB9 for basic blue 9 and BV3 for basic violet 3. Nitrate of lead, zinc, cadmium and nickel, with purity of 99.3, 100, 99.6 and 99.9%, respectively from J.T. Baker and Aldrich were used in the preparation of the heavy metal solutions. Standards of HCl and NaOH 1 M (Aldrich) were used for the titration analysis.

2.3. Adsorption tests

2.3.1. Adsorption isotherms of single pollutants

Equilibrium adsorption studies were carried out to evaluate the maximum capacity of the CL and ER as adsorbents of dyes and heavy metals in aqueous solutions using batch contact adsorption mode at 30 °C and pH 5. It is convenient to remark that this pH condition has been used for adsorption experiments to avoid the metal precipitation caused by hydrolysis, which occurs at pH > 6. This operating condition also corresponds to the maximum adsorbent performance for the removal of heavy metals (see Fig. 1 of supplementary information). The experiments were performed in polycarbonate cylindrical cells with a lid containing suspensions of 0.02 g of adsorbent in 10 mL of aqueous solution of dyes or heavy metals. Adsorption reached equilibrium after 72 h, according to results of preliminary kinetic experiments (see Fig. 2 of supplementary information), and the solution was separated from the adsorbent by decantation. Finally, this solution was analyzed using an atomic absorption spectrophotometer (Perkin Elmer AAnalyst 100) to determine the residual heavy metal concentration, whereas the equilibrium concentration of dyes was determined with a UV–Vis HACH DR 5000 spectrophotometer.

At equilibrium, the adsorbed amount of dyes and heavy metals per unit mass of adsorbent (q_e, mg/g) was determined according to the following mass balance:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where V is the liquid volume (L), C_o is the initial concentration in the solution (mg/L), C_e is the equilibrium concentration (mg/L), and W is the amount of the adsorbent sample on a dry basis (g), respectively. Each experiment was carried out at least twice to check reproducibility of the results and average results are reported. Adsorbent-free blanks were used as control. Overall, the reproducibility of all experiments was high and we have estimated a maximum error of 5% between the replicates of adsorption experiments.

2.3.2. Adsorption experiments in dye–metal binary mixtures

The simultaneous adsorption of binary mixtures of dyes and heavy metals was also studied under similar experimental conditions to those used for obtaining the adsorption isotherms of single pollutants. Note that industrial effluents may contain simultaneously both dyes and heavy metals at pH 5. In this case, the following mixtures were analyzed: Pb^{2+} – BB9, Pb^{2+} – BV3, Ni^{2+} – BB9, Ni^{2+} – BV3, Cd^{2+} – BB9, Cd^{2+} – BV3, Zn^{2+} – BB9 and Zn^{2+} – BV3. In these experiments, the initial concentration of both heavy metals and dyes was 2 mM.

3. Results and discussion

3.1. Characterization of natural zeolites

Fig. 1 shows the XRD patterns of the natural zeolites under consideration. The diffraction pattern of the CL sample matches that of a Na-clinoptilolite. Additional reflections have been assigned to quartz, feldspars and montmorillonite impurities. In the case of