

Adsorption of zinc from aqueous solutions to bentonite

Abidin Kaya^{a,b,*}, Ali Hakan Ören^b

^a URS Corporation, 615 Piikoi Street, 9th Floor, Honolulu, HI 96814-3141, USA

^b Dokuz Eylul University, Civil Engineering Department, Kaynaklar Yerleskesi, 35160 Buca-Izmir, Turkey

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Abstract

The adsorptive properties of natural and Na-enriched bentonite in zinc rich aqueous environment have been studied. The results show that adsorption behavior of both bentonites was strongly depending on the pH. At low pH values, the mechanisms that govern the adsorption behavior of bentonites are dissolution of crystal structure and competition of the metal ions with the H⁺. Between pH 4 and 7, the basic mechanism is an ion exchange process. The alkaline and alkaline earth metals located in the exchangeable sites of bentonites are replaced with Zn²⁺ cations present in the aqueous solution. At higher pH values (i.e. pH 8), formation of zinc hydroxyl species may result either participation to the adsorption or precipitation onto the bentonites. Therefore, a rapid increase in the equilibrium removal of zinc was obtained above pH 7. Increase in the initial metal ion concentration led to the increase in equilibrium adsorption to a certain degree; then, a plateau was obtained at higher concentrations. The rate of zinc removal depends also on the solid concentration of the suspension. Reducing the slurry concentration allows particles to get in the more dispersed form, resulting higher available sorption sites for zinc. As a result, the adsorption performance of Na-enriched bentonite is better than the natural bentonite in all physical and chemical changes. The data were fitted both Langmuir and Freundlich isotherms.

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1. Introduction

Releasing industrial wastewaters and flooding of ore mines into the environment results in contamination of soils and groundwater. Moreover, many inorganic and organic substances that may cause health problems can be detected in agricultural products as a result of contamination transport and pesticide usage. The remediation technologies used for clean up processes of polluted areas are time consuming and expensive. Despite their high cost, clay-based barriers are built up at the waste disposal areas to protect the migration of hazardous contaminants through the environment. Hence, plumes generated by the leachates are capped and immobilized into a clay liner.

The natural materials widely used in liner applications are (i) clays and (ii) bentonite/sand mixtures. The suitable compaction of liner material reduces the permeability and strengthens the barrier system. The utilization of clays as a liner material has been applied for the last few decades [1–4]. In addition, Kleppe and Olson [5] and Kenney et al. [6] proposed the bentonite/sand mixture as an alternative material to the clay liners. Recent studies showed that bentonite/zeolite mixtures could be used in a barrier system as well [7,8].

On account of higher surface area and cation exchange capacity, bentonite (mainly montmorillonite) is the most preferable clay mineral for barrier applications. Bentonite is a 2:1 mineral with one octahedral sheet and two silica sheets, which forms a layer. Layers are held together by van der Waals forces. Because of these weak forces and some charge deficiencies in the structure, water can easily penetrate between layers and cations balance the deficiencies [9].

Since it is an important constituent in a barrier system, the physical and chemical performance of bentonite should

* Corresponding author. Tel.: +1 808 593 1116; fax: +1 808 593 1198.

E-mail addresses: Abidin.Kaya@urscorp.com (A. Kaya), ali.oren@deu.edu.tr (A.H. Ören).

Table 1
Mineralogical compositions of bentonites with their specific surface area and cation exchange capacity values

| Materials | SSA (EGME) (m ² /g) | CEC (meq/100 g) | Mineralogical compositions |
|-----------------------|--------------------------------|-----------------|---|
| Natural bentonite | 393.44 | 132.33 | Montmorillonite, illite, feldspar, quartz |
| Na-enriched bentonite | 441.96 | 67.11 | Montmorillonite, illite, carbonate, feldspar, kaolinite |

be known before using it as a liner material. For evaluating its behavior against chemical attack, bentonite attracted the researcher's concern for a long time and has been studied extensively. Most of these studies considered the adsorption characteristics of bentonite for some toxic elements. It is well documented that bentonite is an efficient adsorbent for some heavy metals, especially for lead [10,11], copper [12], cadmium [10,12,13] and zinc [14]. In addition to bentonite's great tendency for adsorbing heavy metals, it is also effective for adsorbing the phenols and related compounds from the wastewaters [15–17].

Detailed adsorption studies for bentonite were given in the literature for some heavy metals, i.e. lead, copper and nickel [10–13]. However, studies of its behavior in the presence of zinc ions under different pH conditions, slurry and heavy metal concentrations are very scarce. The main purpose of this study is to fill the gap for zinc uptake for bentonite under different physical and chemical conditions. For this reason, a detailed study was conducted in order to determine the influence of initial pH, initial metal ion concentration and slurry concentration on adsorption characteristics of natural and Na-enriched bentonites. Langmuir and Freundlich isotherms were also compared with the experimental data.

2. Materials and methods

2.1. Materials

The natural and commercially available Na-enriched bentonites were obtained from Süd-Chemie Co., Balıkesir, Turkey. Bentonites were in the clod sized forms when first received. Later, they were powdered in a mortar and sieved from no. 200 (75 μm) sieve to obtain finer grains. Powdered bentonites were dried for 1 week in an oven at 60 °C before the experiments. The mineralogical and chemical compositions of the materials were determined by X-ray diffractometer (XRD) and inductively coupled plasma (ICP). The cation exchange capacity and specific surface area were obtained by the Na-method [18] and ethylene glycol monoethyl ether (EGME) method [19]. The results of the mineralogical and chemical compositions of the bentonites are presented in Tables 1 and 2, respectively.

Table 2
Chemical compositions of materials

| Materials | SiO ₂ (%) | Al ₂ O ₃ (%) | Fe ₂ O ₃ (%) | MgO (%) | CaO (%) | Na ₂ O (%) | K ₂ O (%) |
|-----------------------|----------------------|------------------------------------|------------------------------------|---------|---------|-----------------------|----------------------|
| Natural bentonite | 54.30 | 19.54 | 1.25 | 4.13 | 2.09 | 0.13 | 0.73 |
| Na-enriched bentonite | 47.28 | 10.97 | 1.28 | 6.81 | 7.90 | 2.81 | 0.22 |

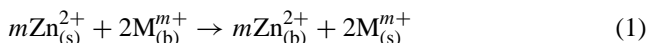
2.2. Methods

Puls and Bohn [20] stated that zinc adsorption onto the calcium saturated bentonite was higher for Cl⁻ solution than that of ClO₄⁻ and SO₄²⁻ because the formation of limited zinc–chloro complexes were due to the incompatibility of the harder Zn²⁺ with the soft Cl⁻. Therefore, ZnCl₂ solution was used in the batch experiments. A volume of 100 cm³ of zinc solutions with various amounts of bentonites was placed in an Erlenmeyer flask to commence the experiments. The initial metal ion concentration used in the tests ranged between 12.5 and 200 mg/l for both clays. Since it was intended to obtain the slurry concentrations in the range of 1.0–10.0 g/l, bentonites were weighed between 0.1 and 1 g. The batch adsorption experiments were also conducted at different pH levels (i.e. pH 3–8) and solution pHs were adjusted by adding diluted NaOH and HCl solutions. NaOH and HCl were prepared in 0.01N stock solutions and diluted with water in another flask and then, added to the solutions to arrange the pH. The pHs of the solutions were adjusted before adding the bentonites. This is because bentonite had a tendency to increase the solution pH after adding into the solution. The agitation speed was constant and fit 100 rpm during the test. The experiments were terminated at a contact time of 2 days. Most of the zinc ions were adsorbed by the bentonites in the first 6 h. After centrifugation, the supernatant liquid was used in UNICAM atomic adsorption spectrophotometry in order to determine the equilibrium zinc concentration in the solution.

3. Results and discussions

3.1. Determining the amount of adsorbed zinc ions, q_e

The interaction between the zinc ion and bentonite can be given by the equilibrium:



where m is the exchangeable cation valence M (Na, K, Ca, Mg) and subscripts (s) and (b) denote solution and bentonite phases, respectively.

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