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Interaction of metal ions with clays: I. A case study with Pb(II)

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Abstract

Pb(II) adsorption was studied under different conditions (pH, time, metal ion concentration, clay amount, temperature) on kaolinite, montmorillonite, and their poly(hydroxo)zirconium (ZrO–kaolinite, ZrO–montmorillonite) and tetrabutylammonium (TBA–kaolinite, TBA–montmorillonite) derivatives. All samples were calcined (ZrO-derivatives at 773 K, TBA-derivatives at 973 K) before using as adsorbents. The data were interpreted assuming first- and second-order kinetics. The rate constants including the pore diffusion rate constant are reported. The adsorption data could be fitted with Freundlich and Langmuir isotherms, and the coefficients indicated favorable adsorption of Pb(II) on the clays. Determination of the thermodynamic parameters, ΔH, ΔS, and ΔG showed the adsorption to be exothermic accompanied by decrease in entropy and Gibbs energy.

Keywords: Kaolinite; Montmorillonite; Poly(hydroxo)zirconium clay; Tetrabutyl-ammonium clay; Adsorption

1. Introduction

Ion exchange and adsorption mechanisms of clays and clay minerals are utilized to remove different types of pollutants. For example, china clay removes cadmium from hazardous waste (Sarma et al., 1991) and natural bentonite is used for removal of zinc from aqueous solution (Mellah and Chegrouche, 1997). Yavuz et al. (2003) reported the use of raw kaolin for adsorption of Mn(II), Co(II), Ni(II) and Cu(II) from aqueous solution. A few studies have also been reported for sorption of heavy metal cations on modified clays (Lin and Juang, 2002; Alvarez-Ayuso and Garcia-Sanchez, 2003).

Pb(II) has become one of the major environmental pollutants (Rawat et al., 1991) due to its presence in automobile fuel and subsequent emission into the atmosphere in the exhaust gases. It enters the water environment through effluents from lead smelters, battery manufacturers, paper and pulp industries, boat and ship fuels and ammunition industries. Many methods have been suggested for its removal and one of the favorite methods is ion exchange and adsorption. The present study investigates the efficiency of two important clay minerals, kaolinite and montmorillonite, and their poly(hydroxo)zirconium

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and tetrabutylammonium derivatives for removal of Pb(II) in aqueous medium.

2. Experimental

2.1. Reagents

Reagent grade chemicals, $ZrOCl_2$ $8H_2O$ (Loba Chemie, Mumbai) and tetrabutylammonium bromide, $(C_4H_9)_4N^+Br^-$ (CDH, Mumbai) were used. A stock solution of Pb(II) was prepared by dissolving $Pb(NO_3)_2$ (Glaxo, Mumbai) in twice distilled water.

2.2. Preparation of the adsorbents

Kaolinite, Kga-1b (C1) and montmorillonite, Swy-2 (C2) were obtained from the University of Missouri-Columbia, Source clay Minerals Repository, USA. Poly(hydroxy)zirconium modified kaolinite (C3) and montmorillonite (C4) were prepared by standard procedure (Burch and Warburton, 1986).

For preparing the ZrO-clays, a suspension was made by mixing 4 g of the clay with 100 ml of double distilled water followed by slow addition of 100 ml of 0.1 mol dm^{-3} solution of $ZrOCl_2$ under constant stirring. Stirring was continued for 24 h after which the suspension was filtered and the clay was washed with water till it was free of Cl^- ion. The clay was dried in an air oven at 373 K for 30 min.

For preparing TBA-clays (Mortland et al., 1986), the clays were Na^+-saturated by stirring 10 g of the sample with 1 l of 1 M NaCl solutions for 12 h and then allowed to settle. The supernatant solution was discarded and the process was repeated with fresh 1 M NaCl solutions. This was repeated twice. The clay was separated by centrifugation, washed with water several times to make Cl^- free. The Na^+-saturated clay was then mixed with water to obtain 700 ml, which was stirred for 16 h with a 300 ml aqueous solution containing TBA–Br 5 times the CEC of the clay. The mixture was centrifuged and washed with water several times till it was free of Br^-. The resulting organoclay was dried in air at 373 K for 30 min.

All the clays were calcined before using them as adsorbents (kaolinite, montmorillonite and the ZrO-derivatives at 773 K and the TBA-derivatives at 973 K for 10 h, the higher temperature in case of the TBA-derivatives was necessary to get rid of the organic template).

2.3. XRD measurement

XRD measurements were done with Phillips Analytical X-ray spectrometer (PW 1710) using CuKα.

2.4. Adsorption procedure

Pre-weighted samples of the adsorbent and given volumes of Pb(II) solution were taken in 100 ml conical flasks and the mixtures were agitated in a thermostated water bath for a constant time. The mixtures were then centrifuged (Remi R 24) and Pb(II) remaining in the supernatant was determined with atomic absorption spectroscopy (Varian SpectrAA 220). The experiments were carried out by varying the amount of the adsorbent, initial concentration of Pb(II), pH of the solution, temperature, and agitation time.

2.5. Theoretical basis

The adsorption process is normally described by the (Gharaibeh et al., 1998) Freundlich isotherm:

$$q_e = K_f C_e^n \quad (1)$$

where q_e is the amount adsorbed per unit mass of the adsorbent, C_e is the equilibrium concentration of the adsorbate. K_f and n are the Freundlich coefficients. In the Langmuir isotherm

$$C_e/q_e = 1/(bq_m) + (1/q_m)C_e \quad (2)$$

where b and q_m are the Langmuir coefficients representing the adsorption equilibrium constant and the monolayer capacity.

The linear Freundlich and Langmuir plots are obtained by plotting (i) log q_e vs. log C_e and (ii) C_e/q_e vs. C_e, respectively, from which the adsorption coefficients are evaluated.

A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L (known as the separation factor), which is considered as a more reliable indicator of