Research paper

Uptake of lead by Na-exchanged and Al-pillared bentonite in the presence of organic acids with different functional groups

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ARTICLE INFO

ABSTRACT

This study investigated the uptake of lead (Pb) ions by Na-rich bentonite (Na-bentonite) and Al-pillared bentonite (Al-bentonite) in the presence or absence of organic acids containing different functional groups. Na-bentonite was an effective adsorbent for Pb^{2+} ions. The element was taken up by the mineral through ion exchange mechanism; and the formation of a lead carbonate hydroxide (hydrocerussite) also occurred. Al-bentonite adsorbed a smaller amount of Pb than Na-bentonite. XRD data indicated that the totality of clay interlayers was occupied by the pillaring agent that led to decrease in Pb uptake.

The amount of Pb taken up by Na-bentonite decreased with increasing concentration of citric acid both when Pb and organic acid were added together as a mixture, and when citric acid was added 2 h before the metal ions. Possible reasons for this were the formation of Pb-citrate complexes which had less affinity to Na-bentonite, and also hydrocerussite dissolution at acidic pH. Citric acid, however, did not change Pb uptake by Al-bentonite. Addition of lysine together with Pb did not have any effect on Pb uptake by Na-bentonite and Al-bentonite, which indicated occupation of different adsorption sites by Pb and lysine compared to citrate. However, lysine addition at 1:1 ratio 2 h before Pb decreased the metal uptake, which again may be explained by the effect of lysine in hydrocerussite dissolution. Uptake of Pb in the presence of lysine was also higher when using Na-bentonite compared to Al-bentonite.

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1. Introduction

Adsorption/desorption of trace elements on clay minerals is of great importance in controlling their bioavailability, leaching and toxicity in the soil environment. These processes are influenced by many factors such as nature of the clay adsorbents, pH, presence and concentration of organic and inorganic ligands including humic and fulvic acids, root exudates, microbial metabolites and nutrient elements (Violante et al., 2010).

Large specific surface area, chemical and mechanical stability, layered structure, and high cation exchange capacities (CEC) make clays exceedingly effective in adsorbing a wide range of environmental pollutants. The edges and faces of clay particles can accumulate cationic, anionic, non-ionic and polar contaminants from the liquid phase. They accumulate on clay surfaces leading to their immobilisation through the process of ion exchange, coordination, electrostatic attraction or ion–dipole interaction (Bhattacharyya and Gupta, 2008). Pollutants can also be held through H-bonding, van der Waals interactions and hydrophobic bonding (Bhattacharyya and Gupta, 2008). Both Brönsted- and Lewis-type acidity in clay minerals (Tanabe, 1981) can also boost the adsorption capacity of contaminants.

However, modern technologies require novel adsorbents having increased uptake capacity and high selectivity to the adsorbate. Conventional methods of modifying clay adsorbents by placing chemical functional groups on the surface cannot always achieve a fundamental change in the natural clay properties (Dudina, 2013). For example, clay minerals` pore structure remained unchanged or diminished in many conventional modifications (Sarkar et al., 2011a). The chemical nature of the surface is also expected to be changed by loading a modifying agent in quantities not exceeding 1–5% by weight of the adsorbent (Dudina, 2013).

Many attempts were made to improve the quality and characteristics of clay adsorbents by using different techniques. One of such techniques is known as intercalation and pillaring. Intercalation is the insertion of a guest species into the interlayer region of a clay mineral with preservation of the layered structure (Schoonheydt et al., 1999).

The material obtained is called intercalated or pillared clay. Microporous clay products pillared with metal oxide clusters were obtained by exchanging the interlayer cations of smectitic clay with bulky inorganic cations followed by calcination (Mishra, 2010). This technique not only tailored the micropore structure of the clay, but might also induce intrinsic catalytic activity according to the nature of the pillar (Dudina, 2013). As a result, pillared-clay derivatives have attracted widespread interest as a novel microporous solid that can serve as an effective adsorbent for different pollutants (Bhattacharyya and Gupta, 2008; Mishra, 2010; Gerasin et al., 2013).

Studies previously investigated trace metal uptake by clay minerals pillared with inorganic cations in binary adsorbent–adsorbate systems (Jobstmann and Singh, 2001; Gupta and Bhattacharyya, 2005; Zeng and Jiang, 2005; Bhattacharyya and Gupta, 2006). However, the interactions of metals with pillared-clays in the environment might differ from that predicted by laboratory experiments because of the presence of a variety of inorganic and especially organic ions in natural solutions. Clays would interact with many organic compounds to form complexes of varying stabilities and properties (Kowalska et al., 1994). Clay–organic interactions were multivariable reactions involving the silicate layers, the inorganic cations, water and the organic molecules. The chemical affinity between the organic compound and the solid depends on the structure (molecular weight, chain length, etc.) of the organic molecule, functional groups present in the organic molecule, such as hydrophobic groups (–C–C–C–), positively charged groups (–NH_3^+), negatively charged groups (–COO^-, phenolate, –SO_3^-), electronegative groups (–C=O, –C–O–C–, –OH), pi bonds, (–C–C–, aromatic rings), configuration of the organic molecule and the aqueous phase present (Kowalska et al., 1994). Moreover, organic ligands (e.g., organic acids) able to form different salts and complexes with trace elements could alter the mechanisms and extent of interactions with the clay materials (Tomba'cz et al., 1998). Consequently, investigating heavy metals uptake by pillared-clays in the presence of organic acids containing different functional groups has great theoretical and practical interests.

The objectives of this work are to study (i) the adsorption of Pb on Na-exchanged and Al-pillared bentonite in the absence or presence of low molecular weight organic acids containing different functional groups: citric acid (Cit) and lysine (Lys); (ii) the effect of organic acid concentrations on the adsorption of Pb; and (iii) the influence of sequence of Pb and organic substance addition on the uptake phenomenon.

2. Materials and methods

2.1. Adsorbent preparation

A sample of bentonite (QB) originating in Queensland (AMCOL Australia Pty Ltd), Australia was used in this study. The CEC of this clay determined by an ammonia electrode method (Borden and Giese, 2001) was 66.7 cmol (p$^+$) kg^{-1}. The sample contained 85.3% clay, 3.5% silt and 11.2% fine sand.

All reagents were prepared in ultrapure Milli-Q water (18.2 Ω). Homo-ionic Na-bentonite was prepared by exchanging finely ground (<75 μm) QB with 0.2 M sodium chloride (NaCl) solutions (1:50 w/v) in two consecutive treatments; a 6 h agitation followed by another for 18 h with a fresh NaCl solution. The mineral was then washed several times with deionised water until a negative test for chloride was obtained using silver nitrate (AgNO$_3$) solution. Solid phase was separated from the suspension by centrifuging at 15,000 rpm for 15 min, dried at 60 °C and gently ground in an agate mortar.

The pillaring solution was prepared by adding 0.5 M sodium hydroxide (NaOH) drop wise to 0.2 M AlCl$_3$·6H$_2$0 with vigorous stirring until an OH:A1 ratio of 2.4 was achieved. The intercalated Al-polyhydroxo cation is similar to the ε-Keggin molecule [A1$_{13}$O$_4$(OH)$_{24}$(H$_2$O)$_{12}$]$^{7+}$ (Al$_{13}$ Kε) (Vaughan and Lussier, 1980). At this hydrolysis ratio, A1$_{13}$ Kε is the major species in the solution. At

OH:A1 ratios >2.5, Al$_{13}$ Kε tends to aggregate to a larger polymer (Furrer et al., 1992). To accelerate the formation of Al$_{13}$ Kε, the solution was aged for 3 h at 90 °C (Gil and Montes, 1994), and then held overnight at room temperature.

The pillaring solution was slowly added to a QB suspension (0.5% w/v) under vigorous stirring until Al-loading 20 mol kg^{-1} was achieved. The final suspension was aged overnight at room temperature. Afterwards, the solid was separated by centrifugation and washed with deionised water until the supernatant was chloride-free. The product was dried at 60 °C in a hot-air oven and gently ground in an agate mortar. The product was then calcined in a furnace for 5 h at 400 °C (Gil and Montes, 1994; Matthes et al., 1999).

2.2. Adsorption isotherms

All adsorption experiments were carried out in triplicates. In 50 mL conical flasks, Na- or Al-bentonite (0.2 g) was equilibrated with different amount of 2 mM lead nitrate (Pb(NO$_3$)$_2$) solution. Using 0.02 M potassium nitrate (KNO$_3$) final volume of the experimental solutions was adjusted to 25 mL with concentration of Pb^{2+} 50, 100, 200, 400, 800 and 1200 mmol kg^{-1} of solid material, and pH 5 was adjusted. The suspensions were gently agitated on an end-over-end shaker at 23 °C for 6 h. Preliminary experiments confirmed that equilibrium was reached in 4 h. Each suspension was adjusted to pH 5 by adding either 0.01 M HNO$_3$ or KOH, once immediately after adding the adsorbents and again 3 h after the equilibration started. Clear supernatant was then collected by centrifugation followed by filtering through a 0.2 μm syringe filter and Pb concentration in the filtrate was determined by an Inductively Coupled Plasma Optical Emission Spectrometer (ICP OES) (Optima-5300 V, Perkin-Elmer). The amount of Pb taken up was calculated by the difference between the amount of metal added and that remaining in the supernatant.

2.3. Pb adsorption in the presence of organic acids

Adsorption experiments were carried out at initial pH 5 in the absence or presence of citric acid and lysine. Pb and individual organic acids were added to the adsorbents either (1) simultaneously, or (2) separately by adding the ligand 2 h before Pb. The concentration of Pb was constant (200 mmol kg^{-1} for solid phase) while organic acid concentrations ranged from 0 to 1600 mmol kg^{-1} in order to obtain an initial acid:metal molar ratio (R) of 0, 1, 2, 4, 6 and 8. Following 12 h of agitation, clear supernatant was analysed for the concentration of Pb as described before. Al released and final pH in the equilibrium solution was also determined.

2.4. Adsorbent characterisation

2.4.1. Fourier transform infrared spectroscopy (FTIR)

The original and modified clay samples before and after adsorption of organic molecules and Pb were ground and mixed homogenously with dry KBr and pressed into discs using a hydraulic compressor. Infrared (IR) spectra were obtained employing an Agilent Cary 600 Series FTIR Spectrometer equipped with DRIFT (Diffuse Reflectance Infra-red Fourier Transform) accessories. Spectra over the 4000–400 cm^{-1} range were obtained by the co-addition of 64 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm s^{-1}.

2.4.2. X-ray diffraction (XRD)

Powdered clay samples before and after adsorption of organic molecules and Pb were pressed in a stainless steel sample holder. XRD patterns of the samples were collected through CuKα radiation (λ = 1.5418 Å) by employing a PANalytical, Empyrean X-ray diffractometer operating at 40 kV and 40 mA between 2 and 70° (2θ) at a step size of 0.016°. The basal spacing was calculated from the 2θ value using Bragg's equation, nλ = 2d sinθ; where, n is an integer, λ the wavelength, and θ the scattering angle.