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Synthesis and characterization of a PbO_2-clay nanocomposite: Removal of lead from water with montmorillonite

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ABSTRACT

The aim of this paper is to present the results obtained with Pb(II) sorption on an Algerian Clay. The experiments were carried out using a batch process. Powder X-rays diffraction patterns (PXRD) prove that in the montmorillonite Pb replaces Na ions. A significant restructuring at the particle scale is observed leading to the disappearance of the $d_{0\,0\,1}$ reflection of the clay at high concentrations of lead. The replacement of hydrated Na with Pb ions influenced significantly the thermal behaviour of the montmorillonite samples with regard to their dehydration and dehydroxilation capacities with a lowering of the water content. A PbO_2-clay composite material with good electrical conductivity is synthesized.

1. Introduction

Many of the world's water ways and water sources are polluted and contaminated by heavy metals and organic materials such as pesticides and herbicides, dyes, phenols and phenolic compounds. At a certain concentration, lead among heavy metals is considered to be toxic to plants, animals and humans. Hydration and swelling are the main properties of clays with respect to their role played in landfill sites [1–4]. Clay minerals are alumino-silicates that are very reactive materials due to their small grain size, large surface area and adsorption properties. As they are able to retain inorganic and organic contaminants, clays as raw or composite materials were widely used in many industrial fields [5–12]. The mineral clay, montmorillonite, has a high surface area and cation exchange capacity (CEC). It is a dioctahedral smectite mineral with a 2:1 layer linkage.

The inner layer is composed of an octahedral sheet of a $M_{2-3}(OH)_6$ general form (M is typically Al), which is located between two SiO_4 tetrahedral sheets [13,14]. Replacement of Al^{3+} by Si^{4+} in the tetrahedral layer and Mg^{2+} by Al^{3+} in the octahedral layer results in a net negative charge on the clay surfaces. The charge imbalance is compensated by the exchangeable cations Na^+ or Ca^{2+} in the interlayer. The hydration of inorganic cations on the exchange sites causes the clay mineral surface to be hydrophilic. The distribution of cations in the montmorillonite system is dependent on various parameters such as pH, ionic strength, and the type of adsorbed cation. Recent studies have greatly contributed to the understanding of sorption mechanisms on clay surfaces and showed that all cations do not behave similarly [15–17]. Lead–clay interactions have received the most attention to date and different authors [18–23] investigated the adsorption and desorption behaviours of Pb(II) on montmorillonite. The adsorption experiments were carried out under batch process and varying concentration, amount of clay, ionic strength, pH, time and temperature. The adsorption of metal ions on montmorillonite is pH dependent and the results followed the second order kinetic model. Two isotherm equations due to Langmuir and Freundlich showed good fits with the experimental data. Using X-ray absorption fine structure (XAFS) spectroscopy, Strawn and Sparks [16] studied the adsorption of lead ion by montmorillonite and found there were two different lead adsorption mechanisms. These mechanisms are controlled by ionic strength. The low ionic strength mechanism is pH independent and is consistent with outer-sphere complexation. The high ionic strength mechanism is pH dependent and suggests inner-sphere complexation. The objective of this study is to determine the feasibility of Pb(II) removal from water using an Algerian bentonite. In this paper, we report the results of our studies on the chemical and physical nature of lead ion sorption on Na-montmorillonite and elucidate the mechanisms taking place. The synthesis and characterization of a PbO_2-clay composite is also investigated. Thermogravimetric analysis (TGA), powder X-ray diffraction (PXRD), energy dispersive

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X-ray microanalysis (EDS) and SEM back-scattered electrons were used as techniques. The electrical conductivities of raw, Na-montmorillonite, Pb-montmorillonite and PbO_2-clay pellets were measured using impedance spectroscopy.

2. Experimental

2.1. Materials

The bentonite raw material used in this study is an important mineral resource of Hammam Boughrara (West Algeria). An appropriate amount of bentonite was treated with a hot solution of H_2O_2 to remove any organic contaminants then washed with distilled water several times and dried at 105 °C. This clay is not a single phase but it is composed of more than 90% of montmorillonite, cristobalite and quartz. Its chemical composition was found to be: 69.4% SiO_2, 14.7% Al_2O_3, 1.2% Fe_2O_3, 1.1% MgO, 0.8% K_2O, 0.5% Na_2O, 0.3% CaO, 0.2% TiO_2, 0.05% As and 11% loss of ignition.

Sodium chloride (analytical grade); lead nitrate ($Pb(NO_3)_2$ 98 wt.%), ammonium persulfate ($(NH_4)_2S_2O_8$), sodium hydroxide (NaOH), and ammonia were purchased from Sigma–Aldrich Chemicals.

2.2. Preparation of Na-montmorillonite

The bentonite was converted to Na-montmorillonite (Na-MMt) following this procedure: 5 g of crude bentonite were mixed with 1 M NaCl solution and stirred for 24 h. After three successive treatments, the homoionic bentonite was dialyzed in distilled water until it was free of chloride. Then it was separated by centrifugation to eliminate all other solid phases (quartz and cristobalite). The Na-MMt (fraction <2 μm) was recovered by decantation, dried at 80 °C, then sieved to 38–108 μm. The specific surface area which was measured by the BET method was 82 $m^2\ g^{-1}$. The cation exchange capacity (CEC) determined using bis(ethylenediamine) copper(II) complex method was 80 mequiv./100 g.

2.3. Preparation of Pb-montmorillonite

The (Na-MMt) was treated with 100 ml of $Pb(NO_3)_2$ (with concentration varying from 10^{-5} to 1 M) solutions at room temperature for 24 h under vigorous stirring. The products were washed with distilled water thoroughly and the supernatants were separated by centrifugation. The solid parts were filtered off, washed with distilled water until a negative nitrate test was obtained. The final products (Pb-MMt) were ground to the initial size, sieved and kept under a constant humidity before being analyzed.

2.4. Preparation of PbO_2-montmorillonite

PbO_2-montmorillonite (PbO_2-MMT) and chemical lead dioxide were prepared following the method described by Ruetschi et al. [24]. To convert Pb ions to PbO_2 (Pb-MMt) was treated with 100 ml of a stirred solution containing a mixture of ammonium persulfate, sodium hydroxide and ammonia at room temperature for 24 h. The solid parts obtained were filtered off, washed with distilled water and overnight dried at 105 °C. Chemical lead dioxide, as reference sample was prepared following the same method. An appropriate amount of lead acetate is used as starting material instead of (Pb-MMt). The solution was stirred at room temperature for 24 h. The brown-black powder obtained was filtered off, washed with distilled water then overnight dried at 105 °C.

2.5. Characterization of the prepared samples

Thermogravimetric analysis (TGA) was carried out on a TA Instruments thermobalance TGA Q500. The measurements were carried out in nitrogen flow 80 mL min^{-1}. 30 mg of each sample was weighed and heated from 100 to 800 °C, at a heating rate of 10 °C min^{-1}.

PXRD patterns were taken at ambient temperature using a Bruker D8 advance diffractometer operating at 40 kV and 30 mA with CuK_α radiation (k = 0.15406 nm). Radial scans were recorded in the reflection scanning mode with 2θ being changed from 2° to 80°. Bragg's law, defined as $n\lambda = 2d \sin\theta$, was used to compute the crystallographic distance (d) for the examined montmorillonite samples. The average crystallite size was calculated from the full width at the half maximum (FWHM) using Sherrer equation.

SEM back-scattered electrons images and EDS semi-quantitative analyses were performed using a JEOL 6360 scanning electronic microscope and an EDAX/DX4 analyzer. The samples were prepared by taking a small amount from the conditioned substrates. All samples were coated with a thin carbon layer in order to obtain a conductive surface. The different samples were placed in a vacuum desiccator containing $CaCl_2$ to be dried before being examined with scanning electron microscope.

The electrical conductivities of raw, Na-MMt, Pb-MMt and PbO_2-clay pellets were measured. The pellets were prepared at room temperature under a pressure of 10 tonnes in a stainless steel die of 13 mm diameter and approximately 2 mm thickness. Ac conductivity and dielectric properties were performed using an HP impedance analyzer 4192A Model in the frequency 5 Hz–13 MHz by placing the pellet samples between two parallel plate electrodes. The electrical conductivity of chemical PbO_2 was determined using Dc conductivity measurements by typical four probe method. The samples were connected to a Keithley 2400 source electrometer. The reproducibility of all measurements was checked.

3. Results and discussions

3.1. Thermal analysis data of Na and Pb-montmorillonites

Fig. 1 presents the TG curves of Na and Pb-MMt. The different samples show two plateaus, the first one in the range of temperature comprised between 100 and 300 °C corresponding to the removal of adsorbed and coordinated water species, the

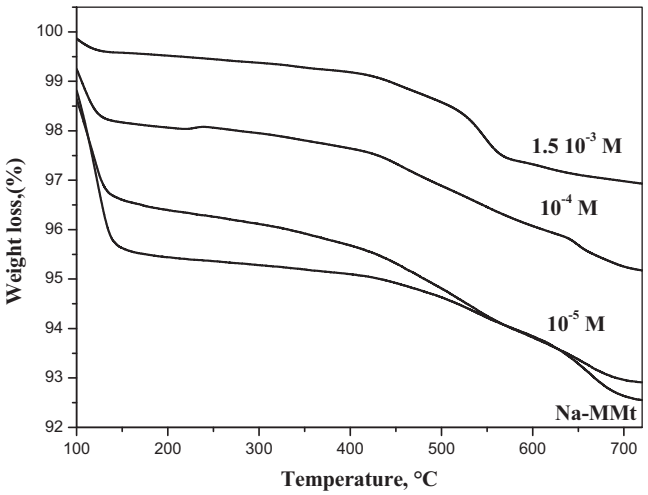

Fig. 1. TG curves of Na-MMt and Pb-MMt samples.