Research paper

Adsorption of lead(II) ions from aqueous solutions onto Cr-pillared clays

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ABSTRACT

The present paper presents the synthesis and characterization of porous nanomaterials, the Cr (III) being the metal oxide used as pillar intercalated between the layers of montmorillonite. The raw material used to obtain the pillared clays was a Romanian natural calcium bentonite, which was provided by S.C. Bentonita S.A. The main parameters were varied (metal ion for ion exchange process, aging temperature and duration for pillaring agent preparation, metal/clay ratio) in the aim of obtaining nanomaterials with high adsorption capacity of lead ions from waters. The modified clays were characterized by: nitrogen adsorption technique, X-ray diffraction (XRD) and scanning electron microscopy (SEM). The determination of Pb(II) ions concentration was realized by atomic absorption spectrophotometry.

The obtained results showed that the basal distance and specific surface area varied with the parameters of materials preparation. The nanomaterial with the best textural, structural and morphological properties was chosen in the aim of its using in Pb(II) adsorption from aqueous solution.

The Langmuir and Freundlich models were used to fit the experimental data and these showed good correlations.

1. Introduction

The retention of toxic heavy metals from wastewaters is an attractive subject in the field of environmental remediation. Currently, there are many technologies used to clean up the contaminated waters with heavy metals, including: ion-exchange, chemical precipitation, evaporation, reverse osmosis, membrane filtration (Gerçel and Gerçel, 2007), but all these methods are generally expensive. The adsorption is a very effective and economical process for heavy metal ions removal from wastewaters. Heavy metals are not biodegradable, so their concentrations should be reduced to acceptable levels before disposal into the environment (Sulaymon et al., 2009). Metals which are toxic pollutants include: mercury, cadmium, lead, cobalt, zinc, nickel, manganese etc. For example, lead presented in the wastewater of many industrial processes, such as the production of dyes, paint coatings, glass and batteries (Li et al., 2010), is potentially toxic to humans and to aquatic environment too. The exposure of humans to lead produces severe acute poisoning when is placed in the digestive tract, edema, learning disabilities for children, damage to organs (liver, kidneys and heart) and immune system disorders (Sreejalekshmi et al., 2009).

The permissible level of lead ions for industrial and urban wastewater discharged into natural receivers is $0.2 \, mg \cdot L^{-1}$, according to

NTPA-001/2002 Romanian normative. For drinking water the limit value of lead ions in Romania is $0.05 \, mg \cdot L^{-1}$.

Natural or synthetic adsorbents can be used in wastewaters remediation, a special attention being accorded to natural clays, which became raw materials in the obtaining of novel adsorbent materials (Volzone, 2004). The using of adsorbent materials based on natural clays, in the decontamination process of wastewaters, has the following advantages: low cost; high availability in native state; ease of using; reusing after adsorbent regeneration; retention of metal ions in a wide pH range. Montmorillonite is the most used type of clay in pillaring process due to its double-layered structure (2:1). The pillaring process consists in the following steps: ion exchange of bentonite, preparation of pillaring agent, intercalation, calcination. The pillared interlayered clays (PILC) present a rigid structure, a high thermal stability given by the oxido-metallic pillars formed after calcination (Schoonheydt et al., 1999).

Chromium pillared clays (Cr-PILC) have attracted attention researchers for their use as catalysts in a wide range of reactions, like: oxidative dehydrogenation of propane (De et al., 2014), catalytic conversion of hydrocarbons (Pinnavaia et al., 1985; Storaro et al., 1997), hydrocracking of heavy liquid fuels (Gyftopoulou et al., 2005), nitration of chlorobenzene (Mishra and Parida, 1998), toluene

disproportionation (Auer and Hofmann, 1993), cumene conversion (Bradley and Kydd, 1993). In this paper we propose to extend the use of Cr-PILC in obtaining of adsorbents with special performances in re-mediation of industrial liquid effluents. To our knowledge, this is the first study that investigates the lead adsorption onto Cr-PILC, by using a Romanian calcium bentonite as raw material. Due to its high mon-tmorillonite content, to its high natural availability and low cost, Ro-manian bentonite, is a good candidate for the development of nano-materials used in environmental remediation.

The synthesis of Cr-PILC was achieved in five stages: purification of bentonite, ion exchange to obtain Na-montmorillonite (Na-Mt) or Cu-montmorillonite (Cu-Mt), preparation of pillaring agent, intercalation of Na-Mt or Cu-Mt with pillaring agent and calcination. Intercalation process involves the use of homoionic clay, Na being the most common cation used in ion exchange step. In our work, the ion exchange was achieved with Na(I) ions or Cu(II) ions. Cation exchange capacity of clays obtained by polyvalent ions exchange is consistently higher than that obtained by monovalent cations, if clays are saturated in aqueous solution (Bower and Truog, 1940). That's why we chose to use Cu(II) ions for montmorillonite ionic exchange process. To our knowledge, this paper is the first study that investigates the comparison between Na-Mt and Cu-Mt in the obtaining of Cr-PILC.

The effects of synthesis parameters on textural, structural and morphological properties have been investigated. The nanomaterial with the best properties was tested on Pb(II) adsorption from aqueous solution. The liquid phase adsorption is influenced by many factors such as pH, the type of adsorbent, the solubility of the adsorbate in the solvent, the temperature, the concentration of the adsorbate, the con-tact time between the adsorbent and adsorbate etc. The parameters varied in the adsorption studies of lead ions onto the most advanced nanomaterial were: contact time between the adsorbent and the aqu-eous solution of Pb(II), pH of aqueous solution, adsorbent dose, Pb(II) ions concentration of initial solution. The experimental data was ana-lyzed by both Freundlich and Langmuir isotherm models.

1.1. Experimental part

1.1.1. Materials and devices

The raw material used to obtain the pillared clays was a natural calcium bentonite, which was provided by S.C. Bentonita S.A. Company, from Satu Mare, Romania. The reagents used in experimental studies were provided by the companies Alfa Aesar (copper(II) sulfate pentahydrate, 99% purity; aluminum chloride hexahydrate, 99.99% purity) and Merck (chromium(III) chloride hexahydrate, 99.97% purity; standard solution of lead(II), $1000 \pm 0.002 \, g \cdot L^{-1}$ Pb; nitric acid, 65%; sodium hydroxide, pellets, 98% purity; silver nitrate, 99.8% purity) and were used without further purification. The water used in kinetic studies was ultra pure water obtained with a Barnstead Easy Pure II device, with a resistivity of 18.2 MΩ·cm at 25°C.

After ion exchange treatment, the modified clays have been sepa-rated from the suspension using a Firlabo SW9/SW12 centrifuge and dried in a Memmert oven. The milling of the bentonite samples was performed in an alumina grinding balls, Pulverisette 6 model. The powders thus obtained were homogenized by means of a three di-mensional mixer Turbula T2F type provided by the WAB Company.

XRD powder patterns were collected on a Siemens Diffraktometer D5000 device, using Cu Kα1 radiation (Ni filter, λ = 0.15401 nm, voltage 40 kV and current 30 mA).

The specific surface area (determined by BET technique) and the nitrogen adsorption-desorption isotherms were measured with a Micromeritics ASAP 2010 device. The samples were degassed at 473 K for 16 h.

The morphological analysis was realized through scanning electron microscope with field emission (FEG-SEM) using a JEOL JSM-7400F type (OXFORD Instruments). Before FEG-SEM analysis, montmor-illonite samples were metalized with carbon, using a Precision Etching

Coating System Gatan (model 682).

The determination of Pb(II) ions concentration was realized by atomic absorption spectrophotometry by using of AAnalyst™ 700 Atomic Absorption Spectrometer device from Perkin Elmer that works with heated graphite furnace atomizers, at a wavelength of 283.3 nm specific to lead lamp. Minimum detection limit of spectrophotometer is $0.002 \, mg \cdot L^{-1}$.

*p*H values adjustment was carried out with a pH meter, M210 Tacussel type previously calibrated with buffer solutions of pH 4.01 and pH 10.01.

1.1.2. Synthesis of Cr-PILC

The preparation of Cr-PILC was achieved in four steps: purification of natural calcium bentonite (CaBent-nat), ion exchange with Na(I) or Cu(II) ions, intercalation of Na- exchanged montmorillonite or Cu(II)-exchanged montmorillonite with pillaring agent and calcination of in-tercalated clay.

Romanian calcium bentonite used as raw material was purified as described in previous papers (Georgescu et al., 2015, 2016). Inter-calation process involves the use of homoionic clay, Na(I) being the most common cation used in ion exchange step. In our work, the ion exchange was achieved with Na(I) ions or Cu(II) ions.

In the case of exchanged clay with Na ions,1 g of montmorillonite sample was treated with 100 mL of 1 M NaCl solution, the suspension being stirred at 80°C, for 3 h (Azzouz et al., 2009). The montmorillonite samples were copper-exchanged, by its treatment with $CuSO_4$ solution, as described in a previous paper (Georgescu et al., 2015). Both proce-dures were repeated three times to obtain a complete Na-montmor-illonite (Na-Mt) or Cu-montmorillonite (Cu-Mt) samples. Between ion-exchanged operations, the Na-Mt and Cu-Mt samples were washed with distilled water, until modified montmorillonite was free of chloride anions (0.1 N $AgNO_3$) or sulfate anions (0.1 N $BaCl_2$). After sample washing, the suspensions were centrifuged. Next, the samples were dried in an oven at 80°C for 16 h, ground and sieved in order to obtain particles size less than 63 μm.

The dilute Cr(III)-pillaring solution was prepared by drop-wise ad-dition of a 0.2 M NaOH solution to a 0.1 M $CrCl_3$ solution, at room temperature with vigorous stirring, till the (OH/Cr) molar ratio was equal to 2.0. The preparation of Cr-pillaring solution was achieved by varying the following parameters: aging temperature and aging dura-tion (Table 1).

For the intercalation of clays with pillaring agent, Na-Mt and Cu-Mt samples were dispersed in distilled water (2 wt% slurry) and the sus-pensions were stirred for 1 h, at room temperature. Further, these slurries were mixed with the pillaring solution at room temperature, until the molar ratio was 10 or 20 mmoles Cr/g clay. The clay was then washed with distilled water for the removal of chloride ions and cen-trifuged. The samples were then dried at 80°C for 15 h, and then hand-ground into a mortar.

The calcination of intercalated samples was realized using a device with a tubular furnace under nitrogen flow, which was maintained at

Table 1
Varied parameters for samples intercalation with pillaring solution.

Nanomaterial	Solution for ion exchange	Parameters for pillaring agent preparation		Cr/clay ratio
		Aging temperature	Aging duration	
		°C	h	mmol/g
Na-Mt-1	1 M NaCl	60	36	10
Na-Mt-2	1 M NaCl	95	108	10
Cu-Mt-1	0.1 M CuSO₄	60	36	10
Cu-Mt-2	0.1 M CuSO₄	95	108	10
Cu-Mt-3	0.1 M CuSO₄	95	84	20