



Research paper

Enhanced heavy metal adsorption on functionalized nanotubular halloysite interlayer grafted with aminoalcohols

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ABSTRACT

Nanotubular halloysite mineral with a 1:1 layered structure was interlayer grafted using diethanolamine and triethanolamine. The tailored materials which were stable in aqueous solutions had a constant interlayer gap equal to 3.1 or 3.6 Å, respectively, and showed no swelling properties. The modification significantly improved the halloysite adsorption capacity with respect to Pb(II), Cd(II), Zn(II), and Cu(II). This was due to a two-step gradual diffusion of the metals into the interlayer space and their subsequent binding by amine nitrogen of the grafted aminoalcohol. In particular, the Cu(II) ions were preferentially removed from solution as they readily form complexes with N-donor ligands. The observed competitive protons adsorption on the amine nitrogen increased the pH of solution in contrast to system with raw halloysite where the pH decreased. The proton release in the latter system was due to domination of an ion-exchange and surface complexation removal mechanisms of the cations on the particles surface. The adsorption efficiency was related to the metal hydrolysis constants and in turn the size of the ions was less relevant. The adsorption isotherms and kinetic data in all cases followed the Langmuir and pseudo-second order equations, respectively. The applied desorption procedure illustrated a complex binding of the metals with the raw and modified mineral and showed that the materials cannot be completely recycled.

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1. Introduction

Heavy metals with toxic properties such as lead and cadmium are not required for the development of living organisms and may lead to serious health problems even at trace concentrations. Although zinc and copper are important nutrients needed in small quantities, the exposure to their excessive amounts is harmful and causes various diseases (Alloway, 2013). The removal of hazardous heavy metals of anthropogenic origin from aqueous media including drinking water, wastewater, and soil solutions is of environmental importance. Several remediation techniques involving the use of structurally different materials were proposed (Babel and Kurniawan, 2003; Bailey et al., 1999; Hua et al., 2012; Wang et al., 2003). Among others, these include activated carbons, zeolites, metal oxides, and raw or modified clay minerals (Bhattacharyya and Gupta, 2008). The removal of metals is mainly based on adsorption and ion-exchange reactions; however, precipitation of highly insoluble metal phases, membrane filtration or electrolytic reduction is also applied (Wang et al., 2003). The adsorption-based remediation is in particular desirable due to the possibility of partial or complete adsorbent regeneration and its further reuse (Hua et al., 2012).

Halloysite in its dehydrated form is a 1:1 layered dioctahedral mineral from the kaolin group with a chemical composition of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. The layer is built from tetrahedral (silicic) and octahedral (aluminum) sheets linked by joint oxygens. In turn, the stacked layers are held by hydrogen bonds formed between tetrahedral basal oxygens and inner surface hydroxyls of the octahedral sheet. Halloysite is a polymorph of kaolinite characterized by a high degree of disorder in the stacking of layers and a small particle size (Joussein et al., 2005). The observed structural misfit between sheets is compensated by layers rolling; thus, naturally occurring particles very often form nanotubes (Singh, 1996). The interlayer space of kaolin minerals is originally not accessible to ions and molecules; however, their insertion becomes possible after prior treatment with e.g. dimethyl sulphoxide, urea or N-methylformamide (Franco and Ruiz Cruz, 2004; Rutkai et al., 2009). Such procedure enabled to synthesize several intercalated and grafted hybrid inorganic/organic structures based on kaolin minerals (de Faria et al., 2010; Komori et al., 2000; Letaief and Detellier, 2007; Letaief et al., 2011; Matusik et al., 2012; Tonlé et al., 2009; Yuan et al., 2008). Their use as adsorbents (de Faria et al., 2009; Li and Bowman, 2001), catalytically active materials (Cho et al., 2006; de Faria et al., 2012), electrochemical sensors (Dedzo and Detellier, 2013; Dedzo et al., 2012; Letaief et al., 2011), luminescent materials (de Faria et al., 2011), and fillers for the production of polymer nanocomposites (Letaief et al., 2011; Matusik et al., 2011; Mu et al., 2007) was illustrated.

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The grafted materials are of particular importance as, in contrast to intercalation compounds, they are stable in aqueous solutions which makes them promising candidates for water treatment. Recently an improved adsorption of aqueous hexavalent chromium by kaolin minerals including halloysite was reported (Matusik and Bajda, 2013). The minerals were previously interlayer grafted with triethanolamine and afterwards reacted with iodomethane. As a result a trihydroxymethylethylammonium iodide was formed in the interlayer space. The modified materials had the ability to attract negative ionic species as the iodide counter ions could be ion-exchanged.

In reference to this study, an attempt was undertaken to examine the possibility of using a nanotubular dehydrated halloysite grafted with aminoalcohols as an adsorbent of selected heavy metals. An assumption was made that the amine nitrogen of aminoalcohol grafted in the interlayer may selectively attract the cations. The adsorption equilibrium and kinetics as well as the desorption both in single-element and multi-element systems were investigated in detail. The paper reports an incorporation and subsequent binding of the cations in the interlayer space of the modified halloysite.

2. Materials and methods

2.1. Synthesis of materials

For the experiments, a halloysite sample (H) from Polish Dunino deposit was used. The sample contained ~60% of halloysite and ~40% of kaolinite as estimated by the formamide test (Churchman et al., 1984). The test assumes that the intercalation of halloysite is rapid and takes place during the first hour after spraying the sample with formamide. After that time the kaolinite structure also undergoes intercalation. Thus, the ratio of kaolinite to halloysite can be calculated from the intensity ratio of the 10.4 Å (basal spacing of the formamide intercalate) and 7.2 Å peaks recorded within 1 h after the reaction. For the test, the mineral sample was prepared as a slurry which was placed on a glass slide and air dried in order to induce preferential orientation of the particles and thus enhance the reflection intensity from basal spacing planes.

The procedure of modification consisted of the two following steps. Firstly, an intercalation with dimethyl sulphoxide–(CH₃)₂SO (DMSO) was carried out by mixing 12.5 g of previously dried (110 °C) H sample with 100 mL of DMSO containing 10% of H₂O at room temperature (22 °C). After 24 h the suspension was centrifuged and the obtained material (HDS) was dried at 65 °C. Secondly, the formed intercalation compound (12 g) reacted with 120 mL of diethanolamine–(CH₂CH₂OH)₂NH (DEA) or triethanolamine–(CH₂CH₂OH)₃N (TEA) at 180 °C under argon flow for 24 h (Letaief and Detellier, 2007). Afterwards, the obtained suspension was centrifuged, washed with isopropanol and subsequently with water, and finally dried at 65 °C. The end products after grafting with DEA and TEA were abbreviated as HD and HT, respectively.

2.2. Characterization methods

The XRD patterns of powdered samples were recorded by a Philips APD PW 3020 X'Pert diffractometer using CuK_α radiation and graphite monochromator. The measurement was performed in the 2–15° 2θ range with a 0.05° step. The FTIR spectra were collected by Nicolet 7600 spectrometer (Thermo Scientific) with 64 scans at 4 cm⁻¹ resolution in the 4000–400 cm⁻¹ mid-region. A mixture of 3 wt.% sample/KBr was analyzed by DRIFT technique using Praying Mantis Diffuse Reflection Accessory (Harrick). The ²⁷Al solid state MAS-NMR spectra were recorded using APOLLO console (Tecmag) at the magnetic field of 7.05 T using 8 KHz spinning speed. The 1 M solution of Al(NO₃)₃ was used as a reference. The UV-Vis spectra of samples aqueous suspensions were collected using UV-Vis Hitachi U-1800 spectrophotometer. Prior to analysis the suspensions were sonicated (20 kHz, 50 W

power, 1 min). The differential thermal analysis (DTA) was performed with a Netzsch STA 449F3 Jupiter instrument. The measurement was carried out using ~30 mg samples in a temperature range of 25–800 °C (heating rate: 10 °C/min, air atmosphere). The N₂ adsorption/desorption measurements were performed at –196 °C in the relative pressure (*p/p*₀) range 10⁻⁴–0.99 using Micromeritics ASAP 2020 instrument. Prior to analysis the samples were outgassed at 150 °C. The specific surface area (*S*_{BET}) was determined by applying the BET equation. The total pore volume (*V*_{TOT}) was calculated for the *p/p*₀ equal to 0.99. The micropore (*V*_{mic}^{DR}) and mesopore (*V*_{mes}^{BJH}) volumes were determined using Dubinin–Radushkevich and BJH models, respectively. In turn, the macropore volume (*V*_{mac}) was calculated using the following formula: *V*_{mac} = *V*_{TOT} – (*V*_{mic}^{DR} + *V*_{mes}^{BJH}). The CEC (cation exchange capacity) was measured using methylene blue method. The powdered samples were shaken in aqueous 2 mmol/L solution of methylene blue. The adsorbed amount of the dye was determined spectrophotometrically for the 660 nm wavelength. The point of zero charge (PZC) was determined using acid-base potentiometric titration experiments performed at 22 °C. The 100 μL portions of 0.05 M HNO₃ were added to 25 mL of sample suspension in 0.05 M KOH until the pH dropped to ~1.5. The suspensions were constantly mixed during the experiment using magnetic stirrer. The PZC for each sample was estimated from the intersection of titration curves obtained for suspension concentrations of 4, 2, and 1 g/L with the titration curve of the blank (0.05 M KOH). The data from potentiometric titration enabled to examine the surface charge changes versus pH using the Eq. (1).

$$Q = FC\Delta V/m \quad (1)$$

where *Q* is the surface charge (C/g), *F* is the Faraday constant: 9.648 × 10⁴ C/mol, *C* is the acid concentration (mol/L), Δ*V* is the difference in acid volume used to reach the same pH in sample suspension and the blank solution (L), and *m* is the suspension concentration (g/L). The isoelectric point (IEP) was estimated as the pH for which the *Q* was equal to 0.0.

The quantitative CHNS elemental analysis was performed through the measurement of purified and separated gaseous products formed during high temperature combustion of the samples using VarioEL III Elementar analyzer. Assuming that the sole cation adsorption center was connected with the amine nitrogen of the aminoalcohol, the adsorption capacity (*AC*_N) in mmol/kg was calculated using Eq. (2).

$$AC_N = (N_G - N_H)/M_N \cdot 10^4 \quad (2)$$

where *N*_G is the nitrogen content in grafted compound (wt.%), *N*_H is the nitrogen content in pure halloysite (wt.%), *M*_N is the molar mass of nitrogen, and 10⁴ is the wt.% to mg/kg conversion factor.

2.3. Adsorption experiments

The equilibrium adsorption experiments of Pb(II), Cd(II), Zn(II), and Cu(II) were carried out in duplicates at 22 °C for the concentration range of 0.005–5.0 mmol/L. The metals were introduced in the form of appropriate nitrates Pb(NO₃)₂, Cd(NO₃)₂·4H₂O, Zn(NO₃)₂·6H₂O, and Cu(NO₃)₂·3H₂O (Sigma-Aldrich). The solid/liquid ratio (*S/L*) was constant and equal to 20 g/L and the initial pH (*pH*_{in}) was set in the 2.0–6.5 range by diluted HNO₃ and/or KOH solutions. The *pH*_{in} range was chosen below the precipitation limit for metal phases (e.g. hydroxides) calculated using hydrochemical PHREEQC software with a MINTEQ.v4 thermodynamic database (Parkhurst, 1995). The materials were shaken in the heavy metal solutions for 24 h. For the kinetic experiments performed for the 1 mmol/L metal concentration at *pH*_{in} 5, the suspended samples were collected after 0.5, 1.0, 1.5, 2, 3, 4, 5, 6, 8, 10, 15, and 20 min from the start of the reaction. The kinetics were examined both for single-element solutions and for a multi-element mixture of all four cations in a ratio of 1:1:1:1 mmol/L. Additionally, the binding

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