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Behaviour of kaolinite intercalation compounds with selected ammonium salts in aqueous chromate and arsenate solutions

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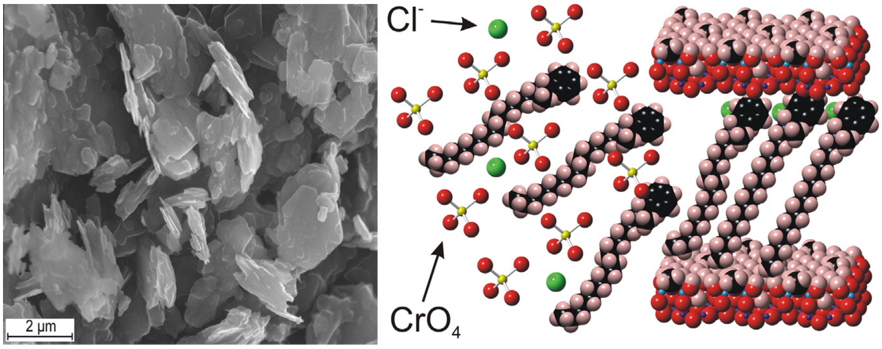
HIGHLIGHTS

- The kaolinite intercalation compounds with selected ammonium salts were obtained.
- The XRD and IR indicated a monolayer or tilted arrangement in the interlayer space.
- The reaction with aqueous Cr(VI) and As(V) lead to deintercalation of molecules.
- A significant improvement of oxyanions immobilization was observed in all cases.
- The removal was due to precipitation of oxyanions alkyl salts and/or ion-exchange.

GRAPHICAL ABSTRACT



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ABSTRACT

The removal of aqueous Cr(VI) and As(V) oxyanions from waters by different materials with sorption properties is of environmental importance. In this study, a methoxy-kaolinite derivative was intercalated with benzyltrimethylammonium (B1), tetramethylammonium (TMA), and benzyldimethylhexadecylammonium (B5) chlorides and the interaction of the obtained materials with oxyanions was examined. The PXRD (powder X-ray diffraction) and IR (Infrared spectroscopy) analyses indicated a monolayer arrangement of the B1 and TMA molecules in the interlayer space of the mineral, while a tilted arrangement was noticed in the case of B5. A complete or partial deintercalation of introduced molecules was observed in the reactions with aqueous solutions of Cr(VI) and As(V). In all studied systems a significant improvement of the oxyanions removal was observed as compared to the pure kaolinite. The highest uptake of oxyanions was noticed in the reaction with B5-intercalated material. This was due to precipitation of organic alkyl salts. The formation of alkylchromate was confirmed using FTIR spectroscopy. The lower uptake of oxyanions by the B1- and TMA-intercalated materials was due to lack of new solid precipitation and resulted from the ion-exchange of chlorides initially compensating the ammonia nitrogen charge. The experimental sorption isotherms for all the reactions were best represented by Langmuir equation. A gradual, two-step removal process of Cr(VI) and As(V) by B1- and TMA-intercalated materials was observed. In turn, the precipitation of alkyl salts in reaction with B5-intercalated material resulted in a rapid immobilization of the oxyanions. The kinetic data modelled using pseudo-second order equation showed very good agreement with experimental results.

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Introduction

The deposits of kaolin group minerals are widespread in the world [1]. Their physical and chemical properties make them useful materials with applications in industry and environmental protection [2]. The structure of kaolinite which is the main component of kaolin sedimentary rock is build from stacked 1:1 layers of $Al_2Si_2O_5(OH)_4$ composition held by hydrogen bonds. The layer is composed of tetrahedral (Si–O) and octahedral (Al–O) sheets bonded through common oxygens. The unmodified mineral does not have swelling properties, however the interlayer can be intercalated using selected organic molecules e.g. dimethyl sulfoxide (DMSO) [3], urea [4], or formamide [5] which could be easily exchanged. Moreover, kaolinite possesses an unique asymmetric interlayer environment with two chemically different surfaces: oxygens of tetrahedral sheet and inner surface hydroxyls of octahedral sheet. In particular the latter surface is susceptible to grafting reactions and formation of new structures [6]. This opens the way to synthesize new kaolinite-based hybrid materials in reactions with organic molecules [7–9]. An appropriate selection of intercalated or grafted organic guest enables to design materials with improved sorption [10–12], luminescent [13], and catalytic properties [14,15]. The obtained organo-functionalized materials may also be used as fillers in the production of polymer–clay nanocomposites due to their chemical compatibility with selected polymers [16,17].

Chromate and arsenate oxyanions are highly mobile and their toxic and/or cancerogenic properties are known [18,19]. The remediation of waters polluted with inorganic oxyanions is often based on sorption processes which include the use of different materials e.g. layered double hydroxides [20], activated carbon [21], oxides [22], modified smectite minerals [23], and organo-zeolites [24–26].

Recently new types of kaolinite intercalation compounds with selected benzylalkylammonium salts were synthesized and characterized [27,28]. The introduced molecules in the form of chlorides may induce immobilization properties of the obtained materials towards oxyanions which are of environmental interest. Thus, the research objective was to investigate the efficiency of Cr(VI) and As(V) removal by intercalation compounds of well ordered kaolinite with selected ammonium salts. The sorption equilibrium and kinetics, pH effect as well as the immobilization mechanism were investigated in detail.

Experimental section

Synthesis of intercalation compounds

A well ordered kaolinite with Hinckley index of 1.31 from Polish "Maria III" deposit (M sample) was chosen for the experiments. A detailed characterization of the mineral sample was reported earlier [29,30]. The chemical compounds: dimethyl sulfoxide (DMSO) and methanol were obtained from POCH company (Polish Chemical Reagents). In turn, the following ammonium salts were purchased from Sigma–Aldrich: benzyltrimethylammonium chloride (B1), tetramethylammonium chloride (TMA) and benzyldimethylhexadecylammonium chloride (B5). The structures and dimensions of the molecules are given as supporting material (Fig. S1).

The synthesis of intercalation compounds followed a three-step procedure described previously [27]. Briefly, the kaolinite pre-intercalated with DMSO was further grafted with methoxyl groups by washing with methanol at room temperature (22 °C). The formed methoxy-kaolinite derivative with hydrophobic character of the interlayer space was sufficient for the insertion of the ammonium salts. The organic compounds in the form of chlorides were dissolved in methanol and the solution concentration was set to 2 mol/L (B1 and TMA salts) and 1 mol/L (B5 salt). The appropriate solutions were mixed with methoxy-kaolinite precursor for 24 h at 22 °C in solid/solution ratio of 125 g/L. The obtained materials were abbreviated in analogy to used salts as MB1, MTMA, and MB5, respectively. Additionally, the MB1 and MTMA derivatives were washed in isopropanol to remove the excess of salts which could have crystallized outside the interlayer space. The washing was not possible in the case of MB5 sample as the isopropanol molecules could destroy the intercalation compound structure.

Immobilization experiments

For the sorption equilibrium experiments the Cr(VI) and As(V) solutions prepared from potassium dichromate $K_2Cr_2O_7$ and sodium arsenate dibasic heptahydrate $Na_2HAsO_4 \cdot 7H_2O$, respectively, covering the 0.02–50.0 mmol/L range were used. The initial pH (pH_{in}) was set in the 3–11 range using diluted solutions of HNO_3 and/or KOH. The sorbent/solution suspensions of 20 g/L concentration were shaken at 22 °C for 24 h. For the kinetic experiments the 5.0 mmol/L starting oxyanion concentration was used and the pH_{in} was set to 5.0. The suspension aliquots were collected within the time interval 0.5–20 min. All collected suspension samples were filtered through 0.22 μm PES filters. The concentration of Cr(VI) was measured colorimetrically by 1,5-diphenylcarbazide method using UV–Vis Hitachi U-1800 spectrophotometer [31]. The As(V) concentration was determined by hydride generation method using GBC SavantAA atomic absorption spectrometer (HG-AAS). The spectrophotometrical measurement of the B1 and B5 salts concentration was carried out using 208 nm band attributed to $\pi \rightarrow \pi^*$ transition.

Methods for structural characterization

The powder X-ray diffraction (PXRD) patterns were recorded using a Philips APD PW 3020 X'Pert instrument with Cu Kα radiation and a graphite monochromator. The powdered samples were analyzed in the range of 1.5–16 °2θ with a step of 0.05 °2θ. FTIR spectra were collected by Nicolet 7600 spectrometer using DRIFT technique (3 wt.% sample/KBr) with 64 scans at 4 cm^{-1} resolution in the 4000–400 cm^{-1} mid-region. Elemental analysis was performed using VarioEL III Elementar CHNS analyzer. The results were used to calculate the formulas of materials. In the case of methoxy-kaolinite, the carbon content was taken for the calculations, while the formulas of intercalation compounds were calculated on the basis of nitrogen content.

Equilibrium and kinetic theoretical models

A detailed description of the equations used for modelling of the experimental equilibrium and kinetic data is given in Table 1.

Results and discussion

Structure of intercalation compounds

The pure M kaolinite exhibits a 7.2 Å peak in the PXRD pattern which is characteristic for a 1:1 layered structure of the kaolin group minerals (Fig. 1). The IR spectrum shows four well resolved bands corresponding to different types of structural OH hydroxyls (3700–3600 cm^{-1} region) characteristic for a well ordered kaolinite (Fig. 2). The DMSO intercalation caused a swelling of the mineral as the initial basal spacing increased to 11.2 Å (MDS sample) (Fig. 1) [32]. Moreover, dramatic changes of the bands attributed to the inner surface OH groups (3700–3600 cm^{-1}) are observed in the IR spectra (Fig. 2). This especially involves an intensity decrease of ~3695 cm^{-1} band as well as the appearance of 3540