

INTERCALATES OF KAOLINITE WITH AMMONIUM SALTS AND THEIR INTERACTION WITH AQUEOUS Cr(VI) IONS

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Kaolinite is a dioctahedral aluminum silicate built from linked octahedral (alumina) and tetrahedral (silica) sheets, which form an asymmetrical 1:1 layer. Kaolinite is more often used as a base for the synthesis of new hybrid materials (Dedzo et al. 2012). Kaolinites modified with selected organic molecules are studied because of their potential application as environmental remediation materials and polymer nanocomposite fillers (Matusik & Bajda 2013). Therefore the purpose of the study was to test the ability of kaolinite intercalation with ammonium salts to remove Cr(VI) from aqueous solution under different conditions. Additionally, information on the removal mechanism was obtained.

Well ordered kaolinite from Polish Maria III deposit (M) was used for the experiments. The mineral intercalated with dimethyl sulfoxide (DMSO) was used as a precursor. The sample portions of 12.5 g were mixed with 90 mL of DMSO and 10 ml of H₂O for 7 days at room temperature (MDS sample). The formed MDS intercalation compound was rinsed with CH₃OH until all DMSO was removed from the interlayer space and the methoxy-kaolinite (KM sample) was synthesized (Matusik et al. 2012). Finally, the KM sample was centrifuged, the excess of methanol was removed and the wet KM was stirred in methanol solutions of the ammonium salts. For the experiments the following chlorides solution were used: 2M tetramethylammonium (TMA), 1M benzyldimethylhexadecylammonium (B5) and 2M benzyltrimethylammonium (B1). The formed materials were abbreviated as the salts. The TMA and B1 samples were washed with isopropanol to remove the excess of ammonium salt crystallized on the surface of the intercalates. In contrast to B1 and TMA, the B5 complex was not washed as isopropanol destroys its structure. All samples were dried at 60°C for 24 h. The products were characterized using powder XRD, IR, and CHNS elemental analysis. The sorption of chromate on the modified kaolinite was

measured spectrophotometrically using 1,5-diphenylcarbazide method as a function of Cr(VI) concentration (0.02–20 mM/L) at pH 5. The intercalates were shaken in prepared chromate solutions (ratio 20 g/L) for 24 h at 22°C. The XRD confirmed that methoxy-kaolinite was intercalated with ammonium salts, which was not possible for the raw kaolinite. The d_{001} peak (7.2 Å) increased to 14.7 Å (B1), 12.6 Å (TMA) and 38.4 Å (B5). The small molecules in the case of B1 and TMA complexes formed a monolayer in the interlayer space while the long chain B5 molecules were tilted with respect to 1:1 layers. The presence TMA, B1 and B5 in the mineral structure was confirmed by infrared spectroscopy (FTIR) as the organic bands in the 3120–2800 cm⁻¹ region attributed to C-H stretching vibrations were registered. The changes in the position and intensity of the bands were also observed in the Si-O vibrations region (1200–900 cm⁻¹) due to salts incorporation. Results of CHNS analyses were used to determine the chemical formulas of the derivatives: $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_{3.79}(\text{OCH}_3)_{0.21}[\text{TMA}]_{0.54}$, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_{3.79}(\text{OCH}_3)_{0.21}[\text{B1}]_{0.38}$, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_{3.79}(\text{OCH}_3)_{0.21}[\text{B5}]_{0.59}$.

The modification by ammonium salts enhanced the sorption capacity as compared to raw kaolinite where the sorption capacity reached only ~2 mM Cr(VI)/kg. For the TMA intercalate the maximum Cr(VI) sorption reached ~23 mM Cr(VI)/kg. For the B1 it was equal to ~73 mM Cr(VI)/kg and for the B5 it was significantly higher equal to ~979 mM Cr(VI)/kg. Two possible Cr(VI) immobilization mechanism could be distinguished: ion exchange of Cr(VI) with Cl⁻ and surface precipitation of organic chromate. In the experimental pH range the HCrO_4^- ionic form of Cr(VI) dominates and it can be exchanged with Cl⁻. The precipitation mechanism undoubtedly dominated in the case of B5 where a yellow precipitate of organic chromate appeared. The XRD studies performed on samples after sorption indicated the lack of d_{001} values characteristic for the intercalates. This confirms that the structures are not stable in aqueous solutions.

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