Removal of selected anions by raw halloysite and smectite clay

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The structure of clay minerals consists of tetrahedral and octahedral sheets, which can form 1:1, 2:1, and 2:1:1 layers. The halloysite, which belongs to the kaolin group, is composed of 1:1 layers while smectite group minerals contains 2:1 dioctahedral layer. The presence of numerous active centers on mineral surfaces and/or in the interlayer spaces allows them to attract and exchange ions from aqueous solutions. This makes them suitable for removal of harmful/toxic ions such as P(V), As(V), and Cr(VI) (Mozgawa et al. 2011, Matusik 2014) or Pb(II), Cd(II), Zn(II), and Cu(II) (Bhattacharyya & Gupta 2008, Matusik & Wcisło 2014) from wastewaters. The aim of this work was to examine the sorption capacity of natural halloysite and smectite clay towards P(V), As(V), and Cr(VI).

Two samples used in this study were collected from Polish deposits. Natural halloysite (H) was obtained from Dunino deposit (located near Legnica in SW Poland), while smectite clay (SC) was obtained from Belchatów Lignine Mine where it forms an overburden cover. For both raw samples the X-ray diffraction (XRD) patterns and infrared absorption (FTIR) spectra were collected. The sorption of P(V), As(V), and Cr(VI) was conducted as a function of anions concentrations ranging from 0.05 to 50 mmol/L for initial pH of 5 in a single-element system. The suspension of H or SC and corresponding aqueous solution (solid/solution ratio: 20 g/L) was shaken for 24 h at 25°C. Afterwards the anions concentration in the supernatant solution was measured using colorimetric methods. The P(V) and As(V) concentration was determined with the molybdenum blue method, whereas Cr(VI) concentration was measured with diphenylcarbazide method.

The XRD pattern of the H sample showed a basal peak at 7.20 Å, which confirms the presence of dehydrated halloysite (7 Å). In turn, the SC exhibited a peak centered at ~12.5 Å with an asymmetric profile starting from ~15.0 Å. Such reflection suggests the presence of smectite which has both Na+ and Ca2+ cations in its interlayer space. The IR spectra of the H showed bands specific for kaolin group minerals related to the OH-stretching region (3700−3620 cm−1), vibrations of water molecules (~1630 cm−1) and bands associated with stretching and bending vibrations of aluminosilicate framework (1200−400 cm−1).

The results of the experiment indicated that the sorption capacity of both H and SC samples was relatively high. The highest uptake of P(V) was measured for both materials and it was equal to 201 and 256 mmol/kg, respectively for H and SC. The sorption capacity of H and SC towards As(V) was 168 and 96 mmol/kg, respectively. The
sorption of Cr(VI) by H and SC equaled 36 and 104 mmol/kg, respectively. The sorption isotherms were fitted to the Freundlich model (Freundlich 1906) with an exception of P(V) which sorption on H sample was described by Langmuir model (Langmuir 1916). The specific surface areas (SBET) of studied materials were similar: H = 49.52 m²/g and SC = 69.10 m²/g. The sorption centers that may attract anions in both H and SC samples were limited due to isomorphic substitutions in tetrahedral and/or octahedral sheets. This will generate positively charged sites and attract cations rather than anions. It is believed that the mechanism responsible for the adsorption of anions on both materials is mainly surface complexation at the crystals edges (Bradl 2004). The sorption capacity of H and SC samples was lower than that reported for hydrotalcite − based anion − exchange materials (HTLc). For comparison, the sorption capacity towards P(V), As(V) and Cr(VI) on uncalcined HTLc was 498 mmol/kg (Kuzawa et al. 2006), 596 mmol/kg (Wu et al. 2013) and 314 mmol/kg (Alvarez-Ayuso & Nugteren 2005), respectively. Nevertheless, the examined mineral samples might be used as sorbents for industrial wastewater treatment involving removal of P(V) and As(V).

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REFERENCES


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