Geology, Geophysics & Environment 2015, vol. 41 (1): 125–126

Removal of selected anions by raw halloysite and smectite clay

Anna Prokop, Paulina Maziarz, Jakub Matusik

AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, Department of Mineralogy, Petrography and Geochemistry; al. Mickiewicza 30, 30-059 Krakow, Poland; e-mail: jakub_matusik@wp.pl

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 Bełchatów 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 Ca^{2+} 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 IR spectrum of SC showed bands specific for smectite minerals; i.e. 3623 cm^{-1} band attributed to OH hydroxyl located inside the 2:1 layer, and broad band centered at ~3400 cm^{-1} due to interlayer water surrounding cations. Also the structural vibrations of the 2:1 layer were observed in the 1200–400 cm^{-1} region.

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

http://dx.doi.org/10.7494/geol.2015.41.1.125 ISSN 2299-8004 | e-ISSN 2353-0790 | Wydawnictwa AGH

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 (S_{BET}) of studied materials were similar: H = 49.52 m^2/g and SC = 69.10 m^2/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).

This project was funded by the Polish National Science Centre; Decision No. DEC-2011/01/D/ST10/06814.

REFERENCES

Alvarez-Ayouso E. & Nugteren H.W., 2005. Purification of chromium(VI) finishing wastewaters using calcined and uncalcined Mg-Al-CO_3-hydrotalcite. *Water Research*, 39, 12, 2535–2542.

Bhattacharyya K.G. & Gupta S.S., 2008. Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: A review. *Advances in Colloid and Interface Science*, 40, 2, 114–131.

Bradl H.B., 2004. Adsorption of heavy metal ions on soil and soil constituents. *Journal of Colloid and Interface Science*, 277, 1, 1–18.

Freundlich H.M.F., 1906. Über die adsorption in lösungen. *Zeitschrift für Physikalische Chemie* (*Leipzig*), 57A, 385–470.

Kuzawa K., Jung Y-J., Kiso Y., Yamada T., Nagai M. & Lee T-G., 2006. Phosphate removal and recovery with a synthetic hydrotalcite as an adsorbent. *Chemosphere*, 62, 1, 45–52.

Langmuir I., 1916. The constitution and fundamental properties of solids and liquids. Part I. Solids. *Journal of the American Chemical Society*, 38, 11, 2221–2295.

Matusik J., 2014. Arsenate, orthophosphate, sulfate and nitrate sorption equilibria and kinetics for halloysite and kaolinites with an induced positive charge. *Chemical Engineering Journal*, 246, 244–253.

Matusik J. & Wcisło A., 2014. Enhanced heavy metal adsorption on functionalized nanotubular halloysite interlayer graf ter with aminoalcohols. *Applied Clay Science*, 100, 50–59.

Mozgawa W., Król M. & Bajda T., 2011. IR spectra in the studies of anion sorption on natural sorbents. *Journal of Molecular Structure*, 993, 109–114.

Wu X., Tan X., Yang S., Wen T., Guo H., Wang X. & Xu A., 2013. Coexistence of adsorption and coagulation processes of both arsenate and NOM from contaminated groundwater by nanocrystallined Mg/Al layered double hydroxides. *Water Research*, 47, 12, 4159–4168.