

A comparative study on the removal of Pb(II), Zn(II), Cd(II) and As(V) by natural, acid activated and calcinated halloysite

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With the intensive development of the global industry trace elements like lead, zinc, cadmium and arsenic spread and infiltrate into soil and water, what results in contamination. Clay minerals play an important role in the environment as natural adsorbents. This is, due to their ability of attracting and accumulating ions from water solutions by their structure, what leads to their immobilization. Halloysite is a clay mineral, belonging to the kaolin group minerals. Its structure is composed of stacked 1:1 layers built from octahedral (alumina) and tetrahedral (silica) sheets. Due to the fact that Poland has several kaolin deposits it is important to undertake research concerning possibility of using them as a natural scavenger of pollutants (Matusik & Bajda 2013, Matusik & Wóscisło 2014). Thus, the purpose of the research was to investigate the sorption affinity of natural, acid activated and calcinated halloysite toward Pb(II), Zn(II), Cd(II) and As(V).

In the study three mineral samples were chosen: natural halloysite – H, acid activated halloysite – HA and calcinated halloysite – HC. The H sample used in the study came from Polish deposit located in Dunino near Legnica which is owned and exploited by the Intermark Company. The last two samples are produced by Intermark on an industrial scale, by modifying H sample. The chemical activation of halloysite was carried out by sulphuric acid treatment at 100°C for 3 h, whereas the calcination temperature was 650°C.

The materials were characterized using XRD and FTIR methods. Additionally the cation exchange capacity (CEC) and specific surface area (S_{BET}) were measured. The CEC of tested materials were measured by adsorption of methylene blue. The S_{BET} was determined on the basis of the low temperature nitrogen adsorption isotherm measured at -196°C and calculated in accordance with the Brunauer-Emmet-Teller (BET) methodology. The materials sorption affinity towards Pb(II), Zn(II), Cd(II) and As(V) was investigated. Experiments were carried out at pH 5. After mixing 50 mg of each material with 2.5 ml of appropriate solution (20 g/L – solid/solution ratio), sample portions were shaken for 24 h at room temperature. The concentration of metals – Pb(II), Cd(II) and Zn(II) in supernatant solutions was determined using AAS method while the As(V) was measured using colorimetric molybdenum blue method.

The XRD pattern of the H sample showed a basal peak at 7.20 \AA , which is attributed to dehydrated halloysite-7(\AA). There were no significant changes in the XRD pattern of HC sample, which indicated that there were no significant changes in the clay structure due to calcination. In contrast, the XRD pattern of HA sample showed a decrease in intensity of $\sim 7.20 \text{ \AA}$ peak of halloysite and the appearance of new peak at 7.63 \AA was observed. Also, there were changes in the $19\text{--}25^{\circ} 2\theta$ region, what is an effect of structural disorder caused by sulfuric acid treatment. It is worth notifying that the FTIR

spectra of H and HC samples did not differ significantly. In turn, the bands changes for the HA are noticeable, which is in accordance with XRD results. After acid treatment the bands shape and intensity in 1300–1000 cm^{-1} region has changed indicating structural disorder of tetrahedral sheet. The spectra revealed that, the octahedral sheet and OH hydroxyls were not significantly altered by acid treatment. The HA sample exhibited the largest S_{BET} (171.6 m^2/g) while the S_{BET} for the H sample was the lowest (49.5 m^2/g). The calcination led to slight increase of S_{BET} value to 52.1 m^2/g in comparison to the H sample. The CEC results showed that differences between H (8.79 ± 0.1 meq/100 g) and HC (8.19 ± 0.2 meq/100 g) samples are insignificant, moreover the CEC of H sample is slightly higher. Such decrease can be explained by the loss of some the cation exchange sites, induced by heat treatment (Ho & Handy 1964). The increase in CEC value was observed for the HA sample (10.69 ± 0.5 meq/100 g). Sorption mechanism for raw halloysite can take place via ion-exchange and surface complexation through silanol Si-OH and aluminol Al-OH groups. The Pb(II) ions are more likely to hydrolyze and create PbOH^+ forms, which may link to deprotonated groups. This process is called surface complexation. Heavy metals such as Zn(II) and Cd(II) tend to adsorb through ion-exchange (Srivastava et al. 2005). The sorption capacity for H sample was found to follow the sequence $\text{As(V)} > \text{Pb(II)} > \text{Cd(II)} > \text{Zn(II)}$. In the case of cations, this behavior reflects the cations hydrolysis constants, which are equal to 7.71, 10.08, and 8.96 respectively. The sorption capacity for H sample reached 168.4 mmol As/kg, 37.2 mmol Pb/kg, 3.7 mmol Cd/kg and 1.9 mmol Zn/kg. The sorption onto HC sample was found to be the following: $\text{Pb(II)} \approx \text{Zn(II)} > \text{Cd(II)} > \text{As(V)}$. Comparing sorption results for HC to the results

for H sample, the increase of sorption for all tested heavy metals was observed. The sorption of cations reached an equilibrium equal to: 219 mmol Pb/kg, 212 mmol Zn/kg and 134 mmol Cd/kg. The sorption of As(V) decreased slightly in comparison to H sample. The acid activation resulted in an increase of active sites capable for Pb(II) adsorption and a decrease of active sites responsible for As(V) adsorption. Sorption equilibrium reached 235 mmol Pb/kg and 66 mmol As/kg. The results obtained for Zn(II) and Cd(II) indicated that sorption was not observed which may be due to lack of ion-exchange sites. The explanation of this behavior requires further studies. It is worth to underline the highest sorption capacity of H sample towards As(V) which is most likely due to surface complexation. The results indicated that depending on the type of pollutants an appropriate type of halloysite-based sorbent needs to be chosen.

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