











Halloysite-LDH heterostructured materials: performance in removal of selected anions from aqueous solutions

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Industrial wastewaters often contain mobile anionic forms of elements which are hazardous for the environment and human health. These cannot be removed by commonly applied precipitation techniques and most of known adsorbents e.g. raw clay minerals which show high affinity to cations. Layered double hydroxides (LDH) are synthetic phases which in contrast to clay minerals are excellent scavengers of anions. However it is reported that their use in real applications devoted to adsorption is of minor importance. This is mainly due to their swelling behavior which is not desired in dynamic column adsorption and high cost of production. Halloysite is a natural 1:1 layered aluminosilicate clay mineral which exhibits a unique tubular morphology. Previous studies showed that in experimental conditions halloysite can remove aqueous As(V) by chemisorption [1]. Therefore, the aim of this work was to synthesize halloysite-LDH composites and to examine their sorption capacity towards As(V), Cr(VI) and S(VI) in different experimental conditions using both artificial and real wastewaters.

The halloysite sample was obtained from Dunino deposit located near Legnica (SW Poland). In turn, LDH materials of Mg-Al and Mg-Fe type were synthesized by co-precipitation method. The halloysite-LDH composites containing LDH were prepared by two different approaches: direct precipitation of LDH in halloysite suspension and physical mixing of the two phases. The materials were characterized with XRD, FTIR, DTA/TG and SEM.

The XRD and FTIR results confirmed the LDH formation in absence and presence of the halloysite as peaks and absorption bands of both mineral components were visible. The LDH peaks intensity increased along with its content in the composite. The same observations were made for the absorption bands in the FTIR spectra. The LDH/halloysite materials in general showed lower efficiency than the raw LDH, however halloysite presence has several benefits in terms of future applications: (i) it significantly reduces the pH, especially in contrast to the calcined LDH, which enables reuse or safe disposal of purified water, (ii) it reduces swelling of the whole composite volume which opens the possibility for applications in column adsorption, (iii) it induces dual adsorption properties through additional cation adsorption and even chemisorption of selected anions e.g. As(V), and (iv) it substantially lowers the overall price of the adsorbent.

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[1] Maziarz, P., Matusik, J. (2016) The effect of acid activation and calcination of halloysite on the efficiency and selectivity of Pb(II), Cd(II), Zn(II) and As(V) uptake. Clay Minerals, 51, 385-394.