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Introduction to the Pieniny Klippen Belt



Efficiency of selected anions removal by Mg/Al and Mg/Fe LDH obtained with different sources of Mg

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The number of methods used for wastewater treatment is constantly growing and includes numerous studies on different materials. With a rapidly growing amount of wastewaters, there is a high demand for low-cost and efficient materials dedicated for specific industrial wastewaters. Adsorption is considered to be a rapid, efficient and relatively cheap wastewater treatment process, therefore adsorption efficiency of different types of adsorbents is studied. However, a minority of them are appropriate for the removal of anions. Layered Double Hydroxides (LDH) are a large group of crystalline non-silicates with general formula: $[\text{Me}^{\text{II}}_{1-x}\text{Me}^{\text{III}}_x(\text{OH})_2]^{x+} [\text{A}^{n-}]_{x/n} \cdot y \text{H}_2\text{O}$, where Me^{II} and Me^{III} are divalent- and trivalent metals, respectively. Their structure comprises of positively charged layers of metal hydroxides with weakly bonded anions counterbalancing the positive charge. As a result LDH have excellent anion-exchange properties. They are rare in nature, but can be easily synthesized in the laboratory, where their structural features and therefore adsorption properties can be controlled. Usually LDH are synthesized with the excessive use of chemical reagents, which generates a high cost of the final material. This study focused on the synthesis of Mg-Al and Mg-Fe LDH, which are the two most common LDH groups, where Mg precursor was replaced with abundant and cheap magnesite (M) (Grochów deposit, Poland). The materials were obtained via a simple co-precipitation method, with 2 h ageing instead of typically used 24 h. The adsorption affinity of the products towards As(V), P(V) and Cr(VI) was studied and compared to the adsorption efficiency of reference samples of Mg/Al and Mg/Fe LDH obtained from chemical reagents.

For the synthesis of the reference samples, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, instead of M, was used as a source of Mg(II). For all materials, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were used as a source of Al(III) or Fe(III) respectively. Prior to the synthesis, chemical reagents were dissolved in water and the M was dissolved in pure HCl to obtain Me^{II} and Me^{III} solutions. Then, appropriate solutions were dropwise added to the 2 M NaCl, with constantly controlled pH=10 with NaOH aqueous solution. The obtained precipitates were aged for 2 h, washed and dried at 60°C overnight. For the adsorption experiments, aqueous solution of $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, KH_2PO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ were used as sources of As(V), P(V) and Cr(VI) respectively, with initial pH set to 5 and concentration range of 2 - 25 mmol/L. The anion concentrations were determined using colorimetric methods: molybdenum blue for As(V) and P(V) and 1,5-diphenylcarbazide for Cr(VI). All the solids before and after adsorption experiments were characterized by XRD and FTIR.

The XRD confirmed the presence of Mg/Al and Mg/Fe LDH as compared to their natural analogues: hydrotalcite (ICDD #14-191) and pyroaurite (ICDD #14-293) standards, respectively. For the M/Al sample, an admixture of gibbsite was also present. Therefore, despite the short ageing time, all materials were successfully synthesized. The FTIR spectra exhibited bands attributed to the presence of water at $\sim 3450 \text{ cm}^{-1}$, Me-O vibrations below 1000 cm^{-1} and bands related to the presence of carbonates in the LDH interlayer space in the $1510\text{-}1360 \text{ cm}^{-1}$ region. Adsorption isotherms indicate that the materials exhibited high adsorption capacity depending



on the studied anionic adsorbate. For the M/Al and M/Fe LDH, adsorption efficiency towards As(V) and Cr(VI) was lower than for the reference samples and did not exceed 600 mmol/kg. However, these materials were equally efficient scavengers of P(V), where adsorption efficiency of the materials derived from magnesite was as high as their analogues derived from chemical reagents and reached ~15 000 mmol/kg.

The XRD patterns after adsorption experiments showed, that the structure of treated LDH did not change significantly. In the case of Mg/Fe and M/Fe materials the LDH peaks intensity decreased as a result of partial dissolution. The diffractograms of Mg/Al after As adsorption and Mg/Fe and M/Fe after P adsorption showed peaks attributed to Mg and Al-As and M-P bearing phases, respectively, suggesting precipitation as an additional mechanism of As and P removal. In turn, the Mg/Al pattern after Cr adsorption exhibited reflections characteristic for Al(OH)₃ and MgCl₂. The FTIR spectra in all cases showed appropriate bands related to the studied elements. Moreover, the bands attributed to carbonates in the spectra of Mg/Fe and M/Fe were of lower intensity, which may indicate either partial dissolution of LDH or anion exchange with adsorbate.

LDH materials were successfully derived via transformation of magnesite. M/Al and M/Fe were less effective than their reference analogues in the removal of As(V) and Cr(VI). However, no significant difference was noticed in the case of P(V) adsorption. In general, all materials showed a good affinity towards As(V), Cr(VI) and P(V).

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