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Mg–Fe LDH derived from magnesite and hematite and its affinity towards sulphates

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With an increasing demand for natural and relatively cheap materials for water purification, modified clay minerals are gaining more attention because of their effectiveness in anions removal (BEALL, 2003). However layered double hydroxides (LDH), called also "anionic clays" due to their similarities to clays, are synthetic and widely used materials with high affinity towards anionic forms (CHUBAR et al., 2017). Both clays and LDH have layered structure and variable layer charge, as well as similar colloidal and rheological properties. LDH with their general formula $[M^{II}_{1-x} M^{III}_{x} OH_2]_x+[A^{n-}]_{x/n}\times yH_2O$ are synthetic forms of natural minerals called hydrotalcites. They are built of positively charged brucite–like layers and hydrated anions between the layers which balance the charge. The LDH synthesis in laboratory conditions is very easy, but the need for using chemical reagents makes the whole process expensive. Therefore, the aim of this study was to use minerals as sources of trivalent and divalent metals to synthesize Mg–Fe LDH as well as their calcined analogues. Moreover, the investigation on their affinity towards sulphates (SO_4^{2-}) was carried out.

For the synthesis, magnesite [M], hematite [H], $MgCl_2\times6H_2O$ [Mg] and $FeCl_3\times6H_2O$ [Fe] were used as sources of magnesium and iron in order to obtain Mg-Fe LDH. Materials were obtained in different combinations: Mg – Fe, M – Fe, Mg – H, M – H. Magnesite and hematite were dissolved in hydrochloric acid before the synthesis to obtain Mg^{2+} and Fe^{3+} chloric solutions. The pH of Mg^{2+} solution was set to 10 by an aqueous NaOH, then the solution containing Fe^{3+} was added dropwise to the solution of Mg^{2+} with constant pH control in the range of 9–10. Solution was aged for 2 h at room temperature, washed with redistilled water and dried at 60˚C overnight. Materials were calcined at 400˚C for 3 h. The obtained materials were characterized by XRD, FTIR and SEM.

The XRD patterns confirmed the presence of LDH in all samples, as compared to magnesium iron carbonate hydroxide standard pattern (JCPDS #14-0293) (FAHAMI & BEALL, 2016). Simultaneously brucite (JCPDS #44-1482) was formed in all samples excluding the M – H sample. This was also confirmed by FTIR (band at 3700 cm^{-1}) (MILLIS et al., 2012). Moreover, characteristic vibrational bands of CO_3^{2-}, Mg-O and Fe-O were observed. The SEM images of obtained materials, compared to the starting mineral substrates, clearly indicated the changes of morphology. Tabular particles with characteristic for LDH layered structure were observed.

The obtained materials were tested in SO_4^{2-} sorption experiments using aqueous solution of K_2SO_4 with concentrations set to 1.0 mM/L and 5.0 mM/L and initial pH = 5. The SO_4^{2-} concentration was determined using turbidimetric method with $BaCl_2$. The sorption capacity measured for the 5 mM/L concentration did not exceed 130 mM/kg for the uncalcined materials. However, the sorption capacity measured for the calcined materials was not lower than 180 mM/kg and did not exceed 210 mM/kg. Thus, it is worth to notice, that the structure reconstruction of the calcined LDH increased the sorption capacity of the investigated materials. The mechanism responsible for the anion uptake by the uncalcined LDH was an anion exchange. Both mechanisms were confirmed by XRD and FTIR.

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