The efficiency and stability of Mg/Al and Mg/Fe as mineral-based adsorbents for the removal of Cr(VI) and Se(VI) from wastewaters

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Abstract:

A growing number of industrial processes leads to increasing loads of wastewaters. The variety of processes generate wastewaters with different chemical composition and other parameters such as pH. The currently applied wastewater treatment techniques are designed for general treatment. Including widely applied flotation, flocculation and precipitation processes, most of the pollutants are removed from the effluent. However, some processes involve the use of the anionic form of elements. Methods used for the removal of anions are difficult to apply, complicated or expensive. One of the methods adequate for anions removal is ion exchange. The bed applied in the ion exchange columns can be, in most cases, reused multiple times. This method, when applied in the industry, may be expensive and have its limitations regarding the initial concentration of elements and pH of the wastewater. However, depending on the conditions, may serve as a separate or complementary method for comprehensive wastewater treatment. In order to lower the price of the adsorbent, mineral-based materials are developed. Layered Double Hydroxides (LDH), are a group of layered minerals with the positive charge of the layer, balanced with the hydrated anions, thus adequate for the anion exchange. The LDH formula is the following: $[M^{II}_{1-x} M^{III}_x OH_2]_x+ [A^{n-}]_{x/n} \cdot y H_2O$, where M^{II} is a divalent metal, M^{III} is a trivalent metal and A is an anion. LDH are rare in nature, but their synthesis in the laboratory is straightforward. Moreover, the use of abundant, easily accessible and cheap materials can significantly lower the final price of an adsorbent. Therefore, the goal of this research was to obtain LDH with different chemical composition with the use of magnesite [M] ($MgCO_3$) (Braszowice deposit, Poland) as a source of M^{II} in the LDH structure, and define their affinity towards Cr(VI) and Se(VI) in comparison to the LDH obtained with the use of chemical reagents.
The materials were synthesized by the co-precipitation method. Chemical reagents used for the synthesis comprised: $MgCl_2 \cdot 6 H_2O$ [Mg], $AlCl_3 \cdot 6 H_2O$ [Al] and $FeCl_3 \cdot 6 H_2O$ [Fe]. Four variants of LDH were obtained: Mg/Al and M/Fe as reference samples, and M/Al and M/Fe as LDH obtained by the M transformation. The materials were tested in static adsorption experiments in the single- and multi-anion systems in order to determine the competition between Cr(VI) or Se(VI) and widespread anions: sulphates and nitrates. The initial concentration of Cr(VI) and Se(VI) was equal to 0.05 mmol/L, and the concentration of sulphates or nitrates was equal to 0.5 mmol/L. To compare the stability of the materials in different conditions, the initial pH was set to 5 or 3. The solid/liquid ratio was set to the lowest effective dose, and varied between 1-4 g/L, depending on the material.
All the materials showed ~100% efficiency in the single-element systems. The low pH did not influence their affinity towards Cr(VI) or Se(VI). However, while in most cases the presence of nitrates did not affect the removal effectiveness significantly, the presence of sulphates visibly lowered the efficiency, by up to 50%, especially at low pH. The stability of the materials was determined as the Mg release from the materials after experiments. The Mg release was not affected by the presence of competitive anions, and depending on the material was in the range of 0.69 - 4.86% at pH = 5, and 2.02 – 6.85% at pH = 3. The elements building the LDH structure are not toxic, and the Mg release is not significant. However, multiple regeneration cycles and further reuse of the materials may result in the decreased efficiency induced by the material dissolution. Despite that fact, because of their high effectiveness in anion exchange, LDH materials can be considered as materials with great potential for industrial wastewater treatment in anion-exchange processes.
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Karolina Rybka, MSc – mineral engineering graduate, interested in mineral-based materials for industrial wastewater treatment. Her research is focused on the synthesis, complex structural characterization of Layered Double Hydroxides, and their application for the anions removal. She is an author of 4 reviewed articles.

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