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Ultrasonic treatment and sorption properties of Mg^{2+}/Fe^{3+} layered double hydroxides

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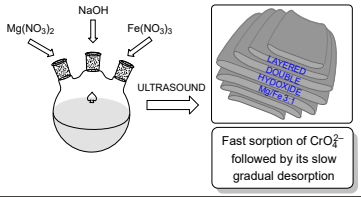
Ultrasonic treatment improved sorption properties of Mg^{2+}/Fe^{3+} (3 : 1) layered double hydroxides towards the chromate ion. The layered double hydroxides demonstrated unusual sorption patterns: fast sorption of up to 100% CrO_4^{2-} ions followed by their gradual complete desorption.



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Layered double hydroxides (LDHs) are inorganic compounds of positively charged layers formed by di- and trivalent metal hydroxides. The interlayer space of LDHs is filled with anions, which compensate for the positive charge of the layers.[1] The layered structure of LDHs is stable with the lability of interlayer anions[2]. The extensive intercalation chemistry of LDHs determines their use as containers for controlled drug release and as sorbents for wastewater treatment.[3]

According to the Scopus database, about 19 000 publications described the synthesis and applications of LDHs. Conventional synthesis of LDHs includes coprecipitation followed by maturation at 80 °C (a conventional method) or at >100 °C and a high pressure under hydrothermal synthesis conditions.[4] Sol–gel and urea methods, microwave synthesis, and cation substitution are also used.[5–12] These methods are just beginning to develop and often show impressive results. Recently, an ultrasonic approach to the synthesis of LDHs was reported.[13,14] The rapidity, ease, and convenience of the ultrasound approach make it promising for LDH preparation. In addition, acoustic conditions (the frequency, power, and amplitude of ultrasound) are easily tunable for elaboration of specific LDHs.[14]

Among the combinations of di- and trivalent metals in LDHs, Mg^{2+} and Fe^{3+} are among the least toxic metal ions.[15,16] Recently, Golubev *et al.*[17] described the ultrasonic synthesis of the Mg^{2+}/Fe^{3+} LDHs and their ability to sorb chromate ions. In this work, we synthesized Mg^{2+}/Fe^{3+} LDHs with a Mg^{2+}/Fe^{3+} ratio of 3 : 1. The LDHs were prepared by (*i*) a conventional coprecipitation method using the treatment of a reaction mixture at 80 °C for 24 (T-24) or 72 h (T-72), and (*ii*) an ultrasonic method in cavitation mode at a frequency of 22 kHz for 5 (US-5), 10 (US-10), and 15 (US-15) min in accordance with the reactions:

$$Mg(NO_3)_2 + 2NaOH = Mg(OH)_2 + 2NaNO_3;$$

$$Fe(NO_3)_3 + 3NaOH = Fe(OH)_3 + 3NaNO_3.$$

The resultant hydroxide-based systems were characterized using FTIR spectroscopy, thermal analysis, and X-ray powder diffraction. The Mg^{2+}/Fe^{3+} ratio of 3 : 1 in the synthesized samples was confirmed by titrimetric chemical analysis.

The IR spectra of LDHs recorded in the range of 4000–400 cm^{-1} were almost identical because of the identity of their chemical structures (Figure S1, see Online Supplementary Materials). A wide intense absorption band at 3750–3200 cm^{-1} corresponded to OH stretching vibrations of water molecules and hydroxyl groups.[18,19] A broadened low-intensity absorption band at 1641 cm^{-1} was due to bending vibrations of water molecules. The high- and low-intensity absorption bands at 1340 and 750 cm^{-1}, respectively, were attributed to vibrations of the nitrate anion,[20] while the medium-intensity band at 549 cm^{-1} was due to metal–oxygen covalent coordination bonds.[21]

The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) data for the LDHs indicated the global similarity of their chemical structures. In general, the thermal decomposition of samples occurred in three stages.[22,23] At the first stage, the loss of interlayer water was accompanied by a pronounced endo effect (weight loss of about 6%). At the second stage, also accompanied by a pronounced endo effect, hydrotalcite-like hydroxide layers were destroyed with their transformation into predominantly oxide layers. The NO_3^- anion also decomposed at the second stage.[24] The weight loss at the second stage was about 18%. The third stage was accompanied by a barely noticeable endo effect; the final decomposition of residual hydroxides and the NO_2^- anion occurred. As a result, a

mixture of iron(III) and magnesium(II) oxides was formed, and the weight loss was about 12%. Figure S2 shows a typical thermogram.

The SEM images of the LDHs were extremely similar (Figure S3) due to the scaly microstructure of the synthesized LDH powders, which, in turn, was a consequence of their layered organization. The SEM data are consistent with published data on other LDHs and their natural analogues, clays, which also have a scaly structure and layered architecture.[25]

Thus, titrimetric chemical tests and ICP, FTIR, TGA/DSC, and SEM analysis confirmed that the resulting compounds were layered double hydroxides. The concentration of nitrate ions was 50% of the total weight of magnesium and iron (in a ratio of 3 : 1). The X-ray powder diffraction analysis revealed differences in the crystal structure of the resulting LDH samples (Figure 1).

The diffraction patterns were typical of LDHs with a characteristic set of basal reflexes. Based on the width at half maximum (FWHM) of the basal reflection (003), we assessed the degree of crystallinity of the LDHs: the lowest FWHM values were observed in the most crystalline samples.[26] The degree of crystallinity increased in the series T-24 (FWHM 1.21), T-72 (FWHM 1.10), US-15 (FWHM 0.95), US-5 (FWHM 0.93), and US-10 (FWHM 0.89). Thus, the ultrasonic irradiation increased the degree of crystallinity of the products in comparison with traditional synthesis. Thus, short (5 min) and prolonged (30 min) exposures to ultrasound resulted in the crystallinity of the hydroxides, while the product US-10 with the highest degree of crystallinity was formed when the reaction was treated with ultrasound for 10 min. In 2002, Seida *et al.*[27] prepared Mg^{2+}/Al^{3+} LDHs under the action of ultrasound and found that the applied ultrasound resulted in an increase in the crystallinity of the LDHs compared to those obtained by the conventional method. Similar results accumulated in the literature were summarized 20 years later in a review by Kalawoun *et al.*[14] There is no consensus among experts in sonochemistry regarding the explanation of the above phenomenon. Among the effects of ultrasound on the synthesis of LDHs, it is believed that (1) vigorous stirring of the reaction mixture by ultrasound during gelation caused a more homogeneous distribution of metal ions than that upon intense mechanical stirring; (2) ultrasound accelerated ion exchange and increased the production of a hydrotalcite-like phase, which crystallized more easily; and (3) cavitation caused by ultrasound accelerated crystallization processes. These effects can increase the crystallite size and degree of crystallinity.[28,29] Thus, optimization allowed us to find the ultrasonic exposure time that led to the highest degree of crystallinity of the product.

This study was also focused on the sorption properties of the LDHs towards chromate anions. Figure 2 demonstrates different quantitative capacities of all samples, but qualitatively the main patterns were similar. The time dependences of the amount of sorbed chromate had two sections: the first section of each curve illustrated intense fast sorption up to a maximum, and the second one corresponded to gradual desorption. According to published data on chromate sorption by LDHs, the kinetics of the process reached a plateau at a sorption maximum.[30–32] As for the Mg^{2+}/Fe^{3+} LDHs, the described kinetics of chromate sorption also had the same pattern, but it was presented only for Mg^{2+}/Fe^{3+} (2 : 1) LDHs.[33,34] Thus, this work showed that the sorption behavior of Mg^{2+}/Fe^{3+} LDHs towards chromate depends dramatically on the metal ratio.

Figure 2 also shows the influence of the preparation method of LDHs on their sorption characteristics. In general, these characteristics correlated with the results of X-ray powder diffraction analysis. The most crystalline samples had the most attractive sorption characteristics. The least crystalline samples T-24 and T-72 exhibited low sorption activity (about 60 and 75% chromate, respectively). They were characterized by higher rates of both sorption and desorption. As the crystallinity of the samples increased, their sorption activity increased in the order T-24, T-72, US-15, US-5, and US-10. These data are not surprising because an improvement in the sorption capacity of LDHs with an increase in their crystallinity was observed.[14] Seida *et al.*[27] noted that Mg^{2+}/Al^{3+} LDHs obtained under ultrasound, which had greater crystallinity, absorbed humic acids better than those prepared by the conventional method.

The results of sorption experiments allowed us to conclude that the undoubtedly leading system was US-10, which completely sorbed chromate ions from an aqueous solution quite quickly (in about 24 h) and then gradually completely desorbed them. This feature can be attractive for the repeated use of US-10 as a spontaneously recyclable sorbent for chromate. We found that the sorption and desorption activity of US-10 remained unchanged even after ten times of use. We believe that the processes of sorption and then desorption observed here are characteristic of CrO_4^{2-} ions since the sorption behavior of other molecules [for example, the dangerous environmental pollutant 2,4-dichlorophenoxyacetic acid (2,4-D)] was different.[35] To explain the observed phenomenon, further research is needed, both mechanistic and using the arsenal of quantum chemistry.

The results of this work can be considered in two principal perspectives. First, we found that the ultrasonic treatment of a reaction mixture significantly improved the sorption properties of layered double hydroxides, and this effect dramatically depended on the acoustic parameters, such as the frequency of ultrasound. Second, we observed for the first time an unusual sorption of chromate by layered double hydroxides. This was a fast and effective sorption of up to 100% of the sorbate followed by the gradual complete desorption for several days.

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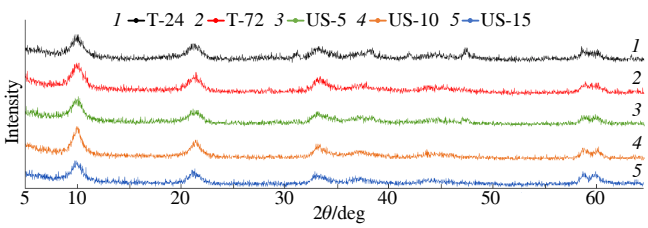

Figure 1 X-ray diffraction patterns of the LDHs.

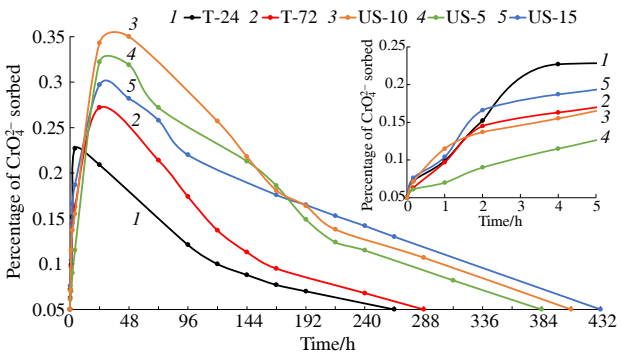

Figure 2 Sorption properties of the LDHs.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7736.

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