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Cr(VI) removal from water by synthesized Mg-Fe layered double hydroxides – Effect of calcination

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In the present study, Mg-Fe layered double hydroxides (Mg-Fe LDHs) have been synthesized by the co-precipitation method at pH 10 and at pH 12 and used for Cr(VI) removal from aqueous solutions. Their characterization by XRD analysis confirms the lamellar structure before calcination and shows the formation of spinel (Mg-Fe_2O_4) and magnesium oxide after calcination at 500°C. Batch experiments reveal that Cr(VI) removal by the prepared LDHs increases with the decrease of the solution pH. Whatever the prepared LDH used, Cr(VI) removal processes is spontaneous and exothermic. The kinetics is well described by the second-order model and the equilibrium data follow the Langmuir model. The lower removal equilibrium time (3 h) is obtained in the case of the uncalcined LDH prepared at pH 12. The calcination of the Mg-Fe LDHs prepared either at pH 10 or at pH 12 implies the decrease in Cr(VI) removal capacity.

Keywords: Layered Double Hydroxydes, Cr(VI) removal, Adsorption, Water treatment

Chromium is used in many industries, such as in the steel industry, surface treatment, wood preservation, leather tanning and in the manufacture of magnetic tapes etc.[1]. In water, chromium can be found in two oxidation states (Cr(III) and Cr(VI)). Cr(VI) is considered as toxic and dangerous pollutant[2]. Chromium speciation in water depends on several parameters such as redox potential, pH, concentration and the presence of complexing agents. Under anoxic conditions, trivalent chromium is expected to be the only form. In oxygenated aqueous solutions and depending on pH, Cr(VI) can be found as dichromate ($Cr_2O_7^{2-}$), bichromate ($HCrO_4^-$) and chromate (CrO_4^{2-})[3]. Numerous treatment methods have been used for the removal of metals from water. The membrane and ion exchange methods are known to be effectives[4,5] but they remain too expensive for their application at large-scale waste water treatment. In contrast, adsorption is recognized as effective and economical. This method is largely used for the removal of pollutants from wastewater[6,7].

Clays have been extensively used as adsorbents for heavy metals removal. They are recognized for their efficiency for removing cationic metals but they are not efficient for removing metals which exist in anionic form like Cr(VI). Recently, the layered double hydroxides (LDHs) also called anionic clays have been tested as new materials in water treatment for removing various pollutants. Their general formula is: $M_{1-x}^{II}M_x^{III}(OH)_2]^{x+}\ X_{x/n}^{n-}\ mH_2O$ [10]; where M^{II} is the divalent cation (Mg^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, Fe^{2+}), M^{III} is the trivalent cation (Al^{3+}, Cr^{3+}, Fe^{3+}, Co^{3+}, Mn^{3+}) and X^{n-} is the interlayer anion. Magnesium and aluminum lamellar double hydroxides have been successfully used in Cr(VI) removal with capacities of 339 mg/g, 246 mg/g and 71.91 mg/g[8,9]. Several studies have been interested in Cr(VI) removal by Mg-Fe LDHs. A high removal rate (above 98%) was obtained by using Mg-Fe (2:1) LDH prepared at pH 9-10 [Cr(VI) initial concentrations 0.2 and 1 mmol/L, pH:5)[10]. Cr(VI) removal capacity of 2.53 mg/g was obtained in the case of Mg-Fe (2:1) LDH prepared at pH 10 (LDH dose: 2g/L, Cr(VI) concentration: 10mg/L, pH: 6)[11]. In the case of Mg-Fe (3:1) LDH prepared at pH: 9, the Cr(VI) removal capacity was 6.2 mg/g at pH: 5 (Cr(VI) concentration: 100 mg/L, LDH dose: 10g/L)[12]. On the other hand, many authors have been interested in the use of calcined layered double hydroxides and various calcinations temperatures have been used[13-15].

In certain studies, it has been demonstrated that the calcined LDHs have more efficiency for pollutants removal as is the case of selenite removal by Mg-Fe (2:1)(Ref: 16). The aim of the present study is to explore of the effect of calcination and the preparation pH on the capacity of Mg-Fe (3:1) lamellar double hydroxides for removing Cr(VI) from water. The temperature 500°C has been used for calcination because for higher temperatures, the formed phases are stable and consequently the property of memory effect is lost; the layer structure cannot be recovered after rehydration. It has been proved that the LDHs calcined at temperatures higher than 500°C do not construct at all upon rehydration[17].

Experimental Details

Preparation and characterization of Mg-Fe LDHs

In the present study, double lamellar hydroxides were prepared by co-precipitation method with a Mg/Fe molar ratio of 3 at pH 10 and at pH 12. Precipitation was occurred by adding NaOH solution (1 M) to iron and magnesium solution ($MgCl_2.6H_2O$ and $FeCl_3$) at room temperature under magnetic stirring. The obtained suspensions were heated at 50°C for 6 h, filtered and washed several times with distilled water and then dried in the oven at 105°C for 24 h giving then the double lamellar hydroxides Mg-Fe(12) and Mg-Fe(10). A calcination is carried out at 500°C for 3 h in order to obtain the calcined double lamellar hydroxides Mg-Fe(12, 500) and Mg-Fe(10, 500).

The prepared LDHs were characterized by X-ray diffraction (XRD) using a PANALYTICAL X'PERT apparatus equipped with a copper anticathode (λ =1.5406 Å). The pH of zero charge point (pH_{PZC}) which corresponds to the pH value for which the net surface charge is zero, was determined by the pH derivative method. This method consists of monitoring the pH evolution of the prepared LDHs suspensions in NaCl (0.01 M) at different pH after shaking for 48 h.

Cr(VI) removal experiments

The Cr(VI) removal experiments were performed in batch in 250 mL bottles. The experimental solutions were prepared by combining the Cr(VI) solution prepared from potassium salt (K_2CrO_4) and a dose of each prepared LDH. The solution pH was adjusted using HCl solution. The formed suspensions were stirred for the desired period of time; the equilibrium pH values were measured and the suspensions were centrifuged at 3000 rpm for 15 min. pH measurements were performed using M210 pH meter equipped with a combined glass electrode. Cr(VI) was determined in the recovered supernatants by the diphenylcarbazide method using Shimadzu 1650 UV-visible spectrophotometer at a wavelength of 540 nm.

Results and Discussion

Characterization of the prepared LDHs

The lamellar structure of the prepared uncalcined Mg-Fe LDHs is confirmed by the presence of the X ray peaks corresponding to (hkl) values (003) and (006)[18]. After calcination at 500°C, the lamellar structure is destroyed and these peaks disappear (Fig. 1). The observed new peaks correspond to magnesium oxide (MgO) and spinel ($Mg\text{-}Fe_2O_4$). The same structures have been identified in the case of other calcined Mg-Fe LDHs[19,20]. The spinel is better crystallized in the case of the LDH prepared at pH 10; the corresponding peaks are more intense (2θ = 35.41; 57.03; 62.48°). In all cases, iron oxides are not detected. This can be due to the high initial concentration of Mg(II) compared to Fe(III) and dispersion of Fe(III) in the structure, making the formation of iron oxides difficult[21,22]. The preparation pH seems to have an effect on the structure of the prepared Mg-Fe LDH(s) after calcination at 500°C.

The prepared Mg-Fe LDHs are characterized by pH_{pzc} values higher than 9. Consequently, their surfaces are positively charged at pH< 9 and they appear to be good physical adsorbents for anions. The values measured in our study (9.96 for Mg-Fe(12) LDH; 9.73 for Mg-Fe(10); 9.91 for Mg-Fe(12, 500) and 10.13 for Mg-Fe(10, 500) are close to those of the reported Mg-Fe LDHs with various Mg/Fe molar ratios[11,22,23].

Cr(VI) removal

Effect of pH and temperature

In the present study, the pH effect on Cr(VI) removal has been studied in the pH range 3-9 with an initial concentration of 5 mg/L. At very acidic pH (pH<3), partial dissolution of the lamellar double hydroxides has been observed in the reported

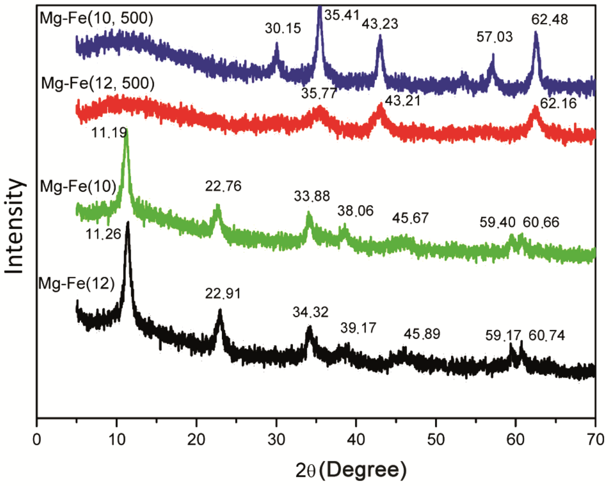

Fig. 1 — XRD patterns of the prepared Mg-Fe LDHs

literature[10,19]. The obtained results show that the uncalcined LDHs are more efficient for Cr(VI) removal. The maximum removal rate is obtained at pH<5 (Fig. 2). In this pH range, the surfaces of the prepared LDHs are positively charged favouring the electrostatic interaction with anionic chromium species. The pH increase implies the decrease of Cr(VI) removal due to the competition effect of OH^- ions. As pH increases to about 8, Cr(VI) removal rate decreases to 27% in the case of Mg-Fe(12), to 31% in the case of Mg-Fe(10), to 5% in the case of Mg-Fe(12, 500) and to 17% in the case of Mg-Fe(10, 500). The obtained experimental data are consistent with those observed in the case of Cr(VI) removal by Ni-Al(2:1) LDH and by Mg-Al(2:1)[24,9]. However, they are not in agreement with what has been observed for sulfate removal. The pH effect was not important on the sulfate removal by Mg-Fe (3:1) LDH prepared at pH 10 and calcined at 400°C[25].

The effect of temperature on Cr(VI) removal by the synthesized LDH(s) has been studied in the range 20°C-45°C with initial concentration of 5 mg/L. The calculated thermodynamic parameters are summarized in Table 1. The free enthalpy values (ΔG) show that the adsorption process is spontaneous. The calculated ΔH values imply the exothermic nature of the removal processes. The negative values of ΔS reflect a decrease of the randomness at the LDHs-solution interface. This result is not in agreement with what has been observed in the case of Cr(VI) removal by Mg-Fe(2:1) LDH[11] and by Mg-Al-NO_3(2:1) LDH[9], in these two cases, the calculated ΔS values were positives.

Kinetic study

For an initial concentration of 5 mg/L, Cr(VI) uptake by the prepared LDHs is characterized by two steps; a first fast step followed by a second slow one (Fig. 3). The lowest equilibrium time (180 min) is obtained in the case of Mg-Fe(12) LDH. In the three other cases, the equilibrium time is higher than 300 min. An equilibrium time of 120 min has been obtained in the case of Cr(VI) removal at pH 6 by Mg-Fe (2:1) LDH (Cr(VI) initial concentration: 10mg/L and LDH dose 2 g/L)[11] The Cr(VI) removal by Mg-Al LDH prepared at pH: 9.5 and calcined at 450°C has been characterized by slower kinetics; an equilibrium time of 600 min was obtained (Cr(VI) concentration of 10.18 meq/L and LDH dose of 0.2 g)[1].

Several models are used to characterize the Cr(VI) removal kinetics. The obtained results (Table 2) show that the experimental data can be described by these models in the order: pseudo-second order > intra-particle diffusion > inter-particles diffusion > pseudo-first order > Elovich. In all cases; the removal capacities at equilibrium calculated by the pseudo-

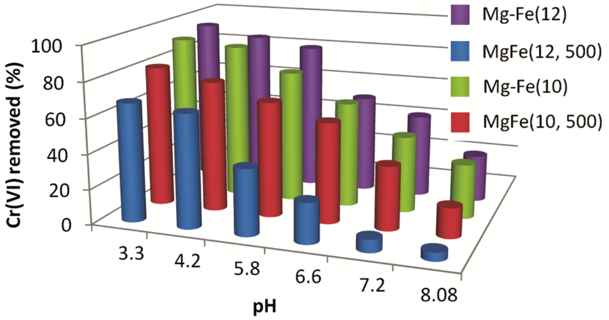

Fig. 2 — Effect of pH on Cr(VI) removal by the prepared LDHs (LDH dose: 0.5 g/L, Cr(VI) concentration: 5 mg/L, time:1 h)

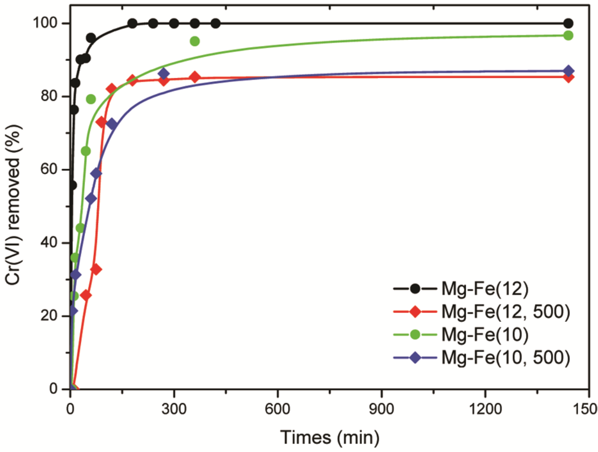

Fig. 3 — Kinetics of Cr(VI) removal by the prepared Mg-Fe LDHs (LDH dose: 0.5 g/L, Cr(VI) concentration: 5 mg/L, pH: 4.25)

Table 1 —Thermodynamic parameters of Cr(VI) removal by the prepared Mg-Fe LDHs (pH: 4.25)

LDH	ΔH (KJ mol^{-1})	ΔS (J $K^{-1}mol^{-1}$)	ΔG (kJ mol^{-1})		
			25°C	35°C	45°C
Mg-Fe (12)	-113.935	-5.082	-3.922	-3.603	-3.333
Mg-Fe(12, 500)	-276.345	-1.197	-1.820	-1.662	-1.568
Mg-Fe(10)	-66.849	-3.013	-5.086	-2.032	-0.963
Mg-Fe(10, 500)	-45.617	-2.113	-2.666	-0.239	0.629

Table 2 — Kinetic parameters of Cr(VI) removal by the prepared Mg-Fe LDHs (pH 4.25)

Model	Linear equation	Parameter	LDH			
			Mg-Fe (12)	Mg-Fe (12, 500)	Mg-Fe (10)	Mg-Fe (10, 500)
First order	$\ln(Q_e - Q_t) = \ln Q_e - Kt$	Q_e (mg/g)	5.14	7.74	6.97	8.57
		K (min^{-1})	0.044	0.0198	0.0109	0.0169
		R	0.824	0.896	0.963	0.985
Second order	$\frac{t}{Q_t} = \frac{1}{KQ_e^2} + \frac{1}{Q_e} t$	Q_e (mg/g)	9.57	8.89	9.85	8.87
		K (g mg^{-1} min^{-1})	0.006	0.008	0.004	0.004
		R	0.992	0.998	0.999	9.999
Elovich	$Q_t = \frac{1}{\beta}\ln(\alpha.\beta) + \frac{1}{\beta}\ln t$	α (mg.g^{-1} min^{-1})	69.574	33.750	1.536	1.437
		β (g mg^{-1})	0.875	1.061	0.671	0.755
		R	0.819	0.537	0.816	0.897
Intraparticle diffusion	$Q_t = K\sqrt{t} + C$	K (mg.g^{-1} $min^{-1/2}$)	0.374	0.041	1.300	0.471
		C (mg g^{-1})	6.716	7.763	2.154	1.459
		R	0.879	0.993	0.945	0.956
Interparticle diffusion	$\ln(1-(Q_t/Q_e)^2) = -K\,t$	K	0.0886	0.0397	0.0219	0.0338
		R	0.886	0.896	0.915	0.985

first order model equation are far from the obtained experimental capacities, implying that this model can not be suitable for describing the kinetics of Cr(VI) removal. However, those calculated by the second order equation coincide well with the experimental data. The same model has been successfully applied to the sorption of Cr(VI) at pH 6 by Mg-Al-NO_3(2:1) LDH prepared by the co-precipitation method at pH 10[9] and by Mg-Al-Fe LDH prepared with different molar ratios by the mechano-chemical method at pH 5[(Ref: 26)]. This model suggests the existence of chemisorption and assumes constant adsorption energy and no interaction between the adsorbed molecules. The rate constants calculated by the pseudo-second order model show that the adsorption is faster in the case of LDHs prepared at pH 12. Cr(VI) diffusion to the prepared LDHs seems to follow the intraparticle diffusion model rather than the interparticle diffusion model.

Equilibrium study

In the concentration range used, the experimental Cr(VI) adsorption isotherms suggest a progressive saturation of the prepared LDHs (Fig. 4). The same behavior has been observed in the case of Cr(VI) removal by Mg-Fe (3:1) LDH prepared at pH 9 and by Mg-Al-Fe LDH prepared with different molar ratios[12,26].

The parameters of Langmuir, Freundlich and Temkin equations applied to the experimental data are summarized in Table 3. According to the correlation coefficients, Cr(VI) removal by the prepared Mg-Fe LDHs can be described by these equations in the order: Langmuir > Temkin > Freundlich. The adequacy of the Langmuir equation confirms that the LDHs surfaces have a finite number of identical sites energetically uniform. Cr(VI) removal by others LDHs has been well described by both Langmuir and Freundlich equations[11,12,27]. In the present study, the calculated Cr(VI) removal capacities show that the uncalcined LDHs are more efficient than calcined ones. The effect of the pH of LDHs preparation on Cr(VI) removal seems to be significant only in the

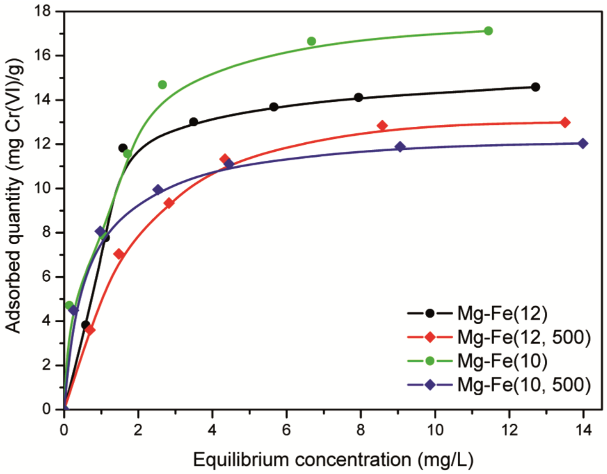

Fig. 4 — Experimental isotherms of Cr(VI) removal by the prepared Mg-Fe LDHs (LDH dose: 0.5 g/L, pH:4.25, time:24 h)

Table 3 — Isotherms parameters ofCr(VI) removal by the prepared Mg-Fe LDHs (pH 4.25)

Model	Linear equation	Parameter	LDH			
			Mg-Fe (12)	Mg-Fe (12, 500)	Mg-Fe (10)	Mg-Fe (10, 500)
Langmuir	$\frac{1}{Q} = \frac{1}{Q_{max} K} \times \frac{1}{C_r} + \frac{1}{Q_{max}}$	R^2	0.900	0.982	0.942	0.996
		K	0.365	0.379	0.485	2.316
		Q_{max} (mg/g)	23.42	17.65	24.19	12.05
Freundlich	$\ln Q = \frac{1}{n} \ln C_r + \ln K$	R^2	0.665	0.848	0.924	0.884
		K	9.164	5.255	8.953	7.197
		n	4.699	2.385	3.153	4.140

case of calcined LDHs. The two uncalcined LDHs give a removal capacity of about 24 mg/g. However, in the case of the calcined LDHs, the removal capacity decreases from 17 mg/g for the LDH prepared at pH 12 to 12 mg/g for the LDH prepared at pH 10.

Conclusion

The results obtained in the present study show that Mg-Fe LDHs prepared with a Mg/Fe molar ratio 3 at pH 10 and at pH 12 can be successfully used for Cr(VI) removal at pH<5. After calcination at 500°C, their efficiency for Cr(VI) removal decreases. The pH of the LDHs preparation has an effect on Cr(VI) removal only in the case of calcined Mg-Fe LDHs. Whatever the Mg-Fe LDH used, Cr(VI) removal decreases with the temperature increase. The obtained Cr(VI) removal capacities are about 24 mg/g in the case of uncalcined LDHs (Mg-Fe(12) and Mg-Fe(10)) and 17 mg/g and 12 mg/g in the case of calcined ones (Mg-Fe(12, 500) and Mg-Fe (10, 500)).

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