

CHROMATE REMOVAL FROM AQUEOUS SOLUTION USING LAYERED DOUBLE HYDROXIDES BEADS

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Abstract

In this study, a novel layered double hydroxides beads (LDHs beads) were developed for removal of chromium. The LDHs beads (MgAl beads and MgFe beads) were generated by impregnating synthetic MgFe-Cl (2:1) and MgAl-Cl (2:1) into alginate/poly(vinyl alcohol)-glutaraldehyde gel bead. The adsorption of chromate (Cr(VI)) onto the 8 % LDHs beads was investigated by performing both equilibrium and kinetic batch tests. Equilibrium tests showed that adsorption of chromate followed Langmuir isotherm and that the 8 % LDHs beads were capable of removing chromate ($q_m = 1.3912-1.4380 \text{ mg Cr.g}^{-1}$). It was further revealed from kinetic tests that removal efficiency of chromate was 92.50 % for 8 % MgAl beads and 90.01 % for 8 % MgFe beads at the initial chromate concentrations of 45 mg Cr.L^{-1} . This indicates that the 8 % LDHs beads developed in this study can be used as promising adsorbents for simultaneous removal of chromate from industrial wastewater or groundwater containing these contaminants.

Keywords. Layered double hydroxides beads, chromate removal, adsorption, kinetics, isotherm.

1. INTRODUCTION

Heavy metal should be removed from wastewater before disposal since they are highly toxic even at low concentrations, persistence, bioaccumulation potential and therefore sources of great concern in aquatic environment. There are number of technologies available for removal of heavy metals from wastewater such as precipitation, filtration, membrane separation, adsorption, etc. For chromium waste treatment, reduction and precipitation technology have been used over the last few decades. Hexavalent chromium (Cr^{VI}) must first be reduced to the trivalent state (Cr^{III}) and then precipitated with lime [1]. Disadvantages of this technology are (i) the reducing agents must be used an excess dosage and the reaction only occurs at acidic pH values (ii) at acidic pH, the quantities of lime required for neutralization and precipitation must be higher than those of basic pH values, (iii)

quantities of sludge produced must be a lot after treatment. Therefore, adsorption has been considered one of the most promising technologies for removing chromate (Cr^{VI}) from wastewater, because of its removal effectiveness, low cost and easy equipment handling.

Layered double hydroxides (LDHs) are a class of nanostructured anionic clays. The general formula of LDHs is $[\text{M}_{1-x}\text{M}_x^{3+}(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$, where M^{2+} is the divalent cation, M^{3+} is the trivalent cation, x is the molar ratio of $\text{M}^{3+}/(\text{M}^{2+}+\text{M}^{3+})$, and A is the interlayer anion of valence n . LDHs consist of positively charged brucite-like sheets which are balanced by the intercalation of anions in the hydrated interlayer regions [2, 3]. LDHs have number of advantages over other materials for environmental remediation applications, as they are nontoxic, cheap and easily to prepare. Their applicability as adsorbents highlights their importance in environmental remediation. Recently,

LDHs have been successfully used for removing of negatively charged species from aqueous solution, due to their high specific surface areas, high anion exchange capacities and flexible interlayer space [3-5]. However, due to low hydraulic conductivity and difficulties encountered in separation such as filtration or centrifugation, the use of a powder form of LDHs remain as major challenges for water and wastewater treatment plant. To overcome these problems, the encapsulation of LDHs powder within the bead of alginate/poly(vinyl alcohol) (PVA) with crosslinker glutaraldehyde would help to solve the separation problem [6-8].

Therefore, this paper focuses on development of a new adsorbent, alginate/PVA-glutaraldehyde beads impregnated with LDHs for removal of chromate in aqueous solution. In order to examine the adsorption capacity of the LDHs beads, both equilibrium and kinetic batch studies were performed.

2. EXPERIMENTAL

2.1. Chemical

All chemicals were of analytical grade. The iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), aluminum chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$), magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), zinc chloride (ZnCl_2), sodium hydroxide (NaOH) and potassium chromate (K_2CrO_4) were purchased from Xilong Chemical Factory, Guang Dong and Shanghai Chemical Company.

2.2. Preparation of LDHs beads

Preparation of LDHs powder: Powders of LDHs (MgAl 2:1 and MgFe 2:1) were prepared by coprecipitation method. First, solutions containing MgCl_2 , AlCl_3 or MgCl_2 , FeCl_3 (molar ratio of $\text{Mg}^{2+}/\text{Al}^{3+}$ or $\text{Mg}^{2+}/\text{Fe}^{3+}$ about 2:1) were added dropwise at 2 mL/min into alkali solution of 1 M NaOH ($\text{pH} = 11 \pm 0.2$) at $65 \pm 5^\circ\text{C}$ under vigorous stirring at 400 rpm. The pH of the solution was maintained at 11 by addition of 2 M NaOH . The mixture was then aged at 65°C for 24 hours in mother liquor. The obtained materials were centrifuged, washed and dried at 65°C for 24 h and calcined at 400°C for 4 h in an electric muffle furnace (Vulcan 3-103). The obtained LDHs are labelled MgAl 2:1 and MgFe 2:1

Preparation of LDHs beads: The LDHs beads (MgAl beads and MgFe beads see in Fig.1) were prepared by entrapped powder of each MgAl 2:1 and MgFe 2:1 into alginate, PVA and glutaraldehyde blend gel. First, a 100 mL solution containing 1 g of

sodium alginate and 0.5 g of PVA and 0.5 mL of glutaraldehyde was stirred by magnetic stirrer at 400 rpm and 70°C for 5 h. Then, the desired amount of each MgAl 2:1 and MgFe 2:1 was added to solution under intensive stirring at 250 rpm for 1 h to give the homogeneous suspension. The suspension contained in plastic syringe was dropped into a stirred reservoir containing a 500 mL solution of 0.3 M CaCl_2 in order to form 4.0 mm spherical beads. The beads were allowed to be cured in the same CaCl_2 solution for 24 h under stirring and then rinsed with deionized water to remove excess Ca^{2+} . The obtained MgAl beads and MgFe beads containing of 2, 4, 6, 8 and 10 % of MgAl 2:1 and MgFe 3:1. For a comparison, 0 % LDHs beads were also prepared by alginate, PVA and glutaraldehyde blend gel without adding LDHs

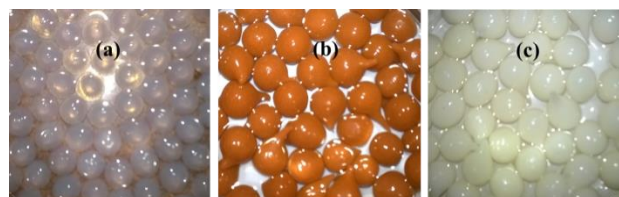


Figure 1: The as-prepared beads of (a) 0 % LDHs, (b) 8 % MgFe and (c) 8 % MgAl

2.3. Characterization of LDHs beads

The X-ray diffraction (XRD) patterns of materials were recorded on a Bruker D8 Advance Diffractometer. The patterns with $\text{CuK}\alpha$ radiation ($\lambda = 1.54051 \text{ \AA}$) at 40 kV and 40 mA were recorded in the region of 2θ from 5° to 70° . Scanning Electron Microscopy (SEM) images were obtained using JEOL with an accelerating voltage of 20 kV.

2.4. Adsorption experiments

The studies of chromate uptake were performed by batch adsorption method and in triplicate. The first batch experiments were conducted to examine the effect of MgAl (2:1) and MgFe (2:1) content in beads on chromate removal. A series of 250 mL Borosil conical flask containing 3 g of each P-P beads, MgAl beads and MgFe beads (2, 4, 6, 8 and 10%) were added to 100 mL of chromate solution at concentration $45 \text{ mg Cr} \cdot \text{L}^{-1}$. The mixture was continuously shaken at 250 rpm for 8 h. Aliquots were taken from the suspension followed by filtered through a $0.45 \mu\text{m}$ membrane filter. The quantity of Cr in filtrate was determined by AAS (AA 6800, Shimadzu, Japan). Further adsorption experiments were performed to observe the effect of solution pH

on chromate removal. The initial chromate concentration and adsorbent dosage were fixed at 50 mg Cr. L⁻¹ and 3 g of 8 % MgAl beads or MgFe beads in 100 mL Cr^{VI} solution, respectively. The initial solution pHs ranged from 6.0 to 9.0 and the contact time was set at 8 h. For sorption kinetics, a series of 250 mL Borosil conical flask containing 3.0 g of adsorbent and 100 mL of chromate solution at concentration 45 mg Cr. L⁻¹ at solution pH of 7.0 was prepared. The mixtures were continuously shaken at 30 °C and 250 rpm). Aliquots were taken at different time interval. Equilibrium batch experiments were conducted with 3.0 g of adsorbent in 100 mL chromate solution in concentration range 4.5-65.0 mg. L⁻¹ at pH of 7.0 and contact time was set at 8 h.

The sorption capacity (q_t , mg. g⁻¹) at any time, t was calculated using the following equation:

$$q = \frac{(C_o - C_t) \times V}{m} \quad (1)$$

where C_o (mg. L⁻¹) is the initial concentration of the chromate in aqueous solution; C_t (mg. L⁻¹) is the chromate concentration in aqueous phase at time t , V (L) is the solution volume and m (g) is the mass of adsorbent.

3. RESULTS AND DISCUSSION

3.1. Characterization of materials

XRD patterns of beads with and without LDHs are shown in figure 2.

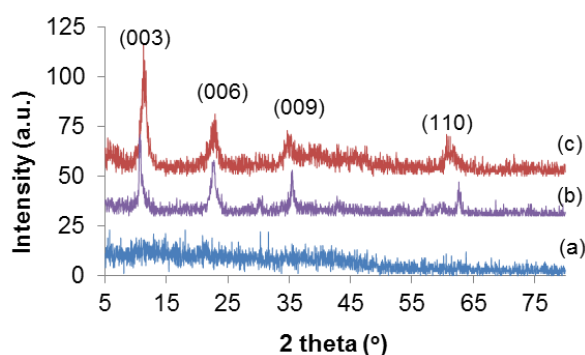


Figure 2: XRD patterns of beads with (a) 0 % LDHs, (b) 8 % MgFe and (c) 8 % MgAl

The measured XRD patterns of all samples fitted well to layered double hydroxide with basal reflections of planes hkl (003), (006), (009) and (110) by comparison with JCPDS card No. 22-0700, then, pure LDHs were obtained. It is obviously seen that almost all the diffraction peaks were sharp and symmetrical, indicating good

crystallinity. The interlayer spacing of the samples corresponding to the (003) and (006) plane recorded at 7.91 and 3.92 Å, respectively, that demonstrated general features of layered double hydroxides[1,9-11].

The morphologies of as-prepared LDHs beads were investigated by SEM and are shown in Figure 3. The analysis of SEM micrographs revealed that the surface of MgAl beads and MgAl beads were not homogenous in comparison with the surface of 0 % LDH beads. It demonstrated that the powders of MgAl 2:1 and MgFe 2:1 were mixed with alginate/PVA-glutaradehyde.

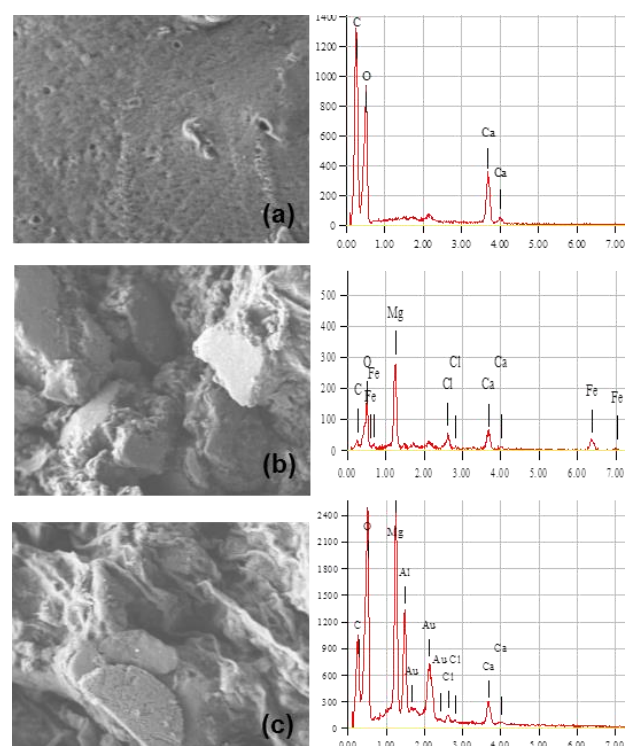


Figure 3: SEM micrographs of beads with (a) 0 % LDHs, (b) 8% MgFe and (c) 8 % MgAl

3.2. Chromate adsorption

3.2.1. Effect of mass of LDHs content and pH

The effect of percentage of MgFe (2:1) and MgAl (2:1) content in beads on chromate removal is presented in figure 4. The average chromate removal efficiency increased sharply with increasing mass of LDHs in the polymer beads. For the experiments, no significant chromate adsorption (≈ 1 %) was observed for the 0 % LDHs beads, whereas the average adsorption of chromate onto 8 % LDHs beads was about 90.0 %. It is well evident that potential for chromate removal of LDHs is high.

There was no significant difference in chromate adsorption by 8 % LDHs beads in comparison with 10 % LDHs beads. Consequently, all subsequent adsorption experiments were conducted with 8 % LDHs beads.

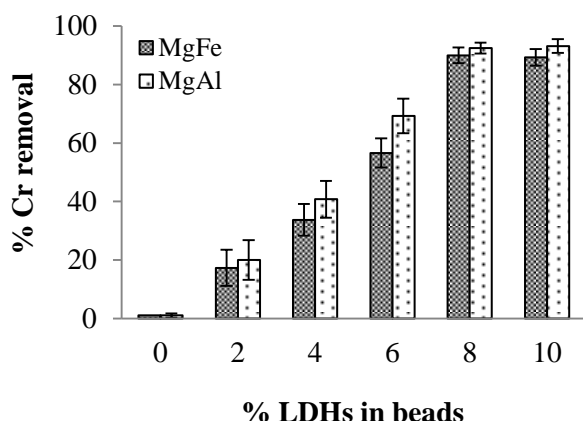


Figure 4: Effect of LDHs content in alginate/PVA-glutaraldehyde beads for chromate adsorption

The sorption of chromate onto 8 % MgAl beads and 8 % MgFe beads was examined at different pH values ranging at initial pH values from 6.0 to 9.0 (6.0, 7.0, 8.0 and 9.0) and is shown in Table 1. Clearly, no significant effect of pH on the Cr^{VI} adsorption was observed for the 8 % MgAl beads and MgFe beads, for further experiments solution pH 7.0 was used.

Table 1: Effect of pH for chromate adsorption on 8 % LDHs beads (mean value ± SD, n=3).

pH	% Cr removal	
	8 % MgFe beads	8 % MgAl beads
6.0	89.27±2.29	92.17±1.59
7.0	90.01±2.66	92.50±1.88
8.0	89.31±2.54	92.02±1.06
9.0	88.98±2.16	92.07±1.00

Adsorption kinetics

The adsorption chromate onto 8 % LDHs beads as function of contact time at constant initial concentration ([Cr] = 45 mg/L) was studied. The equilibrium time required for adsorption of chromate on 8 % LDHs beads was about 8 h. The findings showed that in the first of 8 h, adsorption of chromate onto 8 % MgAl beads was 92.50 % while it was 90.01 % for 8 % MgFe beads. After 8 h, no significant increasing of chromate adsorption onto 8 % LDHs beads was observed, this might be due to

the complete clogging of available adsorption sites on LDHs. Figure 5 shows the adsorption kinetics of chromate onto 8 % LDHs beads.

To evaluate the kinetics of the adsorption process, the Lagergren first-order and Pseudo second-order kinetic models were used to analyze the kinetic experimental. The fittings of the Lagergren first-order and Pseudo second-order kinetic models to the kinetic experimental data for the chromate adsorption onto the 8 % LDHs beads at pH 7.0 are shown in Figure 5. Table 2 summarizes the adsorption kinetic model parameters obtained from these models. It could be seen from Table 2 that the r² values for the pseudo-second order model are close to unity (r² = 0.9936 - 0.9948) and there is significant agreement between q_e calculated and q_e experimental values, indicating that the pseudo-second order model can be applied to simulate the kinetic data of chromate adsorption onto 8 % MgFe beads and 8 % MgAl beads.

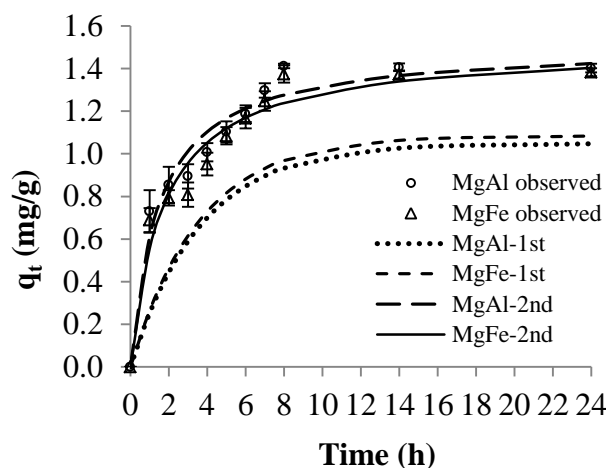


Figure 5: Adsorption kinetics of chromate onto the 8 % MgAl beads and 8 % MgFe beads at pH 7.0

Table 2: Adsorption kinetic parameters of chromate on 8 % LDHs beads

	MgFe beads	MgAl beads
q _{e, exp} (mg. g ⁻¹)	1.3741	1.4117
Lagergren first-order (a)		
k ₁ (h ⁻¹)	0.2789	0.2752
q _e (mg. g ⁻¹)	1.0849	1.0486
r ²	0.9369	0.9195
Pseudo second-order (b)		
k ₂ (g.mg ⁻¹ .h ⁻¹)	0.3873	0.4467
q _e (mg. g ⁻¹)	1.5038	1.5115
r ²	0.9936	0.9948

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (a); \quad \frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (b)$$

where q_t is the amount of chromate removed at time t (mg Cr. g⁻¹); q_e is the amount of chromate removed at equilibrium (mg Cr. g⁻¹); k_1 is the Lagergren first-order rate constant (min⁻¹) and k_2 is the Pseudo second-order velocity constant (g. mg⁻¹. h⁻¹) [12].

3.2.2. Adsorption isotherm

The sorption of chromate by 8 % LDHs beads was studied for a range of initial chromate concentration between 4.5 and 65 mg Cr. L⁻¹. The chromate removal efficiency was between 92.50 and 99.98 % for MgAl beads and between 90.01 and 97.51 % for MgFe beads at initial chromate concentration between 4.5 and 45 mg Cr. L⁻¹. When initial chromate concentration increased from 45 to 65 mg Cr. L⁻¹, the chromate removal decreased from 90 to 60 %. Generally, the removal of chromate decreased with increasing of initial concentration, it might be due to the lack of available adsorption sites for chromate at high concentration on 8 % LDHs beads. The Langmuir and Freundlich parameters and the fittings of these models to experimental data for chromate adsorption onto 8 % LDHs beads are given in table 3 and figure 6.

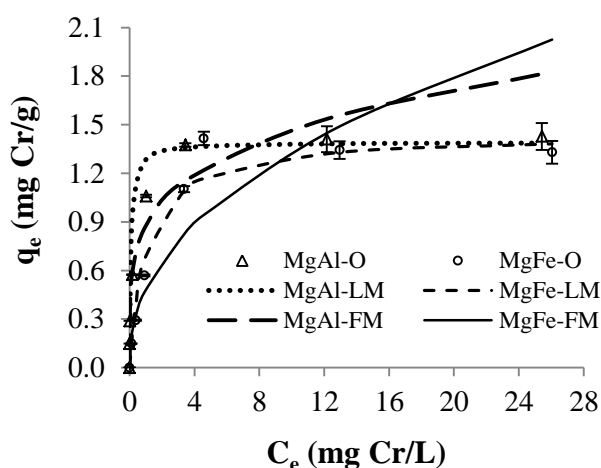


Figure 6: Adsorption isotherms of chromate onto the 8 % MgAl beads and 8 % MgFe beads at pH 7.0 (O: Observed data, LM and FM: Langmuir and Freundlich modeling)

Clearly, the Langmuir isotherm fitted well with the experimental data on both adsorbents, it might be due to homogeneous distribution of active sites onto these adsorbents. The monolayer adsorption capacity (q_m) was 1.4380 mg Cr. g⁻¹ and 1.3912 mg Cr. g⁻¹ for 8 % MgFe beads and 8 % MgAl beads,

respectively. For both adsorbents, the values of $1/n$ obtained from Freundlich model were lying between 0.2 and 0.5, which suggested favorable condition for chromate adsorption. The value of correlation coefficient (r^2) shown in table 3 indicates the better applicability of the Langmuir isotherm model to describe the chromate adsorption capacity of these 8 % LDHs beads.

Table 3: Langmuir and Freundlich parameters for adsorption isotherms of chromate onto 8 % LDHs beads

	MgFe beads	MgAl beads
Langmuir (a)		
K_L (L.mg ⁻¹)	0.9415	12.0201
q_m (mg. g ⁻¹)	1.4380	1.3912
r^2	0.9977	0.9999
Freundlich (b)		
K_F (L. g ⁻¹)	0.4827	0.8744
$1/n$	0.4399	0.2254
r^2	0.9009	0.9466

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (a)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (b)$$

where q_m is the monolayer surface coverage of 8 % LDHs beads surface by the chromate (mgCr.g⁻¹); C_e is the concentration of chromate in the solution at equilibrium (mgCr.L⁻¹); q_e is the amount of chromate removed at equilibrium (mgCr.g⁻¹) and K_L is the Langmuir constant related to the binding energy (L.mg⁻¹); K_F is the distribution coefficient (L.g⁻¹) and n is the Freundlich constant [12, 13].

4. CONCLUSION

In summary, we have reported a simple method for preparation of LDHs beads by entrapped LDHs powder into alginate, PVA and glutaraldehyde blend gel. The adsorption kinetics of chromate onto 8 % LDHs beads are well described by the pseudo second-order kinetic model and adsorption data fit well to a Langmuir isotherm. The chromate removal rate by 8 % LDHs beads is significantly high (more than 90 %) for a such high initial chromate concentration (≈ 45 mgCr.L⁻¹). Therefore, from practical view, the 8 % LDHs beads were expected to be a promising adsorbent for application to chromate decontamination technology.

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REFERENCES

1. W. Wesley Eckenfelder, Jr. *Coagulation, precipitation and metal removal, in Industrial Water Pollution Control*, ed by George Tchobanoglous. McGraw-Hill Publishers, Singapore, 124-157 (1999).
2. Cavani F, Trifirò F and Vaccari A. *Hydrotalcite-type anionic clays: preparation, properties and applications*. *Catalysis Today*, **11**, 173-301 (1991).
3. K. H. Goh, T. T. Lim and Z. Dong. *Application of layered double hydroxides for removal of oxyanions: A review*, *Water Research*, **42**, 1343-1368 (2008).
4. Vaccari A. *Preparation and catalytic properties of cationic and anionic clays*, *Catalysis Today*, **41**, 53-71 (1998).
5. Del Hoyo C. *Layered double hydroxides and human health: An overview*, *Apply Clay Science*, **36**, 103-121 (2007).
6. Bert Gebben, Hans W. A. van den Berg, Dick Bargeman, Cees A. Smolders, *Intramolecular crosslinking of poly(vinyl alcohol)*, *Polymer*, **26**, 1737-1740 (1985).
7. Hossein Hosseinzadeh. *Synthesis and swelling properties of a poly(vinyl alcohol)-based superabsorbing hydrogel*, *Current Chemistry Letters*, **2**, 153-158 (2013).
8. Elisa Campos, Patricia Coimbra, M. H. Gil. *An improved method for preparing glutaraldehyde cross-linked chitosan-poly(vinyl alcohol) microparticles*, *Polymer Bulletin*, **70**, 549-561 (2013).
9. Chibwe K, Jones W. *Intercalation of organic and inorganic anions into layered double hydroxides*. *Journal of the Chemical Society, Chemical Communications*, **14**, 926-927 (1989).
10. Bellotto M., Rebours B., Clause O., Lynch J., Bazin D., Elkaïm E. *A reexamination of hydrotalcite crystal chemistry*, *Journal Physical Chemistry*, **100(20)**, 8527-8534 (1996).
11. Yasin Y., Abdul Malek A. H., Sumari S. M. *The application of response surface methodology for lead ion removal from aqueous solution using intercalated tartrate-Mg-Al Layered Double Hydroxides*, *Oriental Journal of Chemistry*, **26(4)**, 1293-1298 (2010).
12. Hardiljeet K. Boparai, Meera Joseph, Denis M. O'Carroll. *Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles*, *Journal of Hazardous Materials*, **186**, 458-465 (2011).
13. Zhujian Huang, Pingxiao Wu, Yonghong Lu, Xiaorong Wang, Nengwu Zhu, Zhi Dang. *Enhancement of photocatalytic degradation of dimethyl phthalate with nano-TiO₂ immobilized onto hydrophobic layered double hydroxides: A mechanism study*, *Journal of Hazardous Materials*, 246-247, 70-78 (2014).

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