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Hybrid sorbent (LDHs–polymer composite) for the adsorption of chromate from aqueous solution

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ABSTRACT

In this study, the performance of layered double hydroxides–polymer (LDHs–polymer) composite as an adsorbent for the removal of hexavalent chromate ion from aqueous solution was investigated. The LDHs–polymer composite was prepared by immobilizing LDHs into spherical alginate/polyvinyl alcohol (PVA)–glutaraldehyde composite (spherical polymer composite). Approximately 90.0–92.5% of chromium was removed by LDHs–polymer composite from an aqueous solution containing 45 mg Cr/L. The adsorption data were well explained by the pseudo-second-order kinetics model and the Langmuir isotherm model. The adsorption capacities of these LDHs–polymer composite were from 1.358 to 1.471 mg Cr/g at pH 7, as calculated from the Langmuir adsorption isotherm. The adsorption ability of the LDHs–polymer composite decreased by approximately 5–6% after five adsorption–desorption cycles. Significant reduction of the chromate removal was observed in the presence of carbonate and phosphate ions. The effect of co-existing anions on the chromate adsorption capacity followed in the order: $CO_3^{2-} \approx PO_4^{3-} > SO_4^{2-} \approx Cl^-$. A fixed-bed column study was conducted with a real-life chromium-bearing plating wastewater sample. The breakthrough time was found to be from 5.5 to 7.5 h. Under optimized conditions, the LDHs–polymer composite removed more than 83–88% of total chromium in the solution. The results obtained in this study will be useful for further extending the adsorbents to the field scale or for designing pilot plants in future studies. From the viewpoint of environmental friendliness, the LDHs–polymer composite are a potential cost-effective adsorbent for chromate removal in water treatment.

Keywords: Layered double hydroxides–polymer composite; Chromate removal; Adsorption isotherm; Adsorption kinetic; Fixed-bed column

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1. Introduction

Environmental contamination with various heavy metals is currently one of the most urgent problems that both scientific community and general public face. Therefore, various methods for heavy metals decontamination have been studied extensively over the last few decades. Chromium, one of the extremely toxic heavy metals affecting the environment, is present in the waste water as a result of its industrial application such as metal plating, leather tanning, textile industries, battery, and pigment production.

In Vietnam, nowadays, the growing awareness of environmental pollution has been recognized in accordance with evolving the growing needs of the industry, specifically electroplating industry. In Ho Chi Minh City, approximately 26 enterprises specializing in plating are listed enterprises causing serious pollution. The question is how to develop the plating industry with protecting the environment appropriately. There are many solutions to be applied in the plating industry to reduce pollution and save the cost for wastewater treatment while improving productivity [1]. As known, plating process undergoes many stages including stripping, cleaning, plating, and rising. The treatment process of wastewater depends on the nature of the characteristics of wastewater in different stages. Therefore, the search for suitable technology for the removal of chromium in aqueous solution is an important mission of scientific community in context of economic difficulties and ongoing serious environmental pollution. Several methods have been reported for the treatment of chromium-bearing effluents such as reduction and precipitation, electrochemical precipitation, ion-exchange resins, adsorption, and reverse osmosis [2–5]. Among these, adsorption technology is one of the most widely developed and extensively studied, because of its removal effectiveness, low cost, and easy equipment handling [6–13].

Layered double hydroxides (LDHs) have received much attention during the past decades as an emerging material due to their multiple applications such as adsorbent, catalyst, and catalyst support. LDHs have the number of advantages over other materials for environment remediation applications, as they are nontoxic, cheap, and easy to prepare. The general formula of LDHs is $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}$: $y$$H_2O$, where M^{2+} and M^{3+} are divalent (Ca^{2+}, Mg^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+}) and trivalent (Al^{3+}, Fe^{3+}, Cr^{3+}) metal ions, respectively. A^{n-} is intercalate anions (CO_3^{2-}, SO_4^{2-}, NO_3^-, F^-, Cl^-). LDHs consist of positively charged brucite-like sheets which are balanced by the intercalation of anions in the hydrated interlayer regions [14,15]. In recent years, LDHs has been considered as an efficient material for removing negatively charged species due to their high specific surface areas; high anion-exchange capacities, and flexible interlayer space [15–17]. LDHs can remove anion species from solution through three mechanisms: surface adsorption, interlayer anion exchange, and reconstruction of a calcined LDH precursor by the "memory effect." The use of LDHs in the fine powder forms requires follow-on solid/water separation, which substantially increases the cost. The entrapment of functional material within calcium alginate has been developed in recent years because of their economic advantages, high efficiency, and easy handling [18–20]. Our previous studies [21,22] have shown that the encapsulation of LDHs within alginate–polyvinyl alcohol (PVA) beads exhibit superior adsorption of pollutants and separation of beads from aqueous media after treatment. However, the beads were deformed after just one adsorption–desorption cycle. In order to improve the durability of the beads, it was suggested to add cross-linker to alginate–polyvinyl alcohol gel. Glutaraldehyde is commonly used as a cross-linker for PVA. Intra-molecular cross-linking is effective in making the PVA molecules less deformable [23].

Herein, we present a simple and facile method to prepare the hybrid adsorbents, LDHs–polymer composite by immobilizing LDHs into alginate/PVA in the presence of a cross-linker glutaraldehyde for the cost-effective removal of hexavalent chromium ion in aqueous samples. Before testing the performance of LDHs–polymer composite in fixed-bed column, batch adsorption studies were conducted to remove chromate at various times, pH values, initial concentration, and coexisting anions. To clarify the adsorption process, adsorption isotherms and kinetics studies were also performed. The reusability of the LDHs–polymer composite with repeated uses was also evaluated. To show that the LDHs–polymer composite can be used in a dynamic flow system, a fixed-bed column with upward flow was also tested using real-life chromium-bearing plating wastewater sample collected from plating enterprise in Ho Chi Minh city, Vietnam.

2. Materials and methods

2.1. Materials

All chemicals were of analytical grade. The iron (III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), aluminum chloride hexahydrate ($AlCl_3{\cdot}6H_2O$), magnesium chloride hexahydrate ($MgCl_2{\cdot}6H_2O$), sodium hydroxide (NaOH), potassium chromate (K_2CrO_4), sodium alginate, and polyviny alcohol were purchased from Sigma-Aldrich (USA).

2.2. Preparation of hybrid adsorbents (LDHs–polymer composite)

The LDHs containing Mg–Al–Cl and Mg–Fe–Cl used in this study were prepared by the co-precipitation method with a divalent to trivalent molar ratio of 3:1. For Mg–Al–Cl, an $MgCl_2{\cdot}6H_2O$ and $AlCl_3{\cdot}6H_2O$ salt solution was slowly added to a vigorously stirred solution of NaOH (pH 11 ± 0.2) at 65 ± 5˚C. The pH of the solution was maintained at 11 by adding 2 M NaOH. The Mg–Fe–Cl LDH was prepared by the above method using $MgCl_2{\cdot}6H_2O$ and $FeCl_3{\cdot}6H_2O$. The obtained gel was then aged at 65˚C for 24 h in mother liquor. The obtained samples were washed with deionized water, dried in an oven at 65˚C for 24 h, and calcined at 400˚C for 4 h in an electric muffle furnace (Vulcan 3-103, NEY, USA).

To prepare the spherical MgAl–polymer or MgFe–polymer composite with 8 wt% of Mg–Al–Cl or Mg–Fe–Cl (Fig. 1(a)), the following method was used. For this purpose, 8 g of Mg–Al–Cl or Mg–Fe–Cl was added to 100 mL of a solution containing 1 g of sodium alginate, 0.5 g of PVA, and 0.5 mL of glutaraldehyde under intensive stirring at 250 rpm for 1 h to obtain a homogeneous suspension. The obtained mixture was dripped with a syringe into a 500-mL solution of 0.3 M $CaCl_2$ in order to form 4.0 mm spherical beads. The gel beads were allowed to cure in the same $CaCl_2$ solution for 24 h under stirring and were then rinsed with deionized water to remove excess Ca^{2+}. Blank beads were also prepared using an alginate, PVA, and glutaraldehyde blend gel without adding Mg–Al–Cl or Mg–Fe–Cl.

2.3. Characterization of materials

The XRD measurements were conducted on an XRD diffractometer (D8 Advance, Bruker, Germany). Patterns with Cu Kα radiation ($\lambda = 1.54051$ Å) at 40 kV and 40 mA were recorded in the region of 2θ from 5˚ to 80˚. The morphologies of the LDHs–polymer composite were examined by field emission scanning electron microscopy (FESEM) using JSM 7401F (JEOL, USA) with an accelerating voltage of 20 kV. The surfaces of the materials were coated with a thin gold layer to avoid a charging effect.

2.4. Adsorption tests

The chromate adsorption tests were performed by the batch adsorption method in three replicates. For sorption kinetics, 250-mL flasks containing 3 g of each LDHs–polymer composite and 100 mL of a chromate solution at a 45 mg Cr/L concentration were prepared, separately. The mixtures were continuously shaken for 8 h at 30˚C and 250 rpm. Samples were taken at different time intervals and filtered using 0.45-μm Millipore membrane filters to analyze aqueous chromium concentrations. The sorption capacity (q_t, mg/g) at any time, t, was calculated using the following equation:

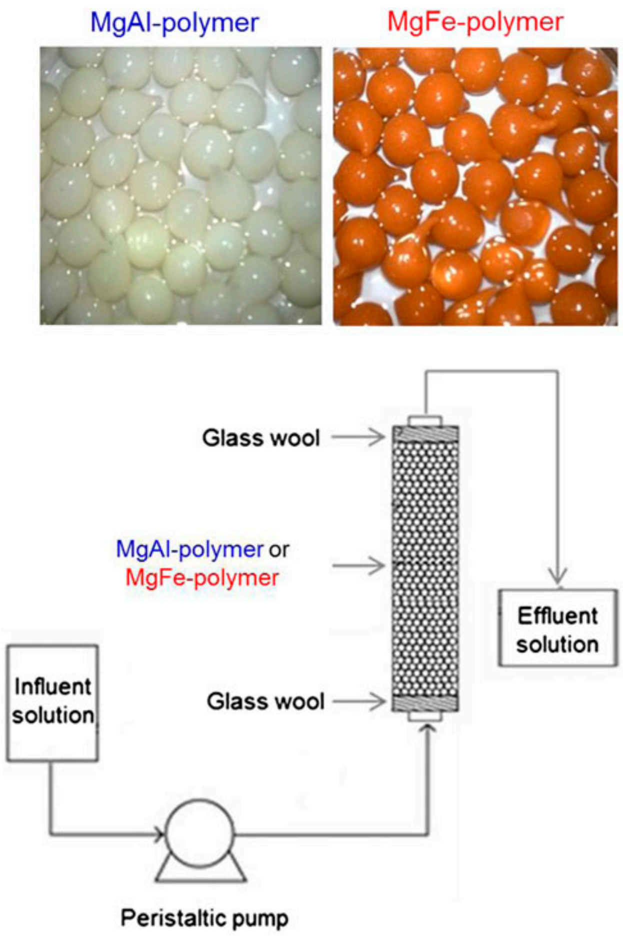

Fig. 1. (a) MgAl–polymer and MgFe–polymer composite and (b) schematic diagram of lab-scale column study.

$$q_t = \frac{(C_o - C_t) \times V}{m} \tag{1}$$

where C_o (mg Cr/L) is the initial concentration of chromate in the aqueous solution, C_t (mg Cr/L) is the chromate concentration in the aqueous phase at time t, V (L) is the solution volume, and m (g) is the mass of the LDHs–polymer composite. For studying the effect of pH on adsorption, 100 mL of a chromate solution with an initial concentration of 45 mg Cr/L was used. The pH was adjusted using 0.1 M HCl and 0.1 M NaOH before adding 3 g of the LDHs–polymer composite to the chromate solution for 8 h. Adsorption isotherms were obtained in batch equilibrium experiments with 3 g of the LDHs–polymer composite in 100 mL of a chromate solution in the concentration range from 4.5 to 65 mg Cr/L at pH 7 ± 0.1. The effects of competing anions on chromate adsorption were also determined. Three grams of LDHs–polymer composite were added to 100 mL of chromate solutions (45 mg Cr/L) containing additional various anions (i.e. Cl^-, SO_4^{2-}, CO_3^{2-}, or PO_4^{3-}) at pH 7, and the molar ratio of Cr to the added anions was 1:5, 1:10, and 1:20. The mixtures were continuously shaken at 30˚C and 250 rpm for 8 h. The concentrations of chromium remaining in the solutions were analyzed.

2.5. Regeneration

Chromate bound to the LDHs–polymer composite was desorbed with a 100-mL solution consisting of 4% NaOH and 2% NaCl for 10 h at 30˚C and 250 rpm. To determine the reusability of the LDHs–polymer composite, consecutive adsorption–desorption cycles were repeated five times using the same beads.

2.6. Fixed-bed column experiments

The real-life wastewater samples were taken from a stage of the downstream for washing product in a chromium-plating process at the Thanh Luan Manufacturing and Trading Ltd. This is one of 26 enterprises causing environmental pollution in Ho Chi Minh city, Vietnam. The composition of chromium-plating wastewater is shown in Table 1. The adsorption experiments in continuous flow system were conducted in a glass column with a 2.5 cm internal diameter and a 45 cm length. The column was packed with the MgAl–polymer or MgFe–polymer composite to a depth of 40 cm (Fig. 1(b)). The column was charged with real-life chromium-bearing plating wastewater in the up-flow mode at a volumetric flow rate of 57.32 $cm^3/(cm^2\ h)$ (3.0 mL/min). The samples were collected at certain time intervals and were analyzed for remaining chromium concentrations.

Table 1
The characteristics of chromium-plating wastewater collected at the Thanh Luan Manufacturing and Trading Ltd, Ho Chi Minh City, Vietnam

Parameter	Quantitative
pH	5.64
Total dissolved solid (mg/L)	70.3
Cl^- (mg/L)	23.4
SO_4^{2-} (mg/L)	35.1
Total Cr (mg/L)	4.96

2.7. Determination of the chromium concentration

The chromium concentrations were determined in duplicate by a graphite furnace atomic absorption spectroscopy using Avanta Ultra Z (GBC, Australia). The limit of detection (LOD), limit of quantification (LOQ), and limit of linearity (LOL) were 0.3×10^{-3}, 10^{-3}, and 15×10^{-3} mg/L, respectively. In the calculations, results below the LOD were assigned a value of 0.3×10^{-3} mg/L.

3. Results and discussion

3.1. Characterization of hybrid sorbents

The XRD patterns of MgAl–polymer, MgFe–polymer and blank polymer are shown in Fig. 2(a). The measured XRD patterns of all of the samples fitted well to LDH with basal reflections of planes *h*, *k*, *l*, (0 0 3), (0 0 6), (0 0 9), and (1 1 0) by comparison with JCPDS card No. 22-0700; thus, pure LDHs were obtained. As seen, almost all of the diffraction peaks were sharp and symmetrical, indicating good crystallinity. The $d_{0\,0\,3}$ crystal planes of MgAl–polymer and MgFe–polymer with basal spacing observed at 7.84 and 7.91 Å, respectively.

The suspension alginate/PVA–glutaraldehyde matrix acted as a bridge that bound Mg–Al–Cl or Mg–Fe–Cl together in the spherical form in the size range of approximately 4.0 mm. The FESEM images of the beads are shown in Fig. 2(b). The analysis of the FESEM micrographs revealed that the surfaces of the MgAl–polymer and MgFe–polymer composite were not homogeneous in comparison with the surface of the blank polymer, demonstrating that Mg–Al–Cl or Mg–Fe–Cl was mixed with the alginate/PVA–glutaraldehyde blend gel.

3.2. Batch adsorption of chromate from aqueous solutions

3.2.1. Adsorption kinetics

The adsorption of chromate onto the LDHs–polymer composite and blank polymer as a function of contact time at a constant initial concentration of 45 mg Cr/L was studied. The chromate removal percentage of blank polymer was approximately 1.0% while it was ≥90.0% for LDHs–polymer composite, indicating the sharp increase of chromate removal in the presence of LDHs.

Fig. 3 shows the adsorption kinetics of chromate on LDHs–polymer composite. The equilibrium time required for adsorption of chromate onto these adsorbents was approximately 8 h. It was found that adsorption of chromate onto LDHs–polymer

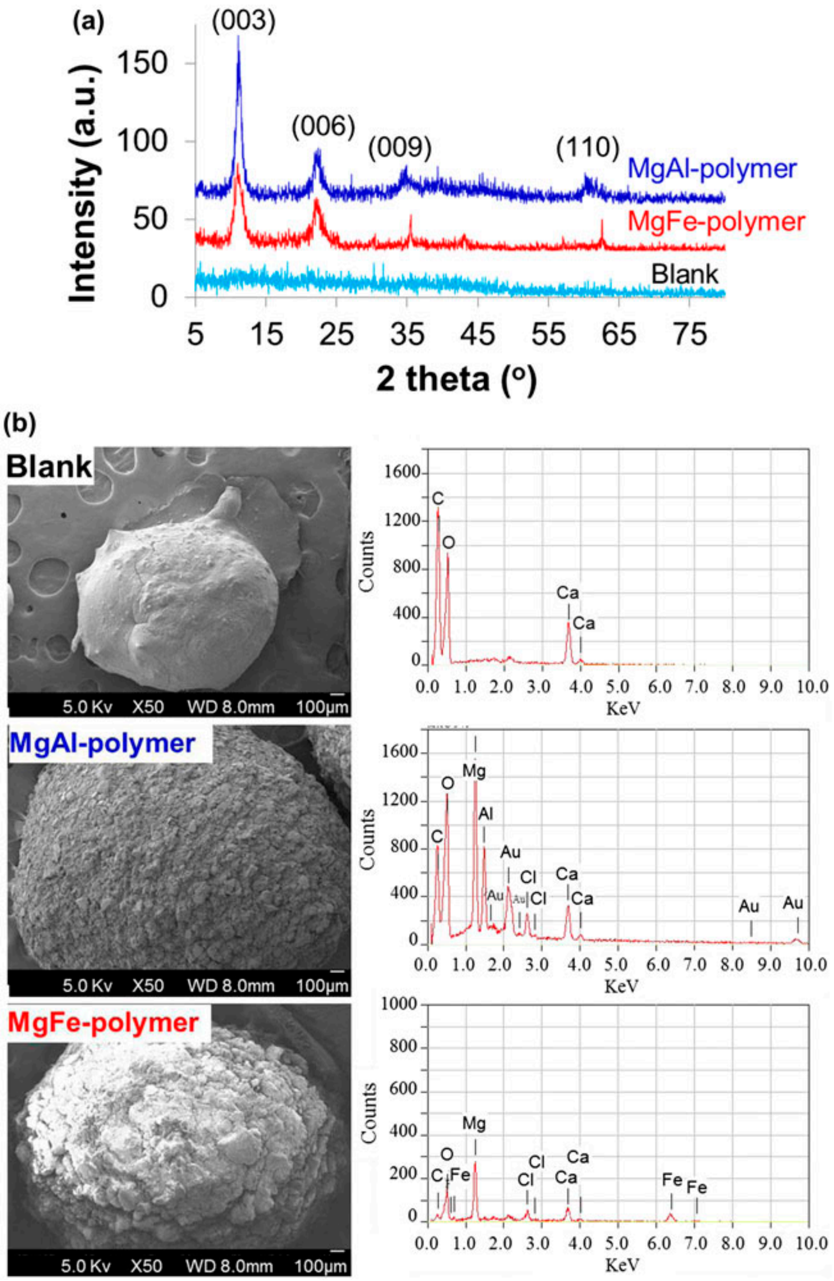

Fig. 2. (a) XRD patterns and (b) FESEM and EDS study of LDHs–polymer, blank polymer.

composite was fast (approximate 50%) in the first 1 h, then slowly increased from 50 to 90% from 1 to 8 h. The adsorption of chromate onto LDHs–polymer composite has not increased significantly after 8 h, which may have been due to complete saturation of available adsorption sites on the surfaces of the LDHs–polymer composite. The adsorption ability of LDHs–polymer was mainly due to the two different mechanisms such as surface adsorption and interlayer anion exchange.

Recently, numerous adsorption processes have been investigated. Adsorption processes are known to be dependent on and controlled by different types of mechanisms, such as diffusion control, mass transfer, and chemical reaction. To evaluate the mechanism of chromate adsorption onto the LDHs–polymer composite, the pseudo-first-order kinetic and pseudo-second-order kinetic were used to test the dynamic experimental data at an initial concentration of 45 mg Cr/L and pH 7 [24,25]. The kinetics parameters

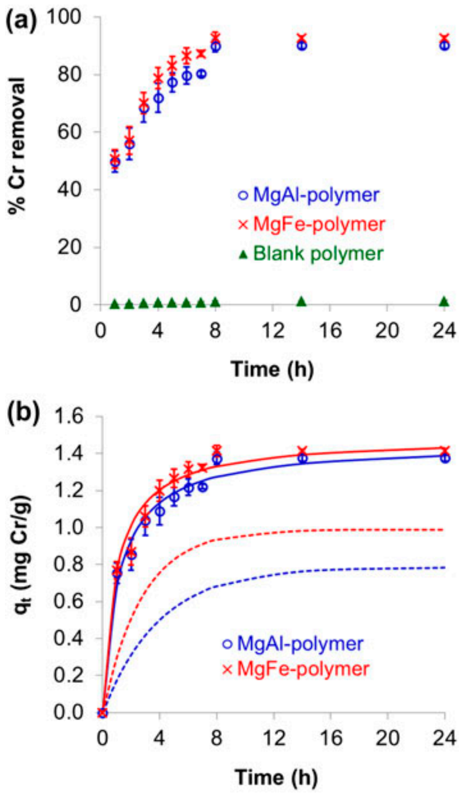

Fig. 3. (a) Effect of contact time on chromate removal by LDHs–polymer and blank polymer at pH 7.0 and (b) adsorption kinetics of chromate onto LDHs–polymer at pH 7.0. Dotted curve: Lagergren first-order kinetic modeling and solid curve: pseudo-second-order kinetic modeling.

obtained from the Lagergren first-order kinetic and pseudo-second-order kinetic models and the fitting of these models to the experimental data for chromate adsorption onto the LDHs–polymer are given in Table 2 and Fig. 3(b).

A linear form of Lagergren first-order equation is expressed as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{2}$$

where q_t is the amount of chromate removed at time t (mg/g); q_e is the amount of chromate removed at equilibrium (mg/g); and k_1 is the Lagergren first-order rate constant (min^{-1}). Using Eq. (2), the Lagergren first-order kinetic constant (k_1) and equilibrium adsorption capacity (q_e) were calculated from the plots of $\log(q_e - q_t)$ vs. t. The predicted kinetics is shown in Fig. 3(b). The correlation coefficient values (r^2) for Lagergren first-order kinetic equation were 0.974 and 0.981 for MgAl–polymer and MgFe–polymer composite, respectively. There were significant different between q_e evaluated from the Lagergren first-order model and q_e experimental values suggested it was highly irrelevant to use a Lagergren first-order kinetics as it violated both theory and the adsorption phenomena.

The pseudo-second-order kinetics can be expressed in a linear form as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{3}$$

where q_t is the amount of chromate, k_2 is the pseudo-second-order velocity constant (g/mg/h). The slope and intercept of plot of t/q_t vs. t was used to calculate q_e and k_2. q_e and k_2 determined from the model are presented in Table 2 along with the corresponding correlation coefficients (r^2).

It could be seen from Table 2 that the r^2 values were close to unity ($r^2 = 0.998$) and there is an agreement between q_e calculated and q_e experimental values for the pseudo-second-order model. Consequently, adsorption process was the best described by the pseudo-second-order kinetic model.

3.2.2. *Effect of pH solution*

pH is one of the most important parameters controlling the metal ion adsorption. The pH affects not only the type of ion in solution, but also the properties of adsorbent surface such as surface active groups [26]. The effects of pH on the level of chromate adsorption on LDHs–polymer composite were assessed using the chromate concentration of 45 mg Cr/L, at the contact time of 8 h and the adsorbent dosage of 3.0 g/L. As it is shown in Table 3, there is no significant different chromate adsorption onto the LDHs–polymer composite, when pH solution increased from 6 to 9. However, the removal percentage significantly decreases with further increase of pH up to 10. The results revealed that pH of the system controls the adsorption capacity due to its influence on the surface properties of the LDHs–polymer, ionic forms of the chromium as well as concentration of hydroxyl ions (OH^-) in the aqueous medium. The movement of chromate to the surface of LDHs–polymer is a pre-requisite of the adsorption reaction and controlled largely by electrostatic attraction or repulsion between chromate species in the aqueous solution and LDHs–polymer surface. The speciation of chromium in aqueous solutions depends mainly on the pH of the solution. The $HCrO_4^-$ predominates at pH range of 1.0–6.0, and CrO_4^{2-}, and $Cr_2O_7^{2-}$ at pH values above 6.0. Hence, pH at point of zero charge (pH_{pzc})

Table 2
Kinetic parameters and correlation coefficients of chromate adsorption onto LDHs–polymer

		Lagergren-first			Pseudo-second		
Adsorbent	$q_{e,exp}$ (mg/g)	q_e (mg/g)	k_1 (h^{-1})	r^2	q_e (mg/g)	k_2 (g/mg/h)	r^2
MgAl–polymer	1.374	0.786	0.254	0.974	1.454	0.611	0.998
MgFe–polymer	1.415	0.989	0.363	0.981	1.488	0.712	0.998

Table 3
Effect of solution pH on chromate removal (initial concentration of 45 mg Cr/L)

	% Cr removal				
Adsorbent	pH 6	pH 7	pH 8	pH 9	pH 10
MgAl–polymer	89.70 ± 1.80	90.00 ± 2.16	89.85 ± 1.68	90.28 ± 1.37	60.22 ± 1.77
MgFe–polymer	91.96 ± 1.72	92.79 ± 1.94	92.01 ± 1.55	92.11 ± 2.63	63.21 ± 2.03

of the LDHs and the chromate species are deciding factors. As known, adsorbent surface is positively charged at pH below pH_{zpc} and negatively charged at pH above pH_{zpc}, resulting in increased electrostatic attraction or repulsion with contaminant, hence leading to more or less readily adsorption. The pH_{zpc} for the LDHs was reported to be in the range 6.8–8.9 [27], below which the LDHs surface is positively charged and normally beneficial for the adsorption of the chromate. Lesser adsorption of Cr(VI) at pH values greater than 9.0 may be due to the dual competition of two anions (CrO_4^{2-} and OH^-) to be adsorbed on the surface of the adsorbent, of which OH^- predominates. This is in accordance with earlier studies on the removal of Cr(VI) by different adsorbents [28]. The fact that chromium removal decreases with the increase in pH may be further in conformity with the mechanism involved, due to the repulsion between the negative de-protonated chromate species and the negative surfaces of the LDHs at higher pH.

3.2.3. Adsorption isotherm

The level of chromate removal was from 99.98 to 64.00% for MgAl–polymer and from 99.86 to 59.33% for MgFe–polymer at pH 7.0, contact time of 8 h, and initial concentration range from 4.5 to 65 mg Cr/L (Fig. 4(a)). The percentage of chromate removal was declined when the concentration increased from 4.5 to 65 mg Cr/L. The observation that chromate removal decreased as the initial concentration was increased may be due to a lack of available adsorption sites for chromate on the surface of the beads at high concentrations, progressively reaching saturation of the adsorbent [29]. Analysis of isotherm data is very important for predicting the adsorption capacity and adsorption behavior of adsorbent. The isotherm results were analyzed using the Langmuir and Freundlich equations [30,31]. The isotherm parameters obtained from the Freundlich and Langmuir models and the fitting of these models to the experimental data for chromate adsorption onto the MgAl–polymer and MgFe–polymer are given in Table 4 and Fig. 4(b).

The Langmuir isotherm model describes monolayer adsorption on homogeneous flat surface without interaction between adsorbed molecules, the expression for the linear Langmuir regression is:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{4}$$

where q_m is the monolayer surface coverage of LDHs–polymer surface by the chromate (mg/g); C_e is the concentration of chromate in the solution at equilibrium (mg/L); q_e is the amount of chromate removed at equilibrium (mg/g); and K_L is the Langmuir constant related to the binding energy (L/mg). Using Eq. (4), q_m and K_L were calculated from gradient of the graph of C_e/q_e vs. C_e and is presented in Table 4. It is noted that the correlation coefficient values obtained from the Langmuir model indicates a significant correlation ($r^2 > 0.99$). The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given by the following equation:

$$R_L = \frac{1}{1 + K_L C_i} \tag{5}$$

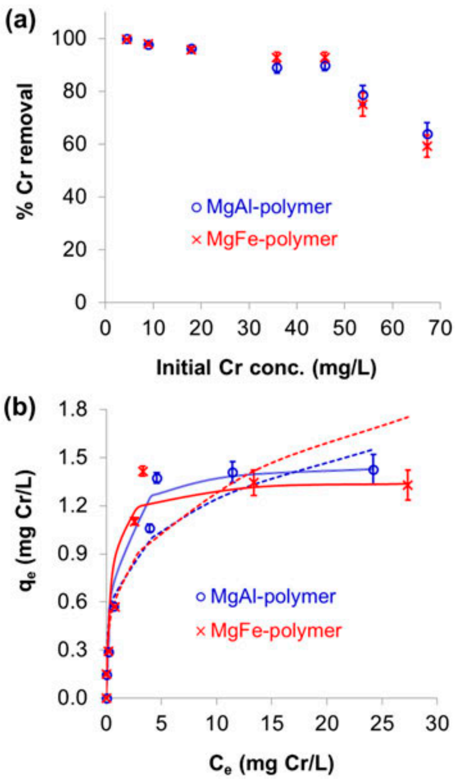

Fig. 4. (a) Effect of initial concentration on the chromate removal by LDHs–polymer at pH 7.0 and (b) adsorption isotherms of chromate onto LDHs–polymer at pH 7.0 (solid curve: Langmuir modeling and dotted curve: Freundlich modeling).

where C_i is the initial concentration of chromate and K_L is the Langmuir constant. The value of R_L indicates the shape of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), irreversible ($R_L = 0$), and R_L values between 0 and 1 indicate favorable adsorption. In this study, the R_L values were found to range between 0.006 and 0.137 (Table 4), indicating the adsorption of chromate on these LDHs–polymer composite is favorable.

The monolayer adsorption capacity (q_m) according to the Langmuir model was calculated to be 1.471 mg Cr/g for MgAl–polymer (≈18.388 mg Cr/g of Mg–Al–Cl) and 1.358 mg Cr/g for MgFe–polymer (≈16.975 mg Cr/g of Mg–Fe–Cl). The fact that the Langmuir isotherm fits the experimental data very well may be due to homogeneous distribution of actives sites onto MgAl–polymer and MgFe–polymer composite.

The Freundlich isotherm model is based on multilayer adsorption characteristics for the heterogeneous surface with interaction between adsorbed molecules, and the model as expressed in Eq. (6):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{6}$$

where C_e is the concentration of chromate in the solution at equilibrium (mg/L); q_e is the amount of chromate removed at equilibrium (mg/g); K_F is the distribution coefficient (L/g); and n is the Freundlich constant. The Freundlich constant gives an indication of the favorability of adsorption and isotherms with $n > 1$ are classified as L-type isotherm reflecting a high affinity between organic compounds and absorbents, indicative of chemisorption [32]. By plotting $\log q_e$ vs. $\log C_e$, the K_F and n values were determined from intercept and slope of the plot, respectively. In this study, $1/n$ values were from 0.2 to 0.3 L/g, which indicate that the chromate could be easy, adsorbed on both of the MgAl–polymer and MgFe–polymer [33]. The correlation coefficient values obtained from the Freundlich model showed significant correlation ($r^2 = 0.914 - 0.922$) (Table 4).

Hence, this isotherm fitting result indicated that the LDHs–polymer composite provided specific homogeneous sites, and chromate adsorption occurred through a monolayer adsorption process.

3.2.4. *Effects of coexisting anions on chromate adsorption*

Industrial effluents usually contain various anions that may influence the adsorption of chromate. The effects of some common anions (Cl^-, SO_4^{2-}, CO_3^{2-}, and PO_4^{3-}) on chromate adsorption by the LDHs–polymer

Table 4
Parameters and correlation coefficients obtained from the analysis of adsorption isotherm

	Langmuir				Freundlich		
Adsorbent	q_m (mg/g)	K_L (L/mg)	r^2	R_L	$1/n$	K_F (L/g)	r^2
MgAl–polymer	1.471	1.402	0.997	0.010–0.137	0.252	0.696	0.922
MgFe–polymer	1.358	2.337	0.998	0.006–0.087	0.298	0.654	0.914

composite were investigated. Regardless of the type of competing anion, increasing the concentration of a coexisting competing anion resulted in decreased chromate adsorption onto the LDHs–polymer composite (Fig. 5). This may be due to the competition between coexisting anions and chromate for the positively charged sites on the surfaces of the LDHs–polymer composite. Among the competing anions considered in this work, CO_3^{2-} and PO_4^{3-} showed more adverse effect on chromate removal in comparison with Cl^- and SO_4^{2-}.

As seen from Fig. 5, at the molar ratio of coexisting anions to chromate was 20, in case of Cl^- or SO_4^{2-}, chromate adsorption decreased approximately 16–19% and 17–20% for MgAl–polymer and MgFe–polymer composite, respectively, whereas in case of CO_3^{2-} or PO_4^{3-}, the chromate adsorption decreased from 34 to 39% for MgAl–polymer and from 39 to 42% for MgFe–polymer composite. Thus, the effects of competing anions on chromate adsorption onto the LDHs–polymer composite followed in the order of $CO_3^{2-} \approx PO_4^{3-} > SO_4^{2-} \approx Cl^-$.

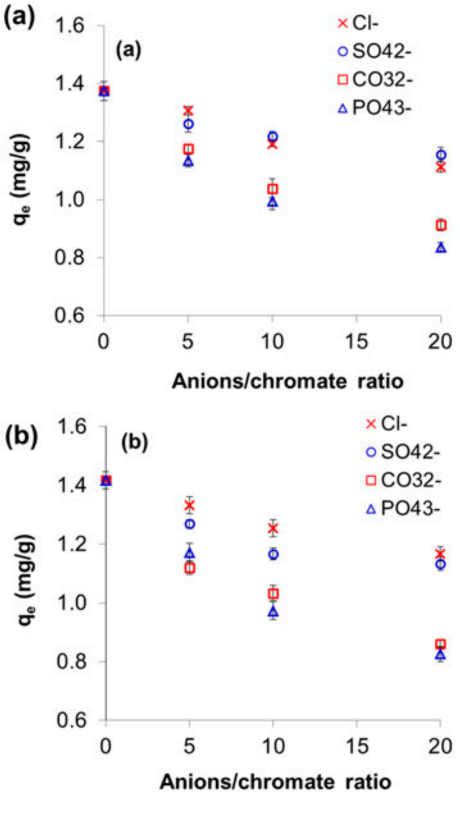

Fig. 5. Effects of coexisting anions on chromate adsorption at pH 7.0 (a) MgAl–polymer composite and (b) MgFe–polymer composite.

3.2.5. Regeneration

Effective use of an adsorbent depends not only on the adsorption capacity, but also on the capability for regeneration and re-use. The adsorption capacity of the LDHs–polymer composites decreased as the number of regeneration cycles increased; however, the adsorption capacity of the LDHs–polymer composites only decreased by approximately 5–6% after 5 adsorption–desorption cycles (Fig. 6). After the fifth regeneration cycle, the chromate removal rates remained at 84.63 and 88.12% for the MgAl–polymer and MgFe–polymer composites, respectively. These results have clearly demonstrated promising attributes for practical application because of the efficient reusability of the LDHs–polymer composite with effective chromate removal.

3.2.6. Fixed-bed column studies

Despite the adsorption in batch systems to available parameters to understand the contaminant–adsorbent interaction and to select the best operational condition, however, the data obtained under batch conditions are generally not applicable to most treatment systems (such as column operation) where contact time is not sufficiently long for attainment of equilibrium [34]. Thus, it is necessary to ascertain the practical applicability of the adsorbent in continuous mode. The fixed-bed column is an effective process for the adsorption application in the industrial scale-up, once that the process can be performed continuously [35,36]. The fixed-bed columns have a series of advantages such as simple operation, large yields treatment, and ease for industrial applications, etc. [37–39].

The efficiency of the treatment technique depends on chromium concentration, the chromium species in

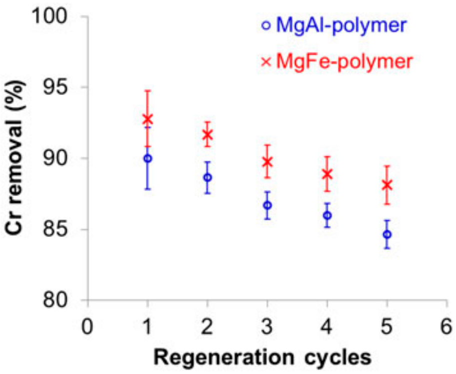

Fig. 6. Chromate removal after different adsorption–desorption cycles.

source water, and other constituents in the water. In order to study the dynamic behavior of adsorption the column, a fixed-bed column study was conducted with real-life chromium-containing wastewater collected from plating enterprise in Ho Chi Minh City using a column of 2.5 cm diameter. The column was charged with real-life chromium-bearing plating wastewater in the up-flow mode with a volumetric flow rate of 36.69 $cm^3/(cm^2 h)$ (3.0 mL/min). The breakthrough curve is shown in Fig. 7.

According to Vietnamese Standards Guidelines and due to the high toxicity of chromium, the breakthrough point was chosen where the chromate concentration reached its maximum allowed value (corresponding to $C_t/C_o = 0.01$, where C is the effluent chromate concentration of 0.05 mg Cr/L, and C_o is the influent chromate concentration of 4.96 ± 0.5 mg Cr/L). When the effluent concentration approaches 90% of C_o (corresponding to $C/C_o = 0.9$), then the adsorbents are considered to be essentially exhausted. For the MgAl–polymer composite, the breakthrough (t_b) and exhaust (t_E) times were found to be 7.5 and 25 h for corresponding volumes of 1.35 and 4.50 L of the treated chromate solution, respectively. For the MgFe–polymer composite, the breakthrough time was at 5.5 h, the corresponding treated volume was 0.99 L, the exhaust time was 20 h and the corresponding treated chromate volume was 3.6 L.

In fixed-bed column experiments, chromate could come in contact with the entrapped LDHs particles by diffusing into the LDHs–polymer composite through the pores in the polymer and subsequently be removed from the solution via two different mechanisms. First, the negatively charged chromate could adsorb to the positively charged brucite-like layer in surface adsorption. Second, the chromate could replace the charge balancing anion (chloride) in the interlayer region in the anion-exchange process.

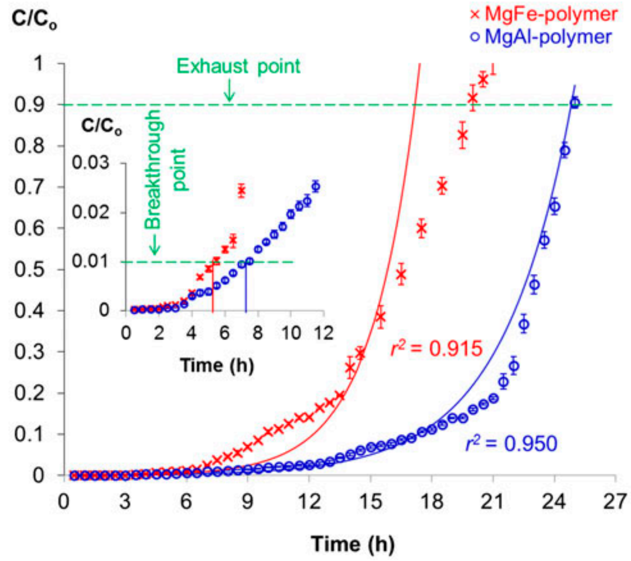

Fig. 7. The breakthrough curve for chromate removal in fixed-bed columns packed with LDHs–polymer.

The total quantity of chromium bound to the adsorbents in fixed-bed columns, q_{total} (mg), at a given flow rate and influent chromium concentration was calculated using the following equation [40]:

$$q_{total} = \frac{Q}{1000}\int_{t=0}^{t=t_{total}} (C_o - C_t)\,dt \tag{7}$$

where Q (mL/min) is the volumetric flow rate, t_{total} (h) is the total time of flow until exhaust, C_o (mg Cr/L) is the initial concentration of chromate, C (mg Cr/L) is the concentration of chromate in the effluent, and m (mg) is the total amount of LDHs–polymer composite in the column.

The total amount of chromate sent to the column, M_{total} (mg), was calculated according to the following equation:

$$M_{total} = \frac{C_o Q t_{total}}{1000} \tag{8}$$

The percentage of chromate removed by the column was calculated as follows:

$$\text{Total removal }(\%) = \frac{q_{total}}{M_{total}} \times 100 \tag{9}$$

In order to properly design and operate a fixed-bed adsorption processes, the concept of the mass transfer zone (MTZ) proposed by Michaels was applied [41,42]. The MTZ is the layer between the equilibrium bed zone and the unused bed zone. During this process, as the feed solution containing the solute passes through the fixed bed of the packed material, the exchange zone moves in the direction of the flow and reaches the exit.

If t_z (min) is the time required for the MTZ to move through its own length up the bed, t_E (min) is the time required for the MTZ to become established and move completely out of the bed, and t_f (min) is the time needed for the MTZ to form, then the height h_z of the MTZ (cm) is given by the following expression:

$$h_z = U_z t_z = \frac{h(t_z)}{(t_E - t_f)} \tag{10}$$

Table 5
Parameters calculated from breakthrough curves for chromate removal in fixed-bed packed with LDHs–polymer composite

Adsorbent	M_{total} (mg)	q_{total} (mg)	Total removal (%)	t_z (h)	h_z (cm)	U_z (cm/h)	Bed saturation (%)	K (L/mg h)	N (mg/L)	x_o (cm)
MgAl–polymer	22.77	19.94	87.59	17.5	31.03	1.77	89.16	0.059	114.58	24.84
MgFe–polymer	17.86	14.80	82.91	14.5	36.56	2.52	73.92	0.089	79.19	23.87

where U_z (cm/h) is the movement rate of the MTZ.

The movement rate of the MTZ is a function of the adsorption capacity of the LDHs–polymer composite, which allows for calculation of the rate of bed saturation. Smaller bed depths of the MTZ lead to faster transfer rates, which increase the saturation of the bed.

The times t_z, t_E and t_f are given by the following expressions:

$$t_z = \frac{(V_E - V_B)}{Q} \quad (11)$$

$$t_E = \frac{V_E}{Q} \quad (12)$$

$$t_f = (1 - F)t_z \quad (13)$$

where F is a parameter that measures the symmetry of the breakthrough curve. F is given by the following ratio:

$$F = \frac{S_z}{S_{\max}} = \frac{\int_{V_B}^{V_E} (C_o - C)\, dV}{C_o(V_E - V_B)} \quad (14)$$

where S_z (mg) is the amount of chromate that has been removed by the adsorption zone from breakthrough to exhaustion and $S_{\max}$ (mg) is the amount of chromate removed by the adsorption zone if the zone is completely exhausted.

The percentage of saturation of the column in the breakthrough point is determined as follows:

$$\text{Bed saturation } (\%) = \frac{h + (F-1)h_z}{h} \times 100 \quad (15)$$

Different parameters, such as the time required for the MTZ to move through its own height (t_z), height of the MTZ (h_z), MTZ moving rate (U_z), and bed saturation (%) for the column studies were calculated using mathematical Eqs. (7)–(15). The results are shown in Table 5. The results obtained indicate that a better column performance was obtained using the fixed-bed of the MgAl–polymer composite. Under the same experimental conditions, a comparison of the fixed-bed columns of the MgAl–polymer composite and MgFe–polymer composite showed that longer service times, larger volumes treated and a higher quantity of chromate removed were obtained using the fixed-bed MgAl–polymer composite. In general, the reported performance using the MgAl–polymer composite for chromate removal in a column was promising compared with the MgFe–polymer composite.

In order to describe the fixed-bed column behavior and to scale the adsorbents up for industrial applications, an Adams–Bohart model was used to fit the experimental data in the column, as follows [43]:

$$\ln\left(\frac{C_t}{C_o}\right) = KC_o t - \frac{KNx}{V} \quad (16)$$

$$x_o = \frac{V}{KN} \ln\left(\frac{C_o}{C_b} - 1\right) \quad (17)$$

where C_t and C_o (mg Cr/L) are the effluent and influent chromate concentrations, respectively, V (cm/h) is the linear flow velocity, x (cm) is the bed depth, K (L/(mg h)) is the kinetic constant, N is the maximum adsorption capacity (mg/L), and x_o (cm) is the minimum column height required to produce an effluent concentration C_b (breakthrough concentration, 0.05 mg Cr/L).

A plot of $\ln(C_t/C_o)$ vs. t yields a straight line with a slope KC_o and an intercept KNx/V from which K and N were calculated. The values of the adsorption rate coefficient (K), adsorption capacity coefficient (N), and minimum bed depth required by the breakthrough concentration (x_o) are shown in Table 5.

These values could be used to design an adsorption column. The fittings of the Adams–Bohart model to the experimental data for chromate removal using LDHs–polymer composite fixed-bed columns are shown in Fig. 7. The calculated maximum adsorption capacity of the MgAl–polymer fixed-bed column was higher than that of the MgFe–polymer fixed-bed column. The obtained results indicate that a better column performance was achieved using the fixed-bed column of MgAl–polymer compared with the fixed-bed column of MgFe–polymer. The fixed-bed column of MgAl–polymer produced longer service times, treated larger volumes, and removed a higher quantity of chromate. However, both fixed-bed adsorbents showed decent removal of problematic chromate. In general, the performance reported using the LDHs–polymer composite for chromate removal in a fixed-bed column was promising for use as an adsorbent.

4. Conclusions

A hybrid sorbent, LDHs–polymer composite, was developed to satisfy the need for a cost-effective, reliable, and reusable material that is easy to separate from effluent water. This combined excellent handling with ready application to conventional fixed-bed adsorption reactors in industry. The adsorption data were well described by the pseudo-second-order kinetics model and the Langmuir isotherm model, and the adsorption capacities of these LDHs–polymer composite at pH 7 calculated from the Langmuir adsorption isotherm were from 1.358 to 1.471 mg Cr/g LDHs–polymer composite (≈16.975–18.388 mg Cr/g LDHs powder). The adsorption ability of the LDHs–polymer composite decreased by approximately 5–6% after five adsorption–desorption cycles. Carbonate and phosphate decreased markedly the removal of chromate. The effects of coexisting anions on the adsorption capacity followed in the order: $CO_3^{2-} \approx PO_4^{3-} > SO_4^{2-} \approx Cl^-$. A fixed-bed column study was performed with real-life chromium-bearing plating wastewater. The breakthrough time was found to be from 5.5 to 7.5 h, and the exhaust time was from 20 to 25 h. The results obtained in this study will be useful for further extending the adsorbents to the field scale or for designing pilot plants in future studies. Therefore, from a practical view, the LDHs–polymer composite developed in this study are a promising adsorbent for application to chromate decontamination technology.

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