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## Arsenate removal by layered double hydroxides embedded into spherical polymer beads: Batch and column studies

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### ABSTRACT

In this study, the performance of poly(layered double hydroxides) [poly(LDHs)] beads as an adsorbent for arsenate removal from aqueous solution was investigated. The poly(LDHs) beads were prepared by immobilizing LDHs into spherical alginate/polyvinyl alcohol (PVA)-glutaraldehyde beads (spherical polymer beads). Batch adsorption studies were conducted to assess the effect of contact time, solution pH, initial arsenate concentrations and co-existing anions on arsenate removal performance. The potential reuse of these poly(LDHs) beads was also investigated. Approximately 79.1 to 91.2% of arsenic was removed from an arsenate solution (50 mg As L<sup>-1</sup>) by poly(LDHs). The adsorption data were well described by the pseudo-second-order kinetics model and the Langmuir isotherm model, and the adsorption capacities of these poly(LDHs) beads at pH 8 were from 1.64 to 1.73 mg As g<sup>-1</sup>, as calculated from the Langmuir adsorption isotherm. The adsorption ability of the poly(LDHs) beads decreased by approximately 5–6% after 5 adsorption-desorption cycles. Phosphates markedly decreased arsenate removal. The effect of co-existing anions on the adsorption capacity declined in the following order: HPO<sub>4</sub><sup>2-</sup> >> HCO<sub>3</sub><sup>-</sup> > SO<sub>4</sub><sup>2-</sup> > Cl<sup>-</sup>. A fixed-bed column study was conducted with real-life arsenic-containing water. The breakthrough time was found to be from 7 to 10 h. Under optimized conditions, the poly(LDHs) removed more than 82% of total arsenic. 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 poly(LDHs) beads are a potential cost-effective adsorbent for arsenate removal in water treatment.

### ARTICLE HISTORY

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### KEYWORDS

Adsorption isotherm; adsorption kinetics; arsenate removal; fixed-bed column; Poly(LDHs) beads; regeneration

## Introduction

Arsenic is a primary concern for water contamination due to its high toxicity and carcinogenicity and is regarded as a first priority issue among toxic substances.<sup>[1]</sup> Industrial wastewaters (metallurgical industry, glassware and ceramic production, tannery operation, dyestuff manufacture, pesticide manufacture, petroleum refining and rare-earth industry) are considered to be the main source of arsenic impurities. Arsenic purification prior to discharge into a recipient is therefore necessary. Various technologies, such as coagulation and filtration,<sup>[2]</sup> reverse osmosis,<sup>[3]</sup> ion exchange,<sup>[4]</sup> and adsorption are currently available to remove arsenic from aqueous solutions.<sup>[5,6]</sup> Among these methods, adsorption is a cost-effective method to remove arsenic from aqueous solution. The effectiveness of adsorption-based methods depends primarily on the adsorbent used.

So far, various adsorbents have been developed for arsenic removal, including activated carbon,<sup>[6,7]</sup> activated alumina,<sup>[8,9]</sup> hydrous zirconium oxide,<sup>[10]</sup> metal-loaded coral limestone,<sup>[11,12]</sup> ferric hydr(oxides),<sup>[13]</sup> metal oxides,<sup>[14]</sup> and zeolite.<sup>[15]</sup> Column

adsorption is the most common and efficient way to purify wastewater. Compared with batch procedures, fixed-bed is more effective for the cycle operation of adsorption/desorption because it allows more efficient utilization of the sorbent capacity and results in a higher quality of the effluent. Additionally, adsorbents can be reused. Hence, the need for good adsorbents that can be used for fixed-bed columns with high effectiveness and low cost is attracting increasing attention in order to meet high demand from the industrial and civil community.

Layered double hydroxides (LDHs) are an emerging material from a class of anionic clays that have received much attention in past decades. LDHs have been widely studied to remove oxyanions, such as phosphate, chromate, selenate and arsenate from aqueous solution.<sup>[16–21]</sup> LDHs have a number of advantages over other materials for environment remediation applications because they are nontoxic, cheap and easy to prepare. The general formula for LDHs is  $[M_{1-x}^{2+} M_x^{3+} (OH)_2]^{x+} (A^{n-})_{x/n} \cdot yH_2O$ , where M<sup>2+</sup> and M<sup>3+</sup> are divalent and trivalent metal ions, respectively, and A<sup>n-</sup> is an intercalate anion. LDHs

consist of positively charged brucite-like sheets that are balanced by intercalation of anions in the hydrated interlayer region.<sup>[22, 23]</sup>

By calcination, the LDHs are transformed into mixed oxides, which are solids with basic properties. There has been considerable interest in using LDHs to remove negatively charged species from aqueous solution due to their high specific surface areas, high anion exchange capacities and flexible interlayer space.<sup>[23,24]</sup> LDHs can remove anion species from solution by three mechanisms: surface adsorption, interlayer anion exchange and reconstruction of a calcined LDH precursor by the “memory effect.”<sup>[23,25]</sup> Use of LDHs in the fine powder form requires follow-on solid/water separation, which substantially increases the cost. If LDHs were easy to remove from aqueous media after treatment, they may be one of the best candidates.

So far, various forms of LDHs have been developed for contaminant removal. These include LDHs-coated sand,<sup>[26]</sup> LDHs-coated zeolites,<sup>[27]</sup> and LDHs supported on cellulose.<sup>[28]</sup> Entrapping iron nanoparticles,<sup>[29]</sup> activated carbon,<sup>[30]</sup> metal hydroxides (Fe<sup>3+</sup> and Ni<sup>2+</sup>),<sup>[31]</sup> and Mg-Al LDH<sup>[32]</sup> within biopolymer matrices have often been used in recent years because of their economic advantages, high efficiency, easy handling, versatility and reusability.

This work aimed to immobilize LDHs in a hybrid polymer system [alginate/polyvinyl alcohol (PVA) in the presence of the cross-linker glutaraldehyde] to form spherical poly(LDHs) beads with less distortion for arsenate removal. Before testing the performance of the poly(LDHs) beads in a fixed-bed column, batch adsorption studies were conducted to remove arsenate at various times, pH values concentrations and co-existing anions. To clarify the adsorption process, adsorption isotherms and kinetics studies were also conducted. The application of the poly(LDHs) beads for repeated use was also determined. To show that the poly(LDHs) beads can be used in a dynamic flow system, a fixed-bed column with upward flow was also tested.

## Experiments

### Materials

All chemicals were of analytical grade. Iron (III) chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O), aluminum chloride hexahydrate (AlCl<sub>3</sub>·6H<sub>2</sub>O), magnesium chloride hexahydrate (MgCl<sub>2</sub>·6H<sub>2</sub>O), sodium hydroxide (NaOH), sodium arsenate (Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O), sodium alginate and PVA were purchased from Sigma Aldrich (St. Louis, MO, USA).

### Synthesis of LDHs

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<sub>2</sub>·6H<sub>2</sub>O and AlCl<sub>3</sub>·6H<sub>2</sub>O 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<sub>2</sub>·6H<sub>2</sub>O and FeCl<sub>3</sub>·6H<sub>2</sub>O. 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).

### Synthesis of spherical poly(LDHs) beads

To prepare the spherical poly(MgAl) or poly(MgFe) beads with 8% wt of Mg-Al-Cl or Mg-Fe-Cl (Fig. 1a), 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<sub>2</sub> in order to form 4.0-mm spherical beads. The gel beads were allowed to cure in the same CaCl<sub>2</sub> solution for 24 h under stirring and were then rinsed with deionized water to remove excess Ca<sup>2+</sup>. Blank beads were also prepared using an alginate, PVA and glutaraldehyde blend gel without adding Mg-Al-Cl or Mg-Fe-Cl.

### Characterization studies

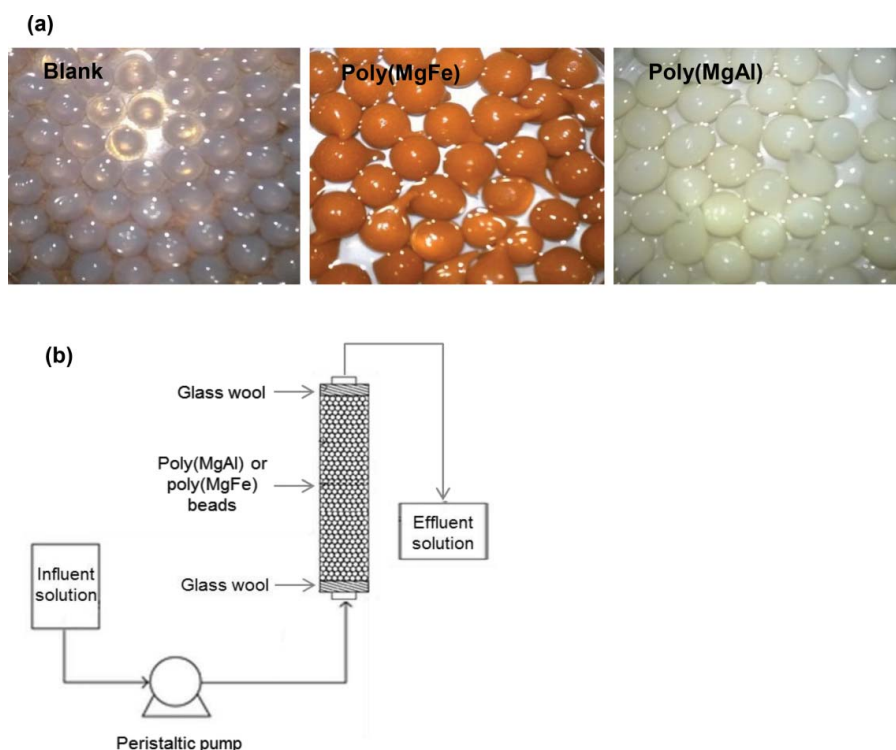
The XRD measurements were conducted on an XRD diffractometer (D8 Advance, Bruker, Germany). Patterns with Cu-K $\alpha$  radiation ( $\lambda = 1.54051 \text{ \AA}$ ) at 40 kV and 40 mA were recorded in the region of  $2\theta$  from 5 to 80°. The morphologies of the poly(LDHs) beads were examined by Scanning Electron Microscopy (SEM) using JEOL (Peabody, MA, 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.

### Adsorption tests

The arsenate adsorption tests were performed by the batch adsorption method in three replicates. For sorption kinetics, 250-mL flasks containing 3 g of each poly(LDHs) and 100 mL of an arsenate solution at a 50 mgAs L<sup>-1</sup> 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- $\mu$ m Millipore membrane filters to analyze aqueous arsenic concentrations. The sorption capacity ( $q_t$ , mg.g<sup>-1</sup>) at any time,  $t$ , was calculated using the following equation:

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

Where  $C_o$  (mg As L<sup>-1</sup>) is the initial concentration of arsenate in the aqueous solution,  $C_t$  (mg As L<sup>-1</sup>) is the arsenate concentration in the aqueous phase at time  $t$ ,  $V(L)$  is the solution volume and  $m$  (g) is the mass of the poly(LDHs) beads. For the experiments studying the effect of pH on adsorption, 100 mL of an arsenate solution with an initial concentration of 50 mg As L<sup>-1</sup> was used. The pH was adjusted using 0.1 M HCl and 0.1 M NaOH before adding 3 g of the poly(LDHs) beads to the arsenate solution for 8 h. Adsorption isotherms were obtained in batch equilibrium experiments with 3 g of the poly(LDHs) beads in 100 mL of an arsenate solution in the concentration range from 5–80 mg As L<sup>-1</sup> at pH 8. The effects of competing anions



**Figure 1.** (a) The as-prepared beads and (b) Schematic diagram of the conventional fixed-bed adsorption reactors.

on arsenate adsorption were also determined. Three grams of poly(LDHs) were added to 100 mL of arsenate solutions ( $50 \text{ mg As L}^{-1}$ ) containing additional various anions (i.e.,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ , or  $\text{HPO}_4^{2-}$ ) at pH 8, and the ratio of As to the added anions was 1:1, 1:5 and 1:10. The mixtures were continuously shaken at  $30^\circ\text{C}$  and 250 rpm for 8 h. The concentrations of arsenic remaining in the solutions were analyzed.

### Regeneration

Arsenate bound to the poly(LDHs) beads was desorbed with a 100-mL solution consisting of 4% NaOH and 2% NaCl for 10 h at  $30^\circ\text{C}$  and 250 rpm. To determine the reusability of the poly(LDHs) beads, consecutive adsorption–desorption cycles were repeated 5 times using the same beads.

### Conventional fixed-bed adsorption reactors

The real-life water samples (water wells) were collected from Dong Thap province, a severely affected area in Mekong

delta, Vietnam. The composition of the water is shown in Table 1. Continuous flow adsorption experiments were conducted in a glass column with a 2-cm internal diameter and a 45-cm length. The column was packed with the poly(MgAl) or poly(MgFe) beads to a depth of 40 cm (Fig. 1b). The column was charged with real-life arsenic-containing water in the up-flow mode at a volumetric flow rate of  $57.32 \text{ cm}^3 (\text{cm}^2 \cdot \text{h})^{-1}$  ( $3.0 \text{ mL min}^{-1}$ ). The samples were collected at certain time intervals and were analyzed for remaining arsenic concentrations.

### Analysis of column data

The total quantity of arsenic bound to the adsorbents in fixed-bed columns,  $q_{total}$  (mg), at a given flow rate and influent arsenate concentration was calculated using the following equation:<sup>[33]</sup>

$$q_{total} = \frac{Q}{1000} \int_{t=0}^{t=t_{total}} (C_o - C_t) dt \quad (2)$$

where  $Q$  ( $\text{mL min}^{-1}$ ) is the volumetric flow rate,  $t_{total}$  (h) is the total time of flow until exhaust,  $C_o$  ( $\text{mg As L}^{-1}$ ) is the initial concentration of arsenate,  $C$  ( $\text{mg As L}^{-1}$ ) is the concentration of arsenate in the effluent and  $m$  (mg) is the total amount of poly(LDHs) beads in the column.

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

$$M_{total} = \frac{C_o Q t_{total}}{1000} \quad (3)$$

**Table 1.** Characteristics of water wells from Dong Thap province in Mekong delta, Vietnam.

Parameter	Quantitative
pH	7.44
$\text{HCO}_3^-$ (mg/L)	35.8
$\text{Cl}^-$ (mg/L)	26.59
$\text{PO}_4^{3-}$ as P (mg/L)	0.03
$\text{SO}_4^{2-}$ (mg/L)	17.0
Total As (mg/L)	0.506

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

$$\text{Total removal (\%)} = \frac{Q_{\text{total}}}{M_{\text{total}}} \times 100 \quad (4)$$

To properly design and operate a fixed-bed adsorption processes, the concept of the Mass Transfer Zone (MTZ) proposed by Michaels was applied.<sup>[34,35]</sup> 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.

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:

$$h_z = U_z t_z = \frac{h(t_z)}{(t_E - t_f)} \quad (5)$$

where  $U_z$  (cm h<sup>-1</sup>) is the movement rate of the MTZ.

The movement rate of the MTZ is a function of the adsorption capacity of the poly(LDHs) beads, 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:

$$t_z = \frac{(V_E - V_B)}{Q} \quad (6)$$

$$t_E = \frac{V_E}{Q} \quad (7)$$

$$t_f = (1 - F)t_z \quad (8)$$

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

$$F = \frac{S_z}{S_{\text{max}}} = \frac{\int_{V_B}^{V_E} (C_o - C) dV}{C_o(V_E - V_B)} \quad (9)$$

where  $S_z$  (mg) is the amount of arsenate that has been removed by the adsorption zone from breakthrough to exhaustion and  $S_{\text{max}}$  (mg) is the amount of arsenate 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:

$$\text{Bed saturation (\%)} = \frac{h + (F - 1)h_z}{h} \times 100 \quad (10)$$

## Determination of the arsenic concentration

The arsenic concentrations were determined in duplicate by a hydride generation atomic absorption spectrophotometer (HG-AAS, Shimadzu Model AA-6800, Japan). The limit of detection (LOD), limit of quantification (LOQ) and limit of linearity (LOL) were  $0.34 \times 10^{-3}$ ,  $10^{-3}$  and  $20 \times 10^{-3}$  mg L<sup>-1</sup>, respectively. In the calculations, results below the LOD were assigned a value of  $0.34 \times 10^{-3}$  mg L<sup>-1</sup>.

## Results and discussion

### Characterization of materials

The XRD patterns of poly(MgAl), poly(MgFe) and blank beads are shown in Figure 2a. The measured XRD patterns of all of the samples fitted well to layered double hydroxide with basal reflections of planes  $h$ ,  $k$ ,  $l$ , (003), (006), (009) and (110) 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 interlayer spacing of the samples corresponded with the (003) and (006) planes that were recorded between 7.84 and 7.91 Å and between 3.85 and 3.92 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 SEM images of the beads are shown in Figure 2b. The analysis of the SEM micrographs revealed that the surfaces of the poly(MgAl) and poly(MgFe) beads were not homogeneous in comparison with the surface of the blank beads, demonstrating that Mg-Al-Cl or Mg-Fe-Cl was mixed with the alginate/PVA-glutaraldehyde blend gel.

### Adsorption kinetics

The adsorption of arsenate onto the poly(LDHs) beads as a function of contact time at a constant initial concentration of 50 mg As L<sup>-1</sup> was studied. The equilibrium time required for adsorption of arsenate onto these beads was approximately 8 h. The findings showed that in the first 8 h, adsorption of arsenate onto the poly(MgAl) and poly(MgFe) beads reached 91.2 and 79.1%, respectively. After 8 h, no significant increase of arsenate adsorption onto the poly(LDHs) beads was observed, which may have been due to complete saturation of available adsorption sites on the surfaces of the poly(LDHs) beads. These results are comparable with a previous study. Lazaridis et al.<sup>[36]</sup> reported that 8 h were required to reach equilibrium when MgAl-CO<sub>3</sub>-LDHs was used as an adsorbent to remove arsenic.

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 arsenate adsorption onto the poly(LDHs) beads, the pseudo-first-order kinetic, pseudo-second-order kinetic and Elovich kinetic models were used to test the dynamic experimental data at an initial concentration of 50 mg As L<sup>-1</sup>



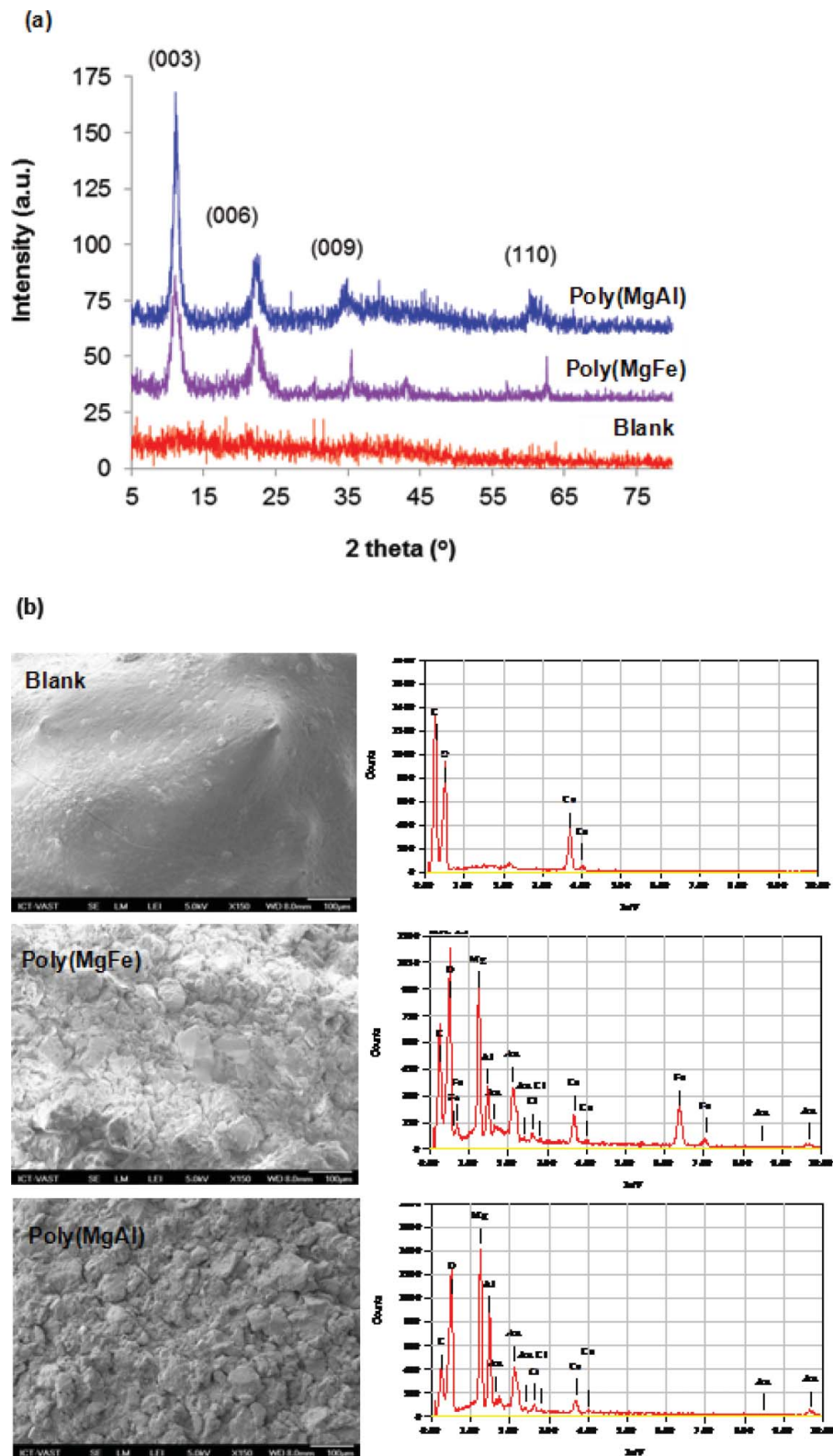
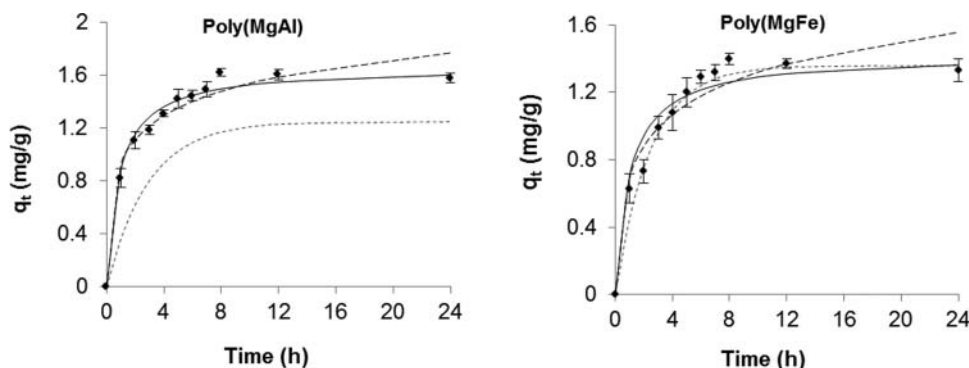


Figure 2. (a) XRD patterns and (b) SEM micrographs and EDX of the as-prepared beads.

and pH 8.<sup>[37-40]</sup> Modeling of these three kinetic models is depicted in Figure 3. The values of the parameters and the correlation coefficients obtained from the three kinetic models are summarized in Table 2. Among these kinetic models, the experimental data showed good agreement with the pseudo-second-order kinetic model. As shown in Table 2, the values of  $r^2$  for

the pseudo-second-order kinetic model were extremely high (all greater than 0.993 for  $r^2$ ), followed by those of the pseudo-first-order kinetic model (all greater than 0.970 for  $r^2$ ) and the Elovich kinetic model (all greater than 0.814 for  $r^2$ ). Consequently, the adsorption process was best described by the pseudo-second-order kinetic model.



**Figure 3.** Adsorption kinetics of arsenate onto the poly(LDHs) beads at pH 8.0. Dotted curve: Lagergren first-order kinetic modeling, solid curve: Pseudo-second-order kinetic modeling, dashed curve: Elovich kinetic modeling.

### Effect of pH

The pH of the aqueous solution is an important parameter in the adsorption process. Therefore, in this study, the adsorption of arsenate onto the poly(LDHs) beads was studied as a function of pH. The initial pH values of the arsenate solution ranged from 6 to 9. The relationship between the initial pH and the amount of arsenate adsorbed onto the poly(LDHs) beads for an initial solution concentration of  $50 \text{ mg As L}^{-1}$  after an 8 h contact time are presented in Figure 4. As shown in Figure 4, pH 8 correlated with maximum adsorption of arsenate. No significantly different amounts of arsenate adsorption onto the poly(LDHs) beads was observed when the solution pH was increased from 6–8; however, the adsorption decreased as the pH was further increased above 9. The pH dependence of arsenic adsorption by LDHs is based on the number of adsorption sites on the surfaces of the beads and the concentration of hydroxyl ions ( $\text{OH}^-$ ) in the aqueous medium.

The movement of arsenate to the LDH surface is a prerequisite of the adsorption reaction, which is largely controlled by electrostatic attraction or repulsion between the arsenate species in the aqueous solution and the LDH surface.<sup>[41]</sup> Therefore, the pH at the point of zero charge ( $\text{pH}_{\text{pzc}}$ ) of the LDHs and the arsenate species are the deciding factors. The species of arsenic in aqueous solutions depend mainly on the pH of the solution. The dissociation constants of arsenate in aqueous solution are  $\text{pK}_{\text{a}1} = 2.3$ ,  $\text{pK}_{\text{a}2} = 6.8$ ,  $\text{pK}_{\text{a}3} = 11.6$ . When the pH increases from the acidic to the alkaline region, the arsenate species changes from  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HAsO}_4^{2-}$  to  $\text{AsO}_4^{3-}$ .<sup>[42]</sup> The adsorbent surface is positively charged at pH values below  $\text{pH}_{\text{zpc}}$  and negatively charged at pH values above  $\text{pH}_{\text{zpc}}$ , resulting in increased electrostatic attraction or repulsion as sites are occupied, thus leading to more or less ready adsorption. The  $\text{pH}_{\text{zpc}}$  of the LDHs has been reported to be in the range from 6.8–8.9,<sup>[43]</sup> below

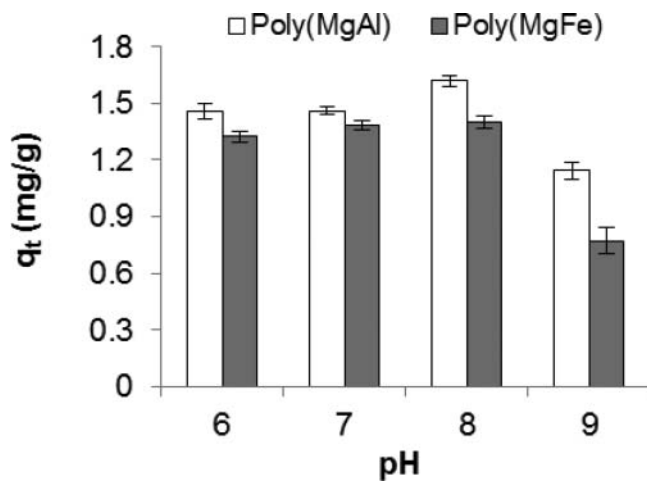
which the LDH surface is positively charged, which is typically beneficial for arsenate adsorption. In the current study, the arsenate adsorption decreased significantly as the pH of the medium ( $\text{pH} > 8.0$ ) was increased due to repulsion between the negative de-protonated arsenate species and the negative surfaces of the LDHs. The decrease in the adsorption of arsenate at a higher pH range may be due to higher pH causing increasing concentrations of hydroxyl ions ( $\text{OH}^-$ ), which have the highest affinity for the poly(LDHs) bead surfaces among monovalent anions.

### Adsorption isotherm

Seven different concentrations of arsenate, that is, concentrations of 5, 10, 20, 40, 50, 60 and  $80 \text{ mg As L}^{-1}$  were selected to investigate the effect of initial arsenate concentrations on the poly(LDHs) beads. The concentrations of arsenate ranged from 5–80  $\text{mg As L}^{-1}$ , which are not environmentally relevant. However, the concentration range was chosen to determine the maximum adsorption capacity of the poly(LDHs) beads. As the initial arsenate concentration was further increased, the residual concentration also increased. The removal efficiency for such a high starting arsenate concentration (5–50  $\text{mg As L}^{-1}$ ) was from 91.2 to 99.0% for the poly(MgAl) beads and from 79.1 to 94.8% for the poly(MgFe) beads. The observation that arsenate removal decreased as the initial concentration was increased may be due to a lack of available adsorption sites for arsenate on the surface of the beads at high concentrations, progressively reaching saturation of the adsorbent. Analyzing isotherm data is very important for predicting the adsorption capacity and the adsorption behavior of an adsorbent. In this work, the Langmuir, Freundlich and Temkin equations were employed to simulate the adsorption isotherms. The fittings of the Langmuir, Freundlich and Temkin models to the experimental data for

**Table 2.** Kinetic parameters and correlation coefficients of arsenate adsorption.

Adsorbent	$q_e, \text{exp mg. g}^{-1}$	Lagergren 1st			Pseudo-2nd			Elovich		
		$q_e \text{ mg. g}^{-1}$	$k_1 \text{ h}^{-1}$	$r^2$	$q_e \text{ mg. g}^{-1}$	$k_2 \text{ mg}^{-1} \cdot \text{h}^{-1}$	$r^2$	$\alpha \text{ mg. g}^{-1} \cdot \text{h}^{-1}$	$\beta \text{ g. mg}^{-1}$	$r^2$
Poly(MgAl)	1.62	1.25	0.344	0.970	1.66	0.687	0.998	8.649	3.769	0.867
Poly(MgFe)	1.40	1.36	0.406	0.989	1.42	0.692	0.993	3.427	3.667	0.814



**Figure 4.** Adsorption of arsenate onto the poly(LDHs) beads as a function of solution pH.

arsenate adsorption on the poly(MgAl) and poly(MgFe) are given in Figure 5.

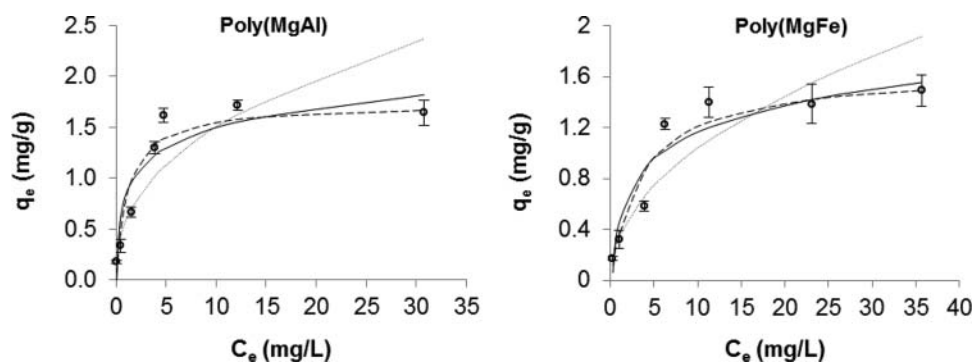
The Langmuir isotherm model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface.<sup>[44]</sup> The Langmuir constants  $q_m$  and  $K_L$  are calculated from the slopes and intercepts of the linear plot of  $C_e/q_e$  versus  $C_e$ , respectively. The parameters of the Langmuir isotherms are listed in Table 3. The calculated maximum adsorption capacities ( $q_m$ ) were not significantly different than the maximum capacities obtained at equilibrium, indicating that the Langmuir isotherm fits the experimental data well ( $r^2 > 0.982$ ). The good fit of the Langmuir isotherm may be due to a homogeneous distribution of active sites on the poly(LDHs) bead surfaces because the Langmuir equation assumes that the surface is homogeneous.

Furthermore, the essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor,  $R_L$ , as follows:<sup>[45]</sup>

$$R_L = \frac{1}{1 + K_L C_0} \quad (11)$$

where  $C_0$  is the initial concentration of arsenate, and  $K_L$  is the Langmuir constant. Favorable adsorption is achieved when  $0 < R_L < 1$ . In this study, all of the  $R_L$  values for arsenate adsorption onto the poly(LDHs) beads were in the range from 0.01–0.41, which indicates a highly favorable adsorption process.

The adsorption capacities of the adsorbents in this study that were calculated from the Langmuir isotherm obtained at an arsenate equilibrium concentration of  $\leq 80$  mg As L<sup>-1</sup> (Fig. 5) were 1.73 mg As g<sup>-1</sup> for poly(MgAl) ( $\approx 21.67$  mg As g<sup>-1</sup> of Mg-Al-Cl) and 1.64 mg As g<sup>-1</sup> for poly(MgFe) ( $\approx 20.55$  mg As g<sup>-1</sup> of Mg-Fe-Cl). These adsorption capacities were higher than adsorption capacities of previously reported adsorbents, such as active carbon prepared from oat hulls (3.1 mg As g<sup>-1</sup>),<sup>[6]</sup> iron-containing ordered mesoporous carbon (7 mg As g<sup>-1</sup>),<sup>[46]</sup> and nano-iron impregnated granulated activated carbon (0.263 mg As g<sup>-1</sup>).<sup>[47]</sup> The adsorption capacities of these beads obtained with arsenate are comparable with the values reported in previous studies. Liu et al.<sup>[48]</sup> reported an arsenate adsorption capacity of 24.2 mg As g<sup>-1</sup> at pH 5 for LiAl-Cl-LDHs at an initial arsenate concentration of 150 mg As L<sup>-1</sup> and a solid/liquid ratio of 2.5 g L<sup>-1</sup>. Lazaridis et al.<sup>[36]</sup> achieved arsenate adsorption capacities of 15.8 and 32.6 mg As g<sup>-1</sup> using MgAl-CO<sub>3</sub>-LDHs at neutral pH with ion strengths of 0.001 and 0.1, respectively. These results and our data indicate that different chemical compositions or types of anions present in the interlayers of LDHs as well as using different experimen-

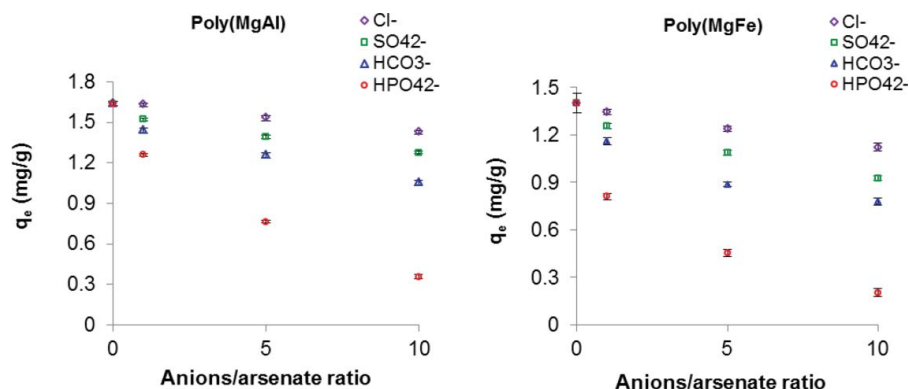


**Figure 5.** Adsorption isotherms of arsenate onto the poly(LDHs) beads at pH 8.0. Dashed curve: Langmuir modeling, dotted curve: Freundlich modeling, solid curve: Temkin modeling.

**Table 3.** Parameters and correlation coefficients obtained from the analysis of adsorption isotherms.

Adsorbent	Langmuir $\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$			Freundlich $\log q_e = \log K_f + \frac{1}{n} \log C_e$			Temkin $q_e = B \ln A_T + B \ln C_e$		
	$q_m$ , mg.g <sup>-1</sup>	$K_L$ , mg <sup>-1</sup>	$r^2$	$1/n$	$K_f$ , g <sup>-1</sup>	$r^2$	$B$ , mol <sup>-1</sup>	$A_T$ , g <sup>-1</sup>	$r^2$
Poly(MgAl)	1.73	0.848	0.994	0.407	0.588	0.917	0.287	18.443	0.857
Poly(MgFe)	1.64	0.275	0.982	0.483	0.341	0.930	0.309	4.316	0.895





**Figure 6.** Effect of co-existing anions on arsenate removal by poly(LDHs) (initial arsenate concentration = 50 mg As L<sup>-1</sup>, pH = 8).

tal procedures (different initial arsenate concentrations, adsorption pHs, ionic strengths and solid to liquid ratios) may affect the arsenate adsorption capacity.

The Freundlich isotherm is based on multilayer adsorption.<sup>[49]</sup> The magnitude of the exponent,  $1/n$ , indicates the favorability of adsorption, and isotherms with  $n > 1$  are classified as L-type isotherms, which reflect a high affinity between pollutants and adsorbents and are indicative of chemisorption.<sup>[50]</sup> By plotting  $\log q_e$  versus  $\log C_e$ , the  $K_f$  and  $n$  values were calculated from the intercept and the slope of the plot, respectively, and are shown in Table 3. In this study,  $1/n$  values were from 0.407 to 0.483 L<sup>-1</sup>g, which indicated favorable sorption.

Linear plots of the Temkin adsorption isotherm are used to visualize chemisorption of a contaminant onto the adsorbents.<sup>[39,51]</sup> Therefore, by plotting  $q_e$  versus  $\ln C_e$ , the Temkin constants  $B$  and  $A_T$  were calculated from the intercept and the slope of the plot, respectively. The values of  $B$  and  $A_T$  obtained are summarized in Table 3. As shown in Table 3, Temkin ( $r^2 > 0.857$ ) was not as adequate as the Freundlich ( $r^2 > 0.917$ ) and Langmuir ( $r^2 > 0.982$ ) models.

Hence, this isotherm fitting result indicated that the poly(LDHs) beads provided specific homogeneous sites, and arsenate adsorption occurred through a monolayer adsorption process.

### Effects of co-existing anions on arsenate adsorption

Drinking water or industrial effluents usually contain various anions that may influence the adsorption of arsenate. The effects of some common anions (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, and HPO<sub>4</sub><sup>2-</sup>) on arsenate adsorption by the poly(LDHs) beads were investigated. Regardless of the type of competing anion, increasing the concentration of a co-existing competing anion resulted in decreased arsenate adsorption onto the poly(LDHs) beads (Fig. 6). This may be due to competition between co-existing anions and arsenate for the positively charged sites on the surfaces of the poly(LDHs) beads. Among the competing anions considered in this work, HPO<sub>4</sub><sup>2-</sup> showed the most adverse effect on arsenate removal. Dahwhal et al.<sup>[52]</sup> reported that sulfate and phosphate severely affected arsenate adsorption onto MgAl-CO<sub>3</sub>-LDH. Violante et al.<sup>[53]</sup> also demonstrated that arsenate adsorption onto MgAl-CO<sub>3</sub>-LDH was decreased in the presence of phosphate. Arsenate adsorption exhibited no significant decrease in the presence of increasing Cl<sup>-</sup> concentrations.

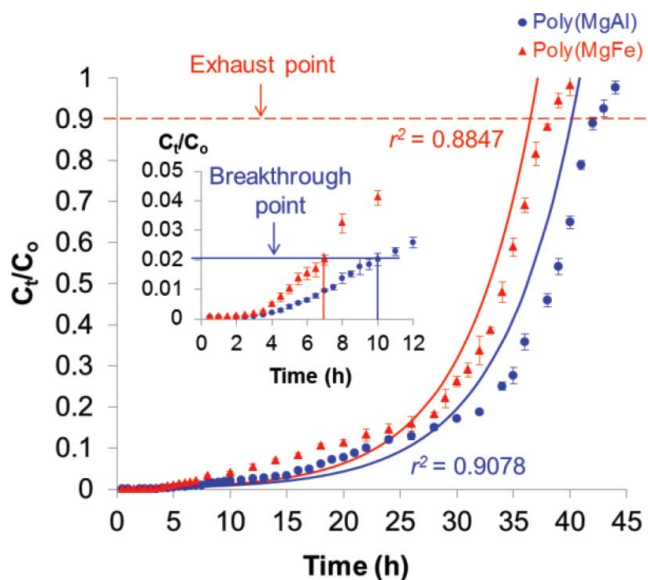
Thus, the effects of competing anions on arsenate adsorption onto the poly(LDHs) beads decreased in the order of HPO<sub>4</sub><sup>2-</sup> >> HCO<sub>3</sub><sup>-</sup> > SO<sub>4</sub><sup>2-</sup> > Cl<sup>-</sup>.

### Regeneration

Effective use of an adsorbent depends not only on the adsorption capacity but also on the capability for regeneration and reuse. The adsorption capacity of the poly(LDHs) beads decreased as the number of regeneration cycles increased; however, the adsorption capacity of the poly(LDHs) beads only decreased by approximately 5–6% after 5 adsorption-desorption cycles. After the fifth regeneration cycle, the arsenate removal rates remained at 85.4 and 72.7% for the poly(MgAl) and poly(MgFe) beads, respectively. These results have clearly demonstrated promising attributes for practical application because of the efficient reusability of the poly(LDHs) beads with effective arsenate removal.

### Conventional fixed-bed adsorption reactor

The efficiency of the treatment technique depends on the arsenic concentration, the arsenic species in the source water and



**Figure 7.** Breakthrough curve for arsenate removal in a fixed-bed of the poly(LDHs) beads.

**Table 4.** Parameters calculated from breakthrough curves for arsenate removal in a fixed-bed.

Adsorbent	M <sub>total</sub> (mg)	q <sub>total</sub> (mg)	Total removal (%)	t <sub>z</sub> (h)	h <sub>z</sub> (cm)	U <sub>z</sub> (cm/h)	Bed saturation (%)
Poly(MgAl)	3.83	3.18	83.03	32	36.06	1.13	81.67
Poly(MgFe)	3.46	2.85	82.37	31	39.55	1.28	78.81

**Table 5.** Calculated constant parameters of the Adam-Bohart equation.

Adsorbent	Linearized Adam-Bohart equation	R <sup>2</sup>	K (L/mg.h)	N (mg/L)	x <sub>o</sub> (cm)
Poly(MgAl)	y = 0.1505 x - 6.9880	0.908	0.297	29.60	25.20
Poly(MgFe)	y = 0.1613 x - 5.9416	0.885	0.319	26.92	25.98

the other constituents in the water. To study the dynamic behavior of the adsorption column, a fixed-bed column study was conducted with real-life arsenic-containing water using a column of 2 cm diameter. The column was packed with the poly(MgAl) or poly(MgFe) beads, and the bed depth was 40 cm. The column was charged with real-life arsenic-containing water in the up-flow mode with a volumetric flow rate of 57.32 cm<sup>3</sup> (cm<sup>2</sup>.h)<sup>-1</sup> (3.0 mL min<sup>-1</sup>). The breakthrough curve is shown in Figure 7.

According to WHO guidelines and due to the high toxicity of arsenic, the breakthrough point was chosen where the arsenate concentration reached its maximum allowed value (corresponding to C/C<sub>0</sub> = 0.02, where C is the effluent arsenate concentration of 0.01 mg As L<sup>-1</sup>, and C<sub>0</sub> is the influent arsenate concentration of 0.5 mg As L<sup>-1</sup>). When the effluent concentration approaches 90% of C<sub>0</sub> (corresponding to C/C<sub>0</sub> = 0.9), then the adsorbents are considered to be essentially exhausted. For the poly(MgAl) beads, the breakthrough (t<sub>b</sub>) and exhaust (t<sub>E</sub>) times were found to be 10 and 42 h for corresponding volumes of 1.8 and 7.56 L of the treated arsenate solution, respectively. For the poly(MgFe) beads, the breakthrough time was at 7 h, the corresponding treated volume was 1.26 L, the exhaust time was 38 h and the corresponding treated arsenate volume was 6.84 L.

Different parameters, such as the time required for the MTZ to move through its own height (t<sub>z</sub>), height of the MTZ (h<sub>z</sub>), MTZ moving rate (U<sub>z</sub>), and bed saturation (%) for the column studies were calculated using Equations (2–10). The results are shown in Table 4. The results obtained indicate that a better column performance was obtained using the fixed-bed of the poly(MgAl) beads. Under the same experimental conditions, a comparison of the fixed-bed columns of the poly(MgAl) and poly(MgFe) beads showed that longer service times, larger volumes treated and a higher quantity of arsenate removed were obtained using the fixed-bed poly(MgAl) beads. In general, the reported performance using the poly(MgAl) beads for arsenate removal in a column was promising compared with the poly(MgFe) beads.

To describe the fixed-bed column behavior and to scale the adsorbents up for industrial applications, the Bohart-Adams model was used to fit the experimental data in the column, as follows:<sup>[54]</sup>

$$\ln\left(\frac{C_t}{C_o}\right) = KC_o t - \frac{KNx}{V} \quad (12)$$

$$x_o = \frac{V}{KN} \ln\left(\frac{C_o}{C_b} - 1\right) \quad (13)$$

where C<sub>t</sub> and C<sub>o</sub> (mg As L<sup>-1</sup>) are the effluent and influent arsenate concentrations, respectively, V (cm h<sup>-1</sup>) is the linear flow velocity, x (cm) is the bed depth, K [L (mg.h)<sup>-1</sup>] is the kinetic constant, N is the maximum adsorption capacity (mg L<sup>-1</sup>), and x<sub>o</sub> (cm) is the minimum column height required to produce an effluent concentration C<sub>b</sub> (breakthrough concentration, 0.01 mg As L<sup>-1</sup>).

A plot of ln(C<sub>t</sub>/C<sub>o</sub>) versus t yields a straight line with a slope KC<sub>o</sub> 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<sub>o</sub>) are shown in Table 5. These values could be used to design an adsorption column. The fittings of the Bohart-Adams model to the experimental data for arsenate removal using poly(LDHs) fixed-bed columns are shown in Figure 7. The calculated maximum adsorption capacity of the poly(MgAl) fixed-bed column was higher than that of the poly(MgFe) fixed-bed column. The obtained results indicate that a better column performance was achieved using the fixed-bed column of poly(MgAl) compared with the fixed-bed column of poly(MgFe). The fixed-bed column of poly(MgAl) produced longer service times, treated larger volumes and removed a higher quantity of arsenate. However, both fixed-bed adsorbents showed decent removal of problematic arsenate. In general, the performance reported using the poly(LDHs) beads for arsenate removal in a fixed-bed column was promising for use as an adsorbent.

## Conclusion

A hybrid sorbent, poly(LDHs), 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 poly(LDHs) beads at pH 8 calculated from the Langmuir adsorption isotherm were from 1.64 to 1.73 mg As g<sup>-1</sup> beads (≈ 20.55–21.67 mg As g<sup>-1</sup> LDHs powder). The adsorption ability of the poly(LDHs) beads decreased by approximately 5–6% after 5 adsorption-desorption cycles. Phosphate and carbonate markedly decreased the removal of arsenate. The effects of co-existing anions on the adsorption capacity declined in the following order: HPO<sub>4</sub><sup>2-</sup> >> HCO<sub>3</sub><sup>-</sup> > SO<sub>4</sub><sup>2-</sup> > Cl<sup>-</sup>. A fixed-bed column study was performed with real-life arsenic-

containing water. The breakthrough time was found to be from 7 to 10 h, and the exhaust time was from 38 to 42 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 poly (LDHs) beads developed in this study are a promising adsorbent for application to arsenate decontamination technology.

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