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Removal of Arsenic (III) from groundwater applying a reusable Mg-Fe-Cl layered double hydroxide

Jia-Qian Jiang,^{a*} S.M. Ashekuzzaman,^a Justin S. J. Hargreaves,^b Andrew R. McFarlane,^b A Borhan M Badruzzaman^c and Mehedi Hasan Tarek^c

Abstract

BACKGROUND: Layered double hydroxide compounds (LDHs) have been applied for the removal of oxyanions including arsenate (As(V)). However, the aim of this present research is to develop a LDH to treat arsenite (As(III)). Both batch and column sorption studies were conducted to assess the effect of LDH dosage, contact time, solution pH and initial As(III) concentrations on the As(III) removal performance. The potential re-use of this sorbent was also investigated.

RESULTS: For 2 g L⁻¹ of Mg-Fe-Cl LDH, As(III) in test solution can be reduced from 400 µg L⁻¹ to <10 µg L⁻¹ after a contact time of 2 h. High As(III) concentration in Bangladesh groundwater can be reduced to meet the national drinking water standards (<50 µg L⁻¹). The maximum adsorption capacity of As(III) by Mg-Fe-Cl LDH is 14.6 mg g⁻¹-LDH. Further, reusability of this sorbent was at least 20 cycles of regeneration with effective As(III) removal between 93.0 and 98.5%. Moreover, As(III) removal was unaffected by the solution pH but affected by the co-existing competing anions and concentration of As(III). Finally, the main mechanism of As(III) removal by Mg-Fe-Cl LDH was suggested to be chemical sorption together with anion and ligand exchange with interlayer Cl⁻ and OH⁻ ions.

CONCLUSION: High efficiency of sorption of As(III) by the developed Mg-Fe-Cl LDH was demonstrated in this study which is generally not the case for most other sorbent materials. Pilot-scale trials are needed to explore the suitability of full application of the developed Mg-Fe-Cl LDH for the removal of As(III).

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Keywords: arsenic removal; layered double hydroxide (LDH); sorption, desorption; drinking water treatment

INTRODUCTION

Arsenic (As) is a contaminant of global concern due to its toxicity, persistence, bioaccumulation potential and its significant contribution to the pollution of water resources including drinking water. Indeed, about 150 million people in 70 countries are at risk of exposure to As contaminated drinking water.¹ Therefore, there is a great demand for low cost, user friendly (i.e. simple design, easy operation) and high efficiency arsenic removal technologies which can easily be applied in these major As affected areas. The maximum permissible limit of total As in potable water has been recommended as 10 µg L⁻¹ by the World Health Organization (WHO).

The various arsenic treatment processes can be grouped as: (1) oxidation and sedimentation; (2) coagulation and filtration; (3) membrane separation; and (4) adsorption.² Among these, adsorption has been found to be promising because of its applicability to small scale treatment plants and household systems, simplicity in design, ease of operation, application to largely sludge free operation and regeneration capability.^{3,4} A number of adsorbents such as zeolite/modified zeolite,^{5,6} activated and mesoporous alumina,^{7,8} activated carbon,⁹ Fe-oxides¹⁰ and ferrihydrite¹¹ have been studied so far for arsenic removal. Of these, minerals

containing iron and aluminium (hydr)oxides, particularly those which are poorly crystalline (hydr)oxides (e.g. ferrihydrite), exhibit relatively high affinity to As oxyanions (i.e. arsenate and arsenite).¹² Sorption on such (hydr)oxide minerals usually takes place only on their external surfaces. However, owing to their relative instability and high solubility, these poorly crystalline (hydr)oxide minerals can pose a risk for secondary contamination of water supplies

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through the dissolution of contaminant-bearing (hydr)oxides. In recent years, layered double hydroxides (LDHs) or hydrotalcite-like compounds have been proposed as a good ion-exchangers and adsorbents, and as a result, these have been widely studied in removing oxyanions such as phosphate, borate, chromate and arsenate from aqueous solution.^{13–16}

The main structure of LDHs consists of positively charged brucite-like ($\text{Mg}(\text{OH})_2$) sheets and negatively charged interlayer regions containing anions and water molecules. Based on the structure of LDHs, positive charges are balanced by interlayer anions that can be exchanged for other anions. Thus, LDHs possess good anion exchange properties. Moreover, LDHs can provide binding sites for contaminants both on their external surfaces and their internal layers. Various isostructural LDH compounds can be prepared with great diversity in metal precursor (i.e. cation pairs), intercalated anion and by a synthesis method; however, Fe-based LDHs are particularly promising candidates for arsenic removal because they comprise Fe-(hydr)oxides, which have high affinity for arsenic.^{1,17} Studies have been reported on the removal of arsenate ($\text{As}(\text{V})$) by Mg-Fe-LDHs,¹⁸ but there have been very few studies directed towards the evaluation of the $\text{As}(\text{III})$ sorption performance of Mg-Fe-LDH. Moreover, for practical use of LDHs, it is pertinent to assess $\text{As}(\text{III})$ removal from real contaminated groundwater using Mg-Fe-LDHs. Hence in this study, Mg-Fe LDH based LDHs were chosen for investigation aimed towards their ability to remove $\text{As}(\text{III})$ from water under realistic operating conditions.

Experiments were conducted applying both batch sorption and column filtration approaches. The potential of the regeneration and reuse of this sorbent material was also investigated. To our knowledge, this study is the first attempt to remove arsenite from real contaminated groundwater by using Mg-Fe-LDH with the evaluation of its potential for repeated use which is a significant consideration.

MATERIALS AND EXPERIMENTAL PROCEDURES

Synthesis of Mg-Fe-Cl LDH and its characterization

Mg-Fe-Cl LDH was synthesized using Cl^- based divalent and trivalent salts. At room temperature, a solution containing $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (initial Mg/Fe molar ratio = 2) was slowly added to a second solution containing 2 mol L^{-1} NaOH under vigorous mechanical stirring. During this mixing process, the pH was between 12.6 and 13.0. After mixing, the resultant thick slurry was aged at 85°C for 2 h, and the pH after ageing was around 8.2. Then, the solid precipitate was separated by centrifugation and dried at 60°C for 20 h, followed by washing with deionized water to free excess Cl^- associated with the LDH product. Finally, the wet LDH solid was dried at 60°C for 24 h, and gently ground and sieved to the fraction of 0.50 to 0.85 mm.

The samples of Mg-Fe-Cl LDH were characterized before and following arsenic adsorption. Arsenic-loaded LDH (As-LDH) samples obtained via the sorption of arsenic from adsorbate solution, were washed with deionised water, followed by drying at 60°C for 20 h. For phase identification, X-ray diffraction (XRD) analyses were performed on a Siemens D5000 Diffractometer, employing Cu K_α radiation with a step size of 0.02° and a counting time of 1 s per step. The measurements were run in the 2θ range $5-85^\circ$, and samples were prepared by compaction into a silicon sample holder.

The composition of the synthesized LDH product was determined using the mass balance protocol. In this case, following the centrifugation step in the synthesis process, the supernatant

was collected by separating from solid precipitates via filtration and measured to record the volume. Finally, the mass difference between the ions dosed in the preparation step and the ion residuals in the supernatant was used to determine the ion content in the LDH product.¹⁸ The concentration of various ions (e.g. Mg^{2+} , Fe^{3+} , Cl^-) in the aqueous phase was determined using a RFID enabled HACH DR3900 spectrophotometer using respective calibrants supplied by HACH Lange, UK.

Batch experiments

The bench experiments were carried out as a function of LDH dosage, contact time, initial pH of solution and initial adsorbate concentration. The description of the materials and procedures are outlined in the following sub-sections.

Adsorbate solution

The working adsorbate solution with the desired concentration for all batch sorption studies was freshly taken from an arsenite ($\text{As}(\text{III})$) stock solution of $10\,000 \mu\text{g-As L}^{-1}$, prepared by diluting 0.05 mol L^{-1} sodium arsenite solution (NaAsO_2 , Sigma) with deionized water. The pH of the working solutions was adjusted manually to the required values with dilute NaOH or HCl solutions.

As(III) uptake assays

The sorption experiments for $\text{As}(\text{III})$ uptake were carried out at room temperature in 50 mL screw-top centrifuge tubes which contained various dosages of LDH compound in 25 mL of adsorbate solution with an initial concentration of $400 \mu\text{g-As L}^{-1}$ and a $\text{pH} \sim 6.2 \pm 0.3$. Mixing of the LDH and the adsorbate solution was performed using a MAXQ 4450 orbital shaker (Thermo Scientific) at 250 rpm for 24 h. After shaking, the suspension was immediately centrifuged for phase separation and the supernatant pH was measured. Finally, the supernatant was collected through filtration using a syringe filter ($0.45 \mu\text{m}$ Whatman filter disc), and analysed to determine the residual As concentration. In this way, to select appropriate LDH dosage, sorption runs were conducted. The same procedures were adopted when determining the equilibrium contact time and the time intervals applied were 0.25, 0.50, 0.75, 1.00, 1.50, 2.00, and 2.50 h. In this case, the initial $\text{As}(\text{III})$ concentration and adsorbent dosage were fixed at $400 \mu\text{g L}^{-1}$ and 2 g L^{-1} , respectively. Moreover, $\text{As}(\text{III})$ sorption studies were performed under different initial $\text{As}(\text{III})$ concentrations and at various initial pH levels to determine the adsorption isotherms and the effect of pH, respectively. The shaking time applied was 2.00 h in both cases, while the adsorbent dose and other procedures adopted were as mentioned previously. All the experiments were conducted in duplicate and the results are within the standard deviation ($< \pm 3\%$).

Analytical approach

pH values were measured by a pH meter (Cyberscan pH 11, Eutech Instruments). Materials were weighed using an Ohaus Analytical Plus balance. The arsenic concentration was determined with the HACH DR3900 spectrophotometer by following the absorbance at 865 nm. The $\text{As}(\text{III})$ concentration was measured based on standard methods.¹⁹ The adsorption capacity (Q_e , $\mu\text{g g}^{-1}$) and removal rate (R) of As were calculated from the following relations:

$$Q_e = \frac{(C_0 - C_e) \cdot V}{m}, R(\%) = 100 \times \frac{C_0 - C_e}{C_0}$$

where C_0 is the initial concentration of the As ($\mu\text{g L}^{-1}$), C_e is the equilibrium or residual As concentration ($\mu\text{g L}^{-1}$), V is the volume of the solution (L) and m is the mass of adsorbent (g).

As(III) desorption and regeneration of LDH

In the first cycle, As(III) sorption was conducted for 2 h at room temperature by adding Mg-Fe-Cl LDH (2 g L^{-1}) to the adsorbate solution ($400 \mu\text{g-As L}^{-1}$). As(III) saturated LDH (As-LDH) was then separated through centrifugation and the supernatant was withdrawn to determine the residual As(III) concentration. Then, the solid phase of As-LDH was treated applying a solid to liquid ratio of 2 g L^{-1} with a desorbing solution consisting of 4% NaOH and 2% NaCl with 2 h shaking. The mixture was then centrifuged and the supernatant was analysed to measure the extent of arsenic release. After the desorption run, the resulting LDH solids were washed with deionized water several times and then, dried at 60°C overnight. In this way, the LDH was regenerated and reused for up to 20 cycles.

The sorption rate (R_{ads}) and desorption rate (R_{des}) were estimated from the following relations:

$$R_{\text{ads}(i)} (\%) = 100 \times \frac{C_0 - C_{(i)}}{C_0}, R_{\text{des}(i)} (\%) = 100 \times \frac{Q_{\text{des}(i)}}{Q_{\text{ads}(i)}}$$

where C_0 is the initial concentration of As ($\mu\text{g L}^{-1}$); $C_{(i)}$ is residual concentration of As in the i th adsorption operation ($\mu\text{g L}^{-1}$); $Q_{\text{ads}(i)}$ is amount of As uptake in the i th adsorption operation ($\mu\text{g-As g}^{-1}$ -LDH); $Q_{\text{des}(i)}$ is the amount of As desorbed in the i th desorption operation ($\mu\text{g-P g}^{-1}$ -LDH).

Laboratory column experiments

These were conducted to assess arsenic contaminated water treatment capacity with a Mg-Fe-Cl LDH packed column. In these studies, both real arsenic contaminated groundwater and As(III) spiked test solutions were used.

Collection of groundwater samples and chemical characterization

Three shallow wells, nearing the village of Sreenagar of Dhaka in Bangladesh, were chosen to collect arsenic contaminated groundwater. Sampling points were from three depths, 50, 65 and 100 ft, respectively. The outflow of sampling tube was connected to an *in situ* filter (0.45 micron medium-capacity disposable filter capsule (Geotech Environmental Equipment, Inc.)). Water quality parameters such as pH, dissolved oxygen (DO) and electrical conductivity (EC) were measured in the field immediately after sample collection using a multi-parameter water quality meter (WTW Multi 3500i, Geotech Environmental Equipment, Inc.). *In situ* arsenic concentration in the samples from each well was assessed by an Arsenic Test Kit (HACH, UK). Some samples (about 500 mL) from each well were collected via acidification using concentrated HNO_3 (8–10 drops).

Collected groundwater samples were analysed to determine the various water chemistry parameters following the standard analytical approaches.¹⁹ The concentrations of phosphorus ($\text{PO}_4^{3-}\text{-P}$), nitrate ($\text{NO}_3^-\text{-N}$), sulfate (SO_4^{2-}), ammonia ($\text{NH}_4^+\text{-N}$) were determined within 1–2 days of sample collection using a HACH DR/4000U Spectrophotometer. The major cations (e.g. Ca^{2+} , Mg^{2+} , Na^+ , K^+) were determined by atomic absorption spectrophotometry (AA-6800, Shimadzu) in the acidified samples. Total arsenic concentration of all samples (acidified) was determined by graphite furnace atomizer (GFA-7000, Shimadzu). Alkalinity, chloride and total iron concentrations were determined respectively by titration, argentometric and colorimetric methods. Bicarbonate was determined by alkalinity.

Set-up of column filtration

Two glass columns, each of size 200 mm length and 11 mm diameter filled with 2 g of Mg-Fe-Cl LDH, were fed separately with groundwater extracted from 65 and 100 ft depths (containing 107 and $402 \mu\text{g-As L}^{-1}$, respectively). The groundwater was filtered using $0.45 \mu\text{m}$ filter paper before being flowed through the column in order to reduce the iron precipitates which resulted in the reduction of original As concentrations. The influent samples were then adjusted by spiking a HACH As(III) Reference Standard solution to achieve values close to the original concentrations (107 and $402 \mu\text{g-As L}^{-1}$, respectively) and pH of 7.4 ± 0.2 . A peristaltic pump (Sci 400/120S, Watson Marlow) was used to deliver a constant downward flow rate of 0.55 mL min^{-1} ($0.35 \text{ m}^3 \text{ m}^{-2} \text{ h}^{-1}$). Effluent samples were collected at various time intervals and were analysed to determine the residual As by graphite furnace atomizer. The inflow was continued until the effluent As concentration reached about $50 \mu\text{g L}^{-1}$. A duplicate sorption study was conducted through a column packed with 1 g Mg-Fe-Cl LDH and fed with groundwater of As concentration $402 \mu\text{g L}^{-1}$.

A column study was also conducted to assess As removal from As(III) test solution with initial concentration of $400 \mu\text{g-As L}^{-1}$ and pH of 6.2 ± 0.3 , and this solution was prepared by spiking As(III) stock solution into deionized water (described previously). In this study, the column was packed with 1 g Mg-Fe-Cl LDH.

Sorption/desorption column study

After the first sorption cycle, deionized water was initially pumped through the packed column for 1 h at 1.7 mL min^{-1} and then desorbing solution was flowed through the column. The extent of As release was analysed. Finally, before commencing the next sorption cycle, the column was washed with deionized water until the effluent pH was below 8. In this way, the sorption experiments with groundwater were repeated three times without any further modifications of the LDH used. Similarly, sorption/desorption repetition was performed up to five times for the As(III) test solution, and arsenic contained desorbing solution was re-used in the subsequent desorption cycles.

RESULTS AND DISCUSSION

Physicochemical characteristics of Mg-Fe-Cl LDH

The structural characteristics of the Mg-Fe-Cl LDH (before and after arsenic removal) were analysed by powder X-ray diffraction (XRD) as presented in Fig. 1. The XRD pattern of the as-synthesized sample LDH is as expected for a typical LDH structure with sharp and symmetric reflections corresponding to the (003), (006), (110) and (113) planes; and broad asymmetric peaks from the (009), (015) and (018) planes. According to the Inorganic Crystal Structure Database (ICSD), these are characteristic planes of hydroxalcalite-like compounds and they match well with the expected reference pattern of ICSD 81963.^{4,16}

The stability of Mg-Fe LDHs in the aqueous phase was assessed in a previous study²⁰ by identifying ion release characteristics during batch sorption runs for phosphate removal, and in this study only 1.2% of the Mg^{2+} or Fe^{3+} ions were released from Mg-Fe LDHs after the first sorption run. Moreover, ion release was almost negligible ($\sim 0.5\%$) during the second sorption run after first regeneration, confirming the stable nature of Mg-Fe LDHs. Based on the mass balance results shown in Table 1, the empirical formula of the Mg-Fe-Cl LDH is proposed to be $\text{Mg}_{1.95}\text{Fe}_{1.15}(\text{OH})_{5.94}\text{Cl}_{2.47} \cdot x(\text{H}_2\text{O})$. This composition is roughly in

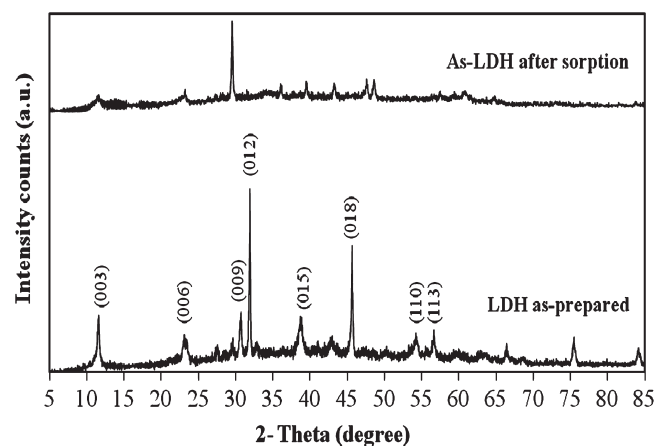


Figure 1. Powder XRD patterns (a) and FT-IR spectra (b) of Mg-Fe-Cl LDH before (as-prepared) and after As removal.

Table 1. Composition of Mg-Fe-Cl-LDH

Ion	Dose in preparation (g)	Residual in the supernatant (g)	Content in LDH	
			(g)	(mol)
Mg ²⁺	4.9	0.161	4.7	0.195
Fe ³⁺	5.6	0.000	5.6	0.100
Cl ⁻	24.9	16.072	8.8	0.247
Na ⁺	13.8	10.350	3.5	0.150
OH ⁻	10.2	–	10.1 ^a	0.594

^a based on mass and electronic balance

accordance with the molar ratio of Mg to Fe (2:1) applied in the synthesis process.

Water chemistry and arsenic species

Since the aqueous solution prepared by spiking sodium arsenite test solution into deionized water had a pH between 6.1 and 6.5, the resultant As(III) species were H₃AsO₃.²¹

Groundwater samples had pH between 6.7 and 6.9 with low dissolved oxygen (DO). HCO₃⁻ (273–453 mg L⁻¹) and Ca²⁺ (57–95 mg L⁻¹) were the dominant ions. The concentration of total As increased with depth, and the values were 83.7, 152.8 and 463.6 µg L⁻¹ at 50, 65 and 100 ft depth, respectively. According to Swartz *et al.*,²² As(III) is the dominant species representing more than 80% of total As at most depths (between 46 and 200 ft) in groundwater. Also, as was the case for the test solution, the As(III) species was in the form of H₃AsO₃.

Uptake of As(III) by Mg-Fe-Cl LDH

Effect of dosage

The As(III) removal efficiency increased sharply with increasing adsorbent dosage, and then levelled off at an adsorbent dosage above 2 g L⁻¹ with about 99% removal efficiency (Fig. 2). In subsequent studies, the adsorbent dosage used was 2 g L⁻¹. The corresponding adsorption capacity and residual As(III) concentration at this dosage were 197 µg-As g⁻¹-LDH and 6 µg L⁻¹, respectively, meaning that the standard of arsenic limit for drinking water can be met. Normalized sorption capacity decreased with increasing dose (Fig. 2), due to the availability of surplus material at higher dosage as observed in other studies.^{18,23}

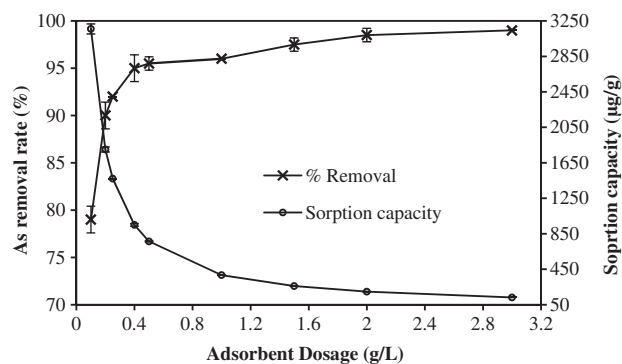


Figure 2. Adsorption of As(III) on LDH as a function of adsorbent dosage. Y error bars indicate the standard deviation at each data point (n = 2).

Effect of contact time and adsorption kinetics

The adsorption as a function of contact time at constant initial concentration ([As₀] = 400 µg L⁻¹) was studied. The equilibrium time required for the adsorption of As(III) on LDH was almost 2 h and the removal rate was about 98%. No significant decrease of As concentration was observed with further increase in time. Consequently, all subsequent adsorption experiments were conducted at 2 h contact time.

First-order and pseudo-second-order kinetic models were used to analyse the sorption kinetics. As shown in Table 2, the theoretical uptake q_e (cal) is in good agreement with the experimental uptake q_e (exp) for the pseudo second-order model. So, the adsorption kinetics of As(III) by the synthesized LDH in this study are well governed by the pseudo-second-order kinetic model.

Effect of adsorbate solution pH

The sorption of As(III) onto Mg-Fe-Cl LDH at initial pH values ranging from 2.5 to 11.0 was assessed. The adsorption efficiency was almost steady (~98%) in the range of pH between 2.5 and 9.0; however, with further increase in pH up to 11.0, there was a steady decline. This can be attributed to the pH dependence of As speciation in aqueous solution as well as to the point of zero charge (pH_{pzc}) of the sorbents. In the present study, the dominant As(III) species in the adsorbate solution was H₃AsO₃ as expected to be the case within an initial pH range between 2.5 and 9.0. Other As(III) species (e.g. H₂AsO₃⁻, HAsO₃²⁻ and AsO₃³⁻) usually dominate at pH > 9.5.²¹ While most of the sorbent materials were found to be ineffective in removing uncharged H₃AsO₃,²⁴ the Mg-Fe-Cl LDH in this study demonstrated excellent steady sorption efficiency. The decrease in sorption of As(III) with increasing pH is in conformity with the fact that higher pH causes increasing concentrations of hydroxyl ions (OH⁻) which have the highest affinity for LDH surfaces among monovalent anions (e.g. H₂AsO₃⁻).²⁵ Also, higher pH (e.g. at pH > 9.0) can cause poor interaction between negatively charged As(III) species (pK_a = 9.2 and 12.1) and LDH, because the pH_{pzc} for uncalcined LDHs was reported to be in the range 7.0–9.0 and the surface of LDH is negatively charged when the solution pH > pH_{pzc}.^{1,17}

Moreover, this study revealed the strong buffering capacity of Mg-Fe-Cl LDH as the final pH remained about 9.0 for the initial pH range of 3.0–9.0, with no significant changes in sorption efficiency.

Effect of initial As(III) concentration and adsorption isotherm

The uptake of As(III) by Mg-Fe-Cl LDH was evaluated for a range of initial As(III) concentrations between 200 and 3000 µg L⁻¹. The residual As concentration after the sorption study was observed

Table 2. Kinetic parameters and correlation coefficients (R^2) for first-order and pseudo-second-order kinetic models

Adsorbent	$q_e, \text{exp} (\mu\text{g g}^{-1})$	First-order ^a			Pseudo-second-order ^b		
		$q_e, \text{cal} (\mu\text{g g}^{-1})$	$k_1 (\text{h}^{-1})$	R^2	$q_e, \text{cal} (\mu\text{g g}^{-1})$	$k_2 (\text{g } \mu\text{g}^{-1} \text{ h}^{-1})$	R^2
Mg-Fe-Cl LDH	196.0	64.0	2.32	0.985	202.9	0.07	1

^a $\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$; ^b $\frac{t}{q_t} = \frac{1}{k_2 b q_e^2} + \frac{t}{q_e}$
 where q_e and q_t ($\mu\text{g g}^{-1}$) are the amounts of As(III) adsorbed on the adsorbents at equilibrium and at time t (h). k_1 (h^{-1}) and k_2 ($\text{g } \mu\text{g}^{-1} \text{ h}^{-1}$) are the rate constants of first-order and pseudo-second-order kinetic models.

Table 3. Isotherm model constants for As(III) adsorption on Mg-Fe-Cl LDH

Adsorbent	Langmuir isotherm ^a			Freundlich isotherm ^b		
	$q_0 (\mu\text{g g}^{-1})$	$b (\text{L } \mu\text{g}^{-1})$	R^2	K_f	n	R^2
Mg-Fe-Cl LDH	14591.6	0.002	0.986	46.0	1.35	0.944

^a $\frac{1}{q_e} = \frac{1}{q_0 b C_e} + \frac{1}{q_0}$; ^b $\log q_e = \log K_f + \frac{1}{n} \log C_e$
 where q_0 = maximum adsorption capacity ($\mu\text{g g}^{-1}$), b = adsorption equilibrium constant ($\text{L } \mu\text{g}^{-1}$), q_e = adsorption capacity at equilibrium ($\mu\text{g g}^{-1}$), C_e = equilibrium adsorbate concentration ($\mu\text{g L}^{-1}$), K_f and n are the Freundlich isotherm constants.

to be less than $10 \mu\text{g L}^{-1}$ (arsenic limit in drinking water by WHO) for an initial concentration up to $400 \mu\text{g-As L}^{-1}$. With further increase of initial As(III) concentration, the residual concentration was observed to be increased. The corresponding removal efficiency for such a high starting As(III) concentration (200 to $2000 \mu\text{g L}^{-1}$) was between 97.5 and 98.5%. Generally, it is expected that the removal rate of arsenic will decrease with increase of initial As concentration because of the lack of available sites that can accommodate increased As species at fixed adsorbent dosage.

The data were used to plot linearly transformed Langmuir and Freundlich adsorption relationships, and values of isotherm constants are presented in Table 3. The value of correlation coefficient (R^2) shown in Table 3 indicates the better applicability of the Langmuir isotherm model to describe the As(III) adsorption capacity of Mg-Fe-Cl LDH. The fitness of the Langmuir isotherm to predict As(III) affinity by Mg-Fe-Cl LDH can also be assessed using the Langmuir parameter b and initial As(III) concentration (C_0) to obtain the separation factor R_L ($R_L = 1/(1 + bC_0)$).^{3,18} When $0 < R_L < 1$, the adsorption system is favourable. In the current study, the values of R_L were found to be in the range 0.13 to 0.74 with a decreased separation factor at high As(III) concentrations, which indicates highly favourable adsorption of As(III) by Mg-Fe-Cl LDH.

The maximum arsenic adsorption capacity by the LDHs will be affected by various factors, such as the nature of the arsenic species, i.e. As (V) or As (III); the composition and properties of the LDHs used; the characteristics of co-existing anions in the solution/water studied and the experimental approaches used. On this basis, the variation of the maximum adsorption capacity of As(III) from this study (14.60 mg g^{-1} -LDH, see Table 3) and from the literature¹⁵ can be rationalised.

Desorption and regeneration

Since preliminary studies showed that 4% NaOH was adequate to achieve greater than 98% desorption rate, 4% NaOH in

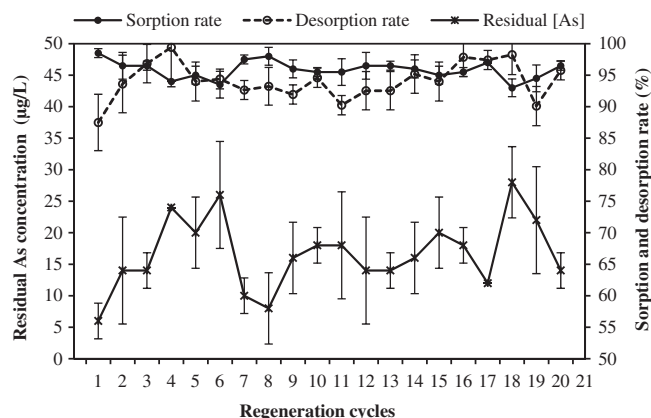


Figure 3. Sorption and desorption profiles of Mg-Fe-Cl LDH after different cycles of regeneration. Y error bars indicate the standard deviation of each data point ($n = 2$).

combination with 2% NaCl was used as the desorbing solution. The reason for the addition of NaCl to the desorbing solution was to re-intercalate Cl^- in the interlayers of the LDH for the regeneration of Mg-Fe-Cl LDH.

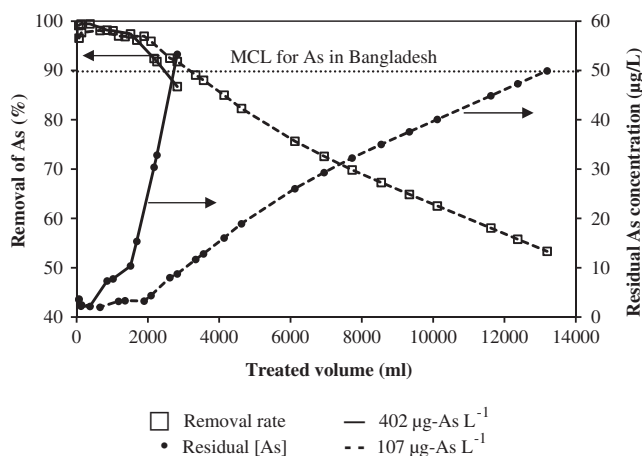
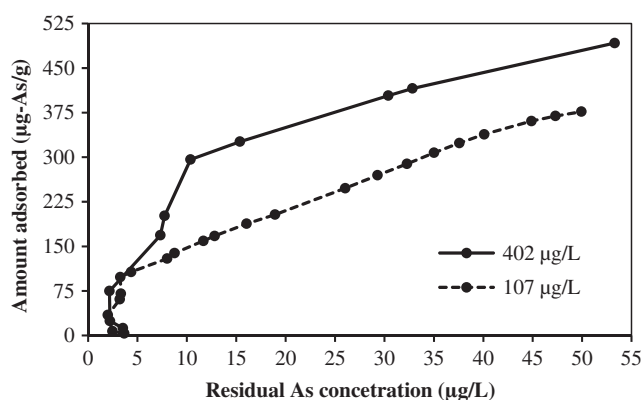
The performance of Mg-Fe-Cl LDH for As(III) removal in repeated cycles of sorption–desorption is shown in Fig. 3. The As(III) removal efficiency (i.e. sorption rate) remained between 93.0 and 98.5% for up to 20 cycles of regeneration of the LDH adsorbent, and the residual As concentration was always below $50 \mu\text{g L}^{-1}$. These results have clearly demonstrated the efficient reusability of the synthesized LDH with effective As(III) removal to meet the drinking water requirement in developing countries such as Bangladesh. The desorption rate of As from As-loaded LDH also remained very stable in the range 87.5 to 99% in consecutive regeneration cycles (Fig. 3). Such a stable sorption and desorption rate resulted in a steady average As(III) sorption capacity of about $191.7 \pm 2.85 \mu\text{g g}^{-1}$ ($n = 20$) with a linear progression in cumulative sorption capacity. The accumulated adsorbed amount of As(III) after 20 cycles of regeneration was about $3051 \mu\text{g-As g-LDH}^{-1}$.

Column studies of sampled ground water

The results for removing As from groundwater via continuous operation with a Mg-Fe-Cl LDH filled column are shown in Figs 4 and 5. On the basis of preliminary measurements, a flow rate of 0.55 mL min^{-1} was used. Groundwater samples with high ($402 \mu\text{g L}^{-1}$) and low ($107 \mu\text{g L}^{-1}$) starting As concentrations were passed through the column until the residual As in the treated volume exceeded the MCL value ($50 \mu\text{g-As L}^{-1}$), and the corresponding treated volumes were observed to be about 2.8 and 13.2 L, respectively (Fig. 4). The arsenic removal rate was decreased

Table 4. Re-use profile of Mg-Fe-C LDH in removing As(III) through column filtration ($[As_0] = 400 \mu\text{g L}^{-1}$)

Cycle no.	Treated volume (mL)	Residual As concentration ($\mu\text{g L}^{-1}$)	Sorption rate (%)	Volume of desorbing solution (mL)	Cumulative released As concentration ($\mu\text{g L}^{-1}$)	Desorption rate (%)
1	2729.5	10.1	97.5	350	2480.5	81.6
2	2512	10.7	97.3	398	4046.8	87.2
3	2528.5	14.7	96.3	520	4801.7	96.6
4	2562.5	20.3	94.9	519	6292.8	94.3
5	1913.0	19.5	95.1	514	7324.3	95.0

**Figure 4.** Removal rate and residual concentration of As with respect to volumes of groundwater containing $402 \mu\text{g-As L}^{-1}$ and $107 \mu\text{g-As L}^{-1}$ passed through column packed with 2 g Mg-Fe-Cl LDH.**Figure 5.** Changes of adsorbed amount of As per g LDH as a function of residual As concentration.

during continuous flow of influent samples and ranged between 50 and 99% before exceeding residual value of $50 \mu\text{g L}^{-1}$. On the other hand, the cumulative adsorbed amount of As increased with increase of residual As concentration upon continued inflow (Fig. 4). The adsorbed amount of As on Mg-Fe-Cl LDH reached 490 and $376 \mu\text{g-As g}^{-1}\text{-LDH}$, respectively, for samples with high and low starting concentrations of As. This could be related to the effect of the competitive sorption of other anions (e.g. PO_4^{3-} , P , HCO_3^-) with the increase of treated volume; this has been reported elsewhere.¹²

A column sorption-desorption was run for up to 5 cycles to assess reusability of Mg-Fe-Cl LDH in terms of the treated volume

with a residual As concentration close to $10 \mu\text{g L}^{-1}$. The residual concentration of As from the third cycle run increased to above $10 \mu\text{g L}^{-1}$ for treatment of a similar volume of As(III) solution (Table 4). However, the sorption and desorption rate were observed to remain high, above 94%. The desorbing solution was reused in the consecutive desorption operation and released As reached $7324 \mu\text{g L}^{-1}$ after the fifth cycle (Table 4). These findings demonstrate the potential reusability of Mg-Fe-Cl LDH over sorption-desorption repetitions as well as the possible recovery of arsenic from As-condensed desorbing liquid.

CONCLUSIONS

A LDH dosage of 2 g L^{-1} is sufficient to reduce the concentration of As(III) in aqueous solution from an initial value of $400 \mu\text{g L}^{-1}$ to $<10 \mu\text{g L}^{-1}$ at an equilibrium contact time of 2 h. Real contaminated groundwater in Bangladesh with high arsenite concentration can be treated to meet the national drinking water standards. The adsorption kinetics of As(III) onto Mg-Fe-Cl LDH are well described by the pseudo-second-order kinetic model and adsorption data fit well to a Langmuir isotherm. The maximum adsorption capacity of As(III) was $14.6 \text{ mg g-LDH}^{-1}$. The As(III) removal was unaffected by the solution pH but affected by the co-existing competing anions and concentration levels of arsenic. Further, reusability of this adsorbent was possible for at least 20 cycles of regeneration with effective As(III) removal being between 93.0 and 98.5%. Finally, the uptake mechanism involved chemical sorption together with As(III) interlayer anion/ligand exchange by Cl^- and OH^- . The above findings indicate that Mg-Fe-Cl LDH is an interesting potential adsorbent which is suitable for further exploration under pilot-scale experimentation conditions in order to fully realize its application to arsenic decontamination technology.

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REFERENCES

- Caporale AG, Pigna M, Azam SMGG, Sommella A, Rao MA and Violante A, Effect of competing ligands on the sorption/desorption of arsenite on/from Mg-Fe layered double hydroxides (Mg-Fe-LDH). *Chem Eng J* **225**:704–709 (2013).
- Jiang J-Q, Removing arsenic from groundwater for the developing world. *Water Sci Technol* **44**:89–98 (2001).
- Turk T, Alp I and Deveci H, Adsorption of As(V) from water using Mg-Fe-based hydroxalcalite (FeHT). *J Hazard Mater* **171**:665–670 (2009).

- 4 Goh KH, Lim TT and Dong ZL, Removal of arsenate from aqueous solution by nanocrystalline Mg/Al layered double hydroxide: sorption characteristics, prospects and challenges. *Water Sci Technol* **61**:1411–1417 (2010).
- 5 Chutia P, Shigeru K, Kijima T and Satokawa S, Arsenic adsorption from aqueous solution on synthetic zeolites. *J Hazard Mater* **162**:440–447 (2009).
- 6 Jiang J-Q, Ashekuzzaman SM, Jiang A, Sharifuzzaman SM and Chowdhury SR, Arsenic contaminated groundwater and its treatment options in Bangladesh. *Int J Environ Res Public Health* **10**:18–46 (2013).
- 7 Lin TF and Wu JK, Adsorption of arsenite and arsenate within activated alumina grains: equilibrium and kinetics. *Water Res* **35**:2049–2057 (2001).
- 8 Kim YH, Kim CM, Choi I, Rengaraj S and Yi JH, Arsenic removal using mesoporous alumina prepared via a templating method. *Environ Sci Technol* **38**:924–931 (2004).
- 9 Chuang CL, Fan M, Xu M, Brown RC, Sung S, Saha B and Huang CP, Adsorption of arsenate by activated carbon prepared from oat hulls. *Chemosphere* **61**:478–483 (2005).
- 10 Pigna M, Krishnamurti GSR and Violante A, Kinetics of arsenate sorption-desorption from metal oxides: effect of residence time. *Soil Sci Soc Am J* **70**:2017–2027 (2006).
- 11 Zhu J, Pigna M, Cozzolino V, Caporale AG and Violante A, Sorption of arsenite and arsenate on ferrihydrite: effect of organic and inorganic ligands. *J Hazard Mater* **189**:564–571 (2011).
- 12 Wang SL, Liu CH, Wang MK, Chuang YH and Chiang PN, Arsenate adsorption by Mg/Al-NO₃ layered double hydroxides with varying the Mg/Al ratio. *Appl Clay Sci* **43**:79–85 (2009).
- 13 Jiang J-Q and Ashekuzzaman SM, Development of novel inorganic adsorbent for water treatment. *Curr Opin Chem Eng* **1**:191–199 (2012).
- 14 Violante A, Pucci M, Cozzolino V, Zhu J and Pigna M, Sorption/desorption of arsenate on/from Mg-Al layered double hydroxides: influence of phosphate. *J Colloid Interface Sci* **333**:63–70 (2009).
- 15 Deliyanni EA, Peleka EN, Gallios GP and Matis KA, A critical review of the separation of arsenic oxyanions from dilute aqueous solution. *Int J Environ Waste Manage* **8**:286–304 (2011).
- 16 Kang D, Yu X, Tong S, Ge M, Zuo J, Cao C and Song W, Performance and mechanism of Mg/Fe layered double hydroxides for fluoride and arsenate removal from aqueous solution. *Chem Eng J* **228**:731–740 (2013).
- 17 Guo Y, Zhu Z, Qiu Y and Zhao J, Adsorption of arsenate on Cu/Mg/Fe/La layered double hydroxide from aqueous solutions. *J Hazard Mater* **239–240**:279–288 (2012).
- 18 Jiang J-Q, Xu Y, Quill K, Simon J and Shettle K, Laboratory study of boron removal by Mg/Al double-layered hydroxides. *Ind Eng Chem Res* **46**:4577–4583 (2007).
- 19 APHA: *Standard methods for the examination of water and wastewater*, 21st edn. American Public Health Association, Washington DC (2005).
- 20 Ashekuzzaman SM and Jiang J-Q, Study on the sorption-desorption-regeneration performance of Ca-, Mg- and CaMg-based layered double hydroxides for removing phosphate from water. *Chem Eng J* **246**:97–105 (2014).
- 21 Smedley PL and Kinniburgh DG, A review of the source, behavior and distribution of arsenic in natural waters. *App. Geochem* **17**:517–568 (2002).
- 22 Swartz CH, Blute NK, Badruzzaman B, Ali A, Brabander D, Jay J, Besancon J, Islam S, Hemond HF and Harvey CF, Mobility of arsenic in a Bangladesh aquifer: inferences from geochemical profiles, leaching data, and mineralogical characterization. *Geochimica Cosmochimica Acta* **68**:4539–4557 (2004).
- 23 Xing K, Wang H, Guo L, Song W and Zhao Z, Adsorption of tripolyphosphate from aqueous solution by Mg-Al-CO₃-layered double hydroxides. *Colloid Surf A: Physicochem Eng Aspect* **328**:15–20 (2008).
- 24 Garelick H, Dybowska A, Valsami-Jones E and Priest ND, Remediation technologies for arsenic contaminated drinking waters. *J Soils Sediments* **5**:182–190 (2005).
- 25 Miyata S, Anion-exchange properties of hydrotalcite-like compounds. *Clays Clay Miner* **31**:305–311 (1983).