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Synthesis of mesoporous Cu/Mg/Fe layered double hydroxide and its adsorption performance for arsenate in aqueous solutions

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Abstract
The mesoporous Cu/Mg/Fe layered double hydroxide (Cu/Mg/Fe-LDH) with carbonate intercalation was synthesized and used for the removal of arsenate from aqueous solutions. The Cu/Mg/Fe-LDH was characterized by Fourier transform infrared spectrometry, X-ray diffraction crystallography, scanning electron microscopy, X-ray photoelectron spectroscopy and Brunauer-Emmett-Teller. Effects of various physico-chemical parameters such as pH, adsorbent dosage, contact time and initial arsenate concentration on the adsorption of arsenate onto Cu/Mg/Fe-LDH were investigated. Results showed that it was efficient for the removal of arsenate, and the removal efficiency of arsenate increased with the increment of the adsorbent dosage, while the arsenate adsorption capacity decreased with increase of initial pH from 3 to 11. The adsorption isotherms can be well described by the Langmuir model with \( R^2 > 0.99 \). Its adsorption kinetics followed the pseudo second-order kinetic model. Coexisting ions such as \( \text{HPO}_4^{2-}, \text{CO}_3^{2-}, \text{SO}_4^{2-} \) and \( \text{NO}_3^- \) could compete with arsenate for adsorption sites on the Cu/Mg/Fe-LDH. The adsorption of arsenate on the adsorbent can be mainly attributed to the ion exchange process. It was found that the synthesized Cu/Mg/Fe-LDH can reduce the arsenate concentration down to a final level of less than 10 \( \mu \text{g/L} \) under the experimental conditions, and makes it a potential material for the decontamination of arsenate polluted water.

Key words: arsenate; adsorption; mesoporous layered double hydroxide; anion exchange

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Introduction
Arsenic has been considered as one of the most toxic elements, and it is often introduced into water environment through the dissolution of minerals and ores from industrial effluents and atmospheric deposition (Mandal and Suzuki, 2002; Smedley and Kinniburgh, 2002). Natural sources, such as the dissolution of arsenic-containing bedrock, often contribute significantly to the high arsenic content of drinking water and groundwater (Fawell et al., 2003). Although environmental regulations have limited the production and uses of arsenic and its compounds, arsenic-based products are still extensively used in various industries, including metallurgy, agriculture, forestry, electronics, pharmaceuticals and the glass and ceramic industry (Altundogan et al., 2000). Arsenic can be present in several oxidation states (–3, 0, +3 and +5), but the trivalent arsenite and pentavalent arsenate occur more prominently in the environment (Smedley and Kinniburgh, 2002). The presence of arsenic in drinking water is receiving increasing attention since arsenic is highly carcinogenic after long-term or high-dose exposure, and the current maximum allowable concentration level of arsenic in drinking water specified by World Health Organization is 10 parts per billion (WHO, 2003).

Arsenic cannot be destroyed, but can be transformed into different forms or converted into insoluble compounds in the presence of other substances. It is essential to develop novel and efficient methods for arsenic removal from drinking water. Various technologies have been developed to treat arsenate-containing water including coagulation (Gupta et al., 2005), reverse osmosis (Vrijenhoek and Waypa, 2002), ultra filtration (Iqbal, 2007) and adsorption (Meski et al., 2010; WHO, 1993). Among these methods, adsorption technique is one of the most popular and practical methods due to its high efficiency, low cost and easy equipment handling (Jiang, 2001; Bissen and Rimmel, 2003). More and more attention has been paid to the development of effective adsorbents to control the arsenate pollution including zeolites (Chutia et al., 2009), granular ferric hydroxide (Guan et al., 2008), activated...
alumina (Bellock, 1971), activated carbon (Chuang et al., 2005) and so on. In recent years, a number of studies have also been done on arsenic sorption onto layered double hydroxide materials (Grover et al., 2009; Manju, 2000; You et al., 2001).

Layered double hydroxide (LDH) have relatively large surface areas and high anion exchange capacities. So they have been studied extensively as adsorbents of anionic contaminants, like 2,4-dichlorophenoxyacetic acid (Chaparadza and Hossenlopp, 2011), bromate (Chitrakar et al., 2011), phosphate (Miyauuchi et al., 2009; Saha et al., 2010), and fluoride (Lü et al., 2006; Delorme et al., 2007). LDH can be usually depicted by the formula $[M^{II}(1-x)M^{III}x(OH)_2]^{x+}A^{2-}xZ^{2-}(OH)\cdot xH_2O$, where $M^{II}$ and $M^{III}$ are divalent and trivalent metal cations, and $A^{2-}$ is an interlayer charge compensating anion with $y$ number of water molecules (Yang et al., 2006). The structure of LDH is derived from that of the mineral brucite (Cavani et al., 1991). Brucite comprises a close packing of hydroxyl ions in which $Mg^{2+}$ ions occupy alternative layers of octahedral sites, leading to a stacking of charge-neutral metal hydroxide layers of composition $[Mg(OH)_2]$. When a fraction $X$ of $Mg^{2+}$ ion is replaced by a trivalent ion such as $Al^{3+}$ or $Fe^{3+}$, the positive charge, $X^+$, is generated on the metal hydroxide layer. The positive charge is compensated by the inclusion of anions, $A^{2-}$, in the interlayer region of LDH.

Arsenic has a high affinity for adsorption on iron oxides, which is evident from the observation that arsenic in natural environment often exists on the surface of iron oxides (Nishida et al., 2004). The iron-based LDH are thus promising candidates for arsenic removal (Türk et al., 2009), but studies on synthetic Mg-based LDH for arsenic sorption onto layered double hydroxide and its adsorption performance for arsenate in aqueous solutions were investigated. The possible mechanism for arsenate adsorption onto the Cu/Fe-LDH was also discussed.

1 Materials and methods

1.1 Materials

Analytical reagents for the preparation of Cu/Mg/Fe-LDH, including Cu(NO$_3$)$_2$$\cdot$3H$_2$O, Mg(NO$_3$)$_2$$\cdot$6H$_2$O, FeCl$_3$$\cdot$6H$_2$O, NaOH, and Na$_2$CO$_3$, were purchased from Sinopharm Chemical Regent Co., Ltd. All the chemicals were used without further purification. The arsenate stock solution was prepared from sodium salt heptahydrate (Na$_2$HAsO$_4$$\cdot$7H$_2$O) (Fluka) dissolved in deionized water.

1.2 Cu/Mg/Fe-LDH

Cu/Mg/Fe-CO$_3$ LDH was synthesized using a constant pH co-precipitation method. First, a mixed solution of Cu(NO$_3$)$_2$$\cdot$3H$_2$O (6 mol/L), Mg(NO$_3$)$_2$$\cdot$6H$_2$O (24 mol/L), and FeCl$_3$$\cdot$6H$_2$O (10 mol/L) salts with (Cu$^{2+}$+Mg$^{2+}$)/Fe$^{3+}$ molar ratio of 3 was made in 50 mL deionized water. Solution of NaOH (8 mol/L) and Na$_2$CO$_3$ (20 mol/L) was also made in 50 mL deionized water. These two solutions were added drop-wise into the vigorously-stirred deionized water in a Teflon reaction vessel. Solutions of NaOH and HCl were added simultaneously to maintain a constant pH of 10.5. The synthetic process was carried out at room temperature. After the drop-wise addition of the two solutions, the suspensions were aged at 353 K for 20 hr. Precipitates were filtered and washed with deionized water to remove excessive salts. The collected solids were dried and stored. Thus the LDH material containing Cu$^{2+}$, Mg$^{2+}$, Fe$^{3+}$ and CO$_3^{2-}$ was obtained.

The chemical composition of the Cu/Mg/Fe-LDH was determined by Optima 2100DV ICP-OES (Perkin Elmer Inc., USA) after dissolving the samples in concentrated nitric acid. The X-ray diffraction patterns of the Cu/Mg/Fe-LDH before and after arsenate adsorption were recorded on a D-8 Advance X-ray diffractometer (Bruker-AXS, Germany) with CuKα radiation operated at 40 kV and 40 mA. The pore structure of the Cu/Mg/Fe-LDH was analyzed by N$_2$ adsorption-desorption at 77 K on an Autosorb-Iq-MP Analyzer (Quanta Chrome Instruments, USA). Prior to the analysis, the samples were out-gassed in a vacuum. The surface areas were calculated by the Brunauer-Emmett-Teller (BET) method, and the pore size distribution and total volume were determined by the Brunauer-Joyner-Hallenda method applied to the desorption branch. Fourier transfer infrared (FT-IR) spectra were recorded on a Thermo Nicolet 5700 (USA) FT-IR instrument. The sample was mixed with oven dried spectroscopic grade KBr and pressed into a disc. The spectrum was recorded between 400 and 4000 cm$^{-1}$. A Quanta 200 FEG scanning electron microscope (SEM) Company, Holland) was used for SEM analysis of the Cu/Mg/Fe-LDH. The point of zero charge pH ($pH_{pcu}$) of the Cu/Mg/Fe-LDH was determined by the Zetasizer Nano Zeta potentiometric Analyzer (Malvern Instruments Ltd., England). The X-ray photoelectron spectroscopy (XPS) analyses were performed on a RBD upgraded PHI-5000C ESCA system with AlKα radiation at 1486.6 eV. The energy scale of the XPS spectra was calibrated with the binding energy of the C 1s peak due to the surface contamination.

1.3 Adsorption experiments

Batch equilibrium isotherm studies were conducted at 298 K in a set of Erlenmeyer flasks (100 mL) with different...
concentrations (1–15 mg/L) of As(V). A series of 20 mg dose Cu/Mg/Fe-LDH was put into each of the flasks and the initial pH of the solution was set at 6.0. Thereafter, the flasks were placed in a shaker with a constant speed of 150 r/min for 24 hr. The aqueous samples were filtered, and the residue concentration of As(V) in the solution was determined with Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Optima 2000, Perkin Elmer, UK). The amount of As(V) adsorbed at equilibrium \( q_e \) (mg/g) was calculated using:

\[
q_e = \frac{(C_0 - C_e)V}{W}
\]

where, \( C_0 \) (mg/L) and \( C_e \) (mg/L) are the solution concentration of As(V) at the beginning and equilibrium, respectively; \( V \) (L) is the volume of the solution; and \( W \) (g) is the mass of the dry adsorbent used.

Adsorption kinetics was also studied in batch experiments in which 20 mg of Cu/Mg/Fe-LDH was added to 100 mL of As(V) solution with an initial concentration of 2 mg/L (pH 6.0) and shaken at 150 r/min, 298 K. The aqueous samples were flatted at pre-determined time, and the residue As(V) concentrations in the filtrates were determined.

The effect of initial pH on the adsorption of As(V) by Cu/Mg/Fe-LDH was carried out with the As(V) solutions (100 mL, 2 mg/L) at different pH values (3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0 and 11.0). A dosage of 20 mg of Cu/Mg/Fe-LDH was put into each As(V) solution at 298 K. After 24 hr shaking, the aqueous samples were filtered, and the residue As(V) concentrations in the filtrates were determined.

The effect of Cu/Mg/Fe-LDH dosage on As(V) adsorption was investigated by adding Cu/Mg/Fe-LDH to 100 mL of As(V) solutions with initial concentration of 2 mg/L at pH 6.0 and shaking at 150 r/min, 298 K for 24 hr. The aqueous samples were filtered, and the remaining As(V) concentrations in the filtrates were determined.

The effect of coexisting ions was investigated as following: 2 mg/L of As(V) solutions were prepared with a certain amount of competing ions. The coexisting ions NO\(_3^−\), SO\(_4^{2−}\), HPO\(_4^{2−}\), and CO\(_3^{2−}\) were prepared from their corresponding sodium salts. A dose of Cu/Mg/Fe-LDH adsorbent 0.2 g/L was added to each solution and the samples were shaken at 298 K for 24 hr and then analyzed using the procedure described before.

### 1.4 Desorption experiments

Desorption experiments were conducted after 100 mL of 2 mg/L As(V) solutions were equilibrated with the Cu/Mg/Fe-LDH material. After centrifugation the equilibrated solution was withdrawn for ICP-OES analysis, and the sodium salt solution of HPO\(_4^{2−}\) was used as desorption solution to be mixed with the saturated adsorbent, which was then shaken for 24 hr and centrifuged again. The amount of As(V) desorbed was determined through analysis of As(V) released into the solution.

## 2 Results and discussion

### 2.1 Characterization of LDH

The chemical analysis result of the synthesized Cu/Mg/Fe-LDH is as follows. Molar ratio of (Cu\(^{2+}\) + Mg\(^{2+}\))/Fe\(^{3+}\) is 2.72, which is close to that of the starting salts 3.0. The little difference can be attributed to an incomplete incorporation of cations inside the layers. The Cu\(^{2+}\) content is 11.6 mass%; Mg\(^{2+}\) content is 20.3 mass%; and Fe\(^{3+}\) content is 17.1 mass%.

The XRD patterns of the Cu/Mg/Fe-LDH are presented in Fig. 1 line a. The diffraction peaks of the material are typical of the layered double hydroxides structure (Gregg and Sing, 1982; Busetto et al., 1984). It has sharp and symmetric reflections of the basal (003), (006) and (009) planes. The two reflections of (110) and (113) around 60° can be clearly distinguished. The XRD pattern and chemical analysis result confirmed that the layered structure material containing Cu\(^{2+}\), Mg\(^{2+}\), Fe\(^{3+}\) and with CO\(_3^{2−}\) in the interlayer had been successfully synthesized. The crystal parameters of the LDH before and after As(V) adsorption are shown in Table 1. Results showed that after As(V) adsorption, the \( d \) spacing peak was shifted towards higher value from 11.394° to 11.430°.

The FT-IR spectrum of the Cu/Mg/Fe-LDH is shown in Fig. 2, which indicates that the spectra of the Cu/Mg/Fe-LDH resemble those of hydrotaclcite-like phases with CO\(_3^{2−}\) as the counter anion (Hernandez-Moreno et al., 1985; Kloprogge and Frost, 1999). There is a strong and broad absorption band at 3467 cm\(^{-1}\), which is associated with a superposition of hydroxyl stretching band v(\(OH\))\(_{\alpha}\) arising from metal-oxide groups in the layers and hydrogen-bonded interlayer water molecules. Another absorption band at 1645 cm\(^{-1}\) represents the water deformation, \( \delta (\text{H}_2\text{O}) \). The absorption band observed around

![Fig 1 XRD patterns of the LDH samples before (line a) and after (line b) As(V) adsorption.](image-url)
Table 1  Crystal parameters of the LDH before and after As(V) adsorption (LDH-As(V))

<table>
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<tr>
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<th>2θ (degree)</th>
<th>Basal spacing, (d) (Å)</th>
<th>Metal-metal distance ((a)) (nm)</th>
<th>Interlayer distance ((c)) (nm)</th>
<th>Crystal size (nm)</th>
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<td>LDH</td>
<td>11.394</td>
<td>7.78</td>
<td>0.311</td>
<td>2.337</td>
<td>14.9</td>
</tr>
<tr>
<td>LDH-As(V)</td>
<td>11.430</td>
<td>7.73</td>
<td>0.312</td>
<td>2.318</td>
<td>14.8</td>
</tr>
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</table>

\(a\): average metal-metal distance inside the brucite-like sheets, which is \(2 \times d\) \((110)\). \(c\): interlayer distance regulated by the size and charge of the anion placed between the brucite-like sheets, which is \(3 \times d\) \((003)\). Crystal size was calculated from the average value of full width at half maximum of peak \((003)\) and \((006)\) using Scherrer equation.

1362 cm\(^{-1}\) is the \(v_3\) (asymmetric stretching) of the \(\text{CO}_3^{2-}\) ion in the interlayer. The bands observed in the low frequency 500–1000 cm\(^{-1}\) region of the spectrum are interpreted as the lattice vibration modes of M–O and M–OH (Lagadic et al., 1992; Titulaer et al., 1994).

Adsorption and desorption isotherms of the Cu/Mg/Fe-LDH with \(\text{N}_2\) are presented in Fig. 3. The isotherms followed the type IV adsorption isotherms according to the IUPAC classification with a H3-type hysteresis loop for the desorption isotherm, which was a characteristic of mesoporous materials (Wu et al., 2007). Moreover, the adsorption isotherm did not show a plateau at high \(P/P_0\) values, which suggested that \(\text{N}_2\) physi-sorption occurred between aggregates of platelet particles and led to the lamellar morphology of the LDH.

The surface area of Cu/Mg/Fe-LDH was 70 m\(^2\)/g, the \(C\) value in BET equation was 212, the pores volume was 0.797 mL/g, the absence of micropores was confirmed by the t-plot analysis. The average pore size was calculated as 34.6 nm, following the size range of mesoporous materials. These results indicated the mesoporous structures and high surface area of the Cu/Mg/Fe-LDH synthesized in our experiment.

An SEM image of the Cu/Mg/Fe-LDH is shown in Fig. 4. In general, LDH crystal has plate-like morphology and hexagonal crystallite. Although part of the Cu/Mg/Fe-LDH is coagulated, it showed clearly the plate-like morphology and the hexagonal crystallite.

2.2 Effect of experimental conditions on adsorption

The initial solution pH is important and can affect the adsorption process at the water-adsorbent interfaces. Therefore, the effect of initial solution pH on the adsorption of As(V) was examined at different pH values ranging from 3.0 to 11.0, and the results are shown in Fig. 5. It showed that the amount of As(V) adsorbed on the Cu/Mg/Fe-LDH decreased with increasing pH from 3.0 to 11.0.

The speciation of As(V) changes with the solution pH. The neutral form \(\text{H}_3\text{AsO}_4\) is dominant at acidic pH range (0–2), but \(\text{H}_2\text{AsO}_4^-\) will be the dominant form under mildly acidic conditions (2–7). Main species are \(\text{HAsO}_4^{2-}\)
at pH = 7 to 12.0 and AsO_4^{3-} at pH =12 to 14 (Zhang and Hideaki, 2005). In the pH range of 3–11, H_2AsO_4^- and HAsO_4^{2-} are the dominant species.

The adsorption efficiency on the Cu/Mg/Fe-LDH decreased with increasing pH, which might be related to pH_{pzc} of LDH in aqueous solutions. The pH_{pzc} of the Cu/Mg/Fe-LDH used in this experiment was determined as 8.0. When the solution pH is higher than pH_{pzc}, the surface of the Cu/Mg/Fe-LDH is negatively charged. Therefore, the arsenate anionic species are repelled by the LDH surface. Furthermore, the negative effect of pH at the higher pH range may be further compounded by the increasing competitive effect of OH^- adsorption on LDH. When the solution pH is lower than the pH_{pzc} of LDH, the LDH surface is positively charged, which is beneficial for the adsorption of the negatively charged anionic species.

Meanwhile, under different initial solution pH values, the possibility of metal release from LDH in a solution has been considered and researched. The results showed that the metal ions released from LDH in the aqueous solution were limited and negligible. Furthermore, the XRD patterns of the LDH material after As(V) adsorption under different pH values showed the typical peaks of the layered double hydroxides. It was demonstrated that the layered structure of the LDH material was kept during the adsorption process under different pH values.

The effect of adsorbent dosage on the As(V) adsorption has been examined and the result is shown in Fig. 6. As expected, the As(V) removal increased sharply with increasing adsorbent dose above 1.0 g/L. On the other hand, Fig. 6 also shows that the As(V) adsorption capacity of the LDH decreased with increasing LDH dosage, this is because the increasing amount of LDH dosage caused more unsaturated adsorption sites, which caused the adsorption capacity decreased. Furthermore, when the Cu/Mg/Fe-LDH concentration was 1.0 g/L, the resulting As(V) concentration was lower than 10 μg/L, which can meet the need of the recommended concentration limit of arsenic in drinking water.

### 2.3 Adsorption kinetics

The adsorption kinetics were investigated for As(V) sorption onto the Cu/Mg/Fe-LDH at room temperature. Experiments were carried out with an initial As(V) concentration of 2 mg/L and adsorbent dosage 0.2 g/L (Fig. 7). The adsorption was fast at the first 100 min. As more adsorption sites were filled with arsenate, the adsorption rate slowed down and gradually reached the equilibrium. The pseudo first-order and pseudo second-order kinetic models have been used to fit the experimental data. The pseudo first-order kinetic model can be expressed as follows (Wang et al., 2009):

\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]

where, \(q_e\) (mg/g) represents the amount of adsorbate adsorbed at time \(t\), and \(k_1\) (min\(^{-1}\)) represents the adsorption rate constant. The adsorption rate constant \(k_1\) was calculated from the plot of \(\ln(q_e - q_t)\) against \(t\). For the pseudo second-order kinetic model, it can be expressed as below (Wang et al., 2009):

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

where, \(k_2\) (g/(mg-min)) is the pseudo second-order rate constant of sorption, \(q_e\) and \(k_2\) can be obtained by linear plot of \(t/q_t\) versus \(t\).

The pseudo first- and second-order constants and correlation coefficients were determined from the linear plots of ln(\(q_e-q_t\)) and \(t/q_t\) against time \(t\). It was found that the pseudo second-order model had a relatively high correlation coefficient \(k_2 = 0.002\) g/(mg-min), \(q_{e,cal} = 7.46\) mg/g, \(R^2 = 0.998\) compared with the pseudo first-order model \(k_1 = 0.0005\) min\(^{-1}\), \(q_{e,cal} = 2.75\) mg/g, \(R^2 = 0.829\), therefore the kinetics of As(V) adsorption onto the Cu/Mg/Fe-LDH can be better described by the pseudo second-order model.
2.4 Adsorption isotherms

Adsorption isotherm can describe how adsorbates interact with adsorbents in an adsorption system. The adsorption isotherm for As(V) uptake by the Cu/Mg/Fe-LDH is shown in Fig. 8. The adsorbed As(V) increased rapidly upon increasing As(V) concentration until reaching a plateau. The Langmuir and Freundlich adsorption isotherms were used to analyze the equilibrium adsorption data. These two models are presented as Eqs. (4) and (5), respectively (Hartono et al., 2009; Veli and Alyüz, 2007):

\[ q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \quad (4) \]

\[ q_e = \frac{1}{K_F C_e^n} \quad (5) \]

where, \( K_L \) (L/mg) is the Langmuir adsorption constant related to the energy of adsorption, \( q_m \) (mg/g) is the maximum adsorption capacity, \( K_F \) (L/mg) is the Freundlich constant, and \( 1/n \) is the heterogeneity factor.

The Langmuir isotherm model can be linearized as Eq. (6):

\[ \frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (6) \]

The Langmuir constants \( K_L \) and \( q_m \) can be determined from the linear plot of \( C_e/q_e \) versus \( C_e \). The linearized form of Freundlich isotherm model is given as Eq. (7):

\[ \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (7) \]

The Freundlich constants \( K_F \) and \( 1/n \) are determined from the linear plot of \( \ln q_e \) versus \( \ln C_e \).

The adsorption isotherms of As(V) onto the LDH depicted with the Langmuir and Freundlich models are plotted and shown in Fig. 8. The isotherm constants, calculated from slope and intercept of the linearized plot of the isotherm equations. It was found that the adsorption of As(V) can fit both of the above models. Langmuir isotherm model \((q_e, 15.6 \text{ mg/g}, K_L, 4.57 \text{ L/mg}, R^2 = 0.997)\) produced slightly better fitting than that of Freundlich model \((K_F, 12.05 \text{ mg}^{1-1}/\text{L}^{1/n}, 1/n, 0.997, R^2 = 0.994)\). Based on the Langmuir isotherm model, the calculated maximum capacity of As(V) adsorbed onto the Cu/Mg/Fe-LDH was 15.60 mg/g. Table 2 shows the comparison results of the maximum adsorption capacities of several adsorbents for As(V). It is found that the Cu/Mg/Fe-LDH in this work has a relatively higher adsorption capacity, which makes it to be an potential adsorbent for the As(V) removal from aqueous solutions.

The Langmuir parameter \( K_L \) and initial As(V) concentration \((C_0)\) can be used to obtain the separation factor \( R_L \), which can be used to assess the favorability of the substances on the adsorbent. It can be calculated by the following Eq. (8) (Kundu and Gupta, 2007):

\[ R_L = \frac{1}{1 + K_L C_0} \quad (8) \]

In this experiment, it was found that the \( R_L \) value is less than 1 with a decreased separation factor at a higher As(V) concentration, which indicated a highly favorable adsorption of As(V) on the Cu/Mg/Fe-LDH.

2.5 Possible mechanism of As(V) adsorption

Layered double hydroxide materials possess intrinsic anion uptake capacity because of the presence of facile exchangeable interlayer anions and large external surface, and hence are explored widely for the removal of noxious anions from contaminated water. As discussed in previous reports, anion exchange process may be an important mechanism for the As(V) adsorption onto other LDHs.
The XPS analyses of the LDH material before and after adsorption of As(V) showed crystallinity after adsorption of As(V), which suggested a preservation of the structure proving topotactic exchange mechanism. Xing et al. (2008) used Mg-Al-CO₃ LDH for tripolyphosphate adsorption and also found that features at d(003) and d(006) were essentially retained after P₂O₇³⁻ adsorption, which suggested that the adsorption of P₂O₇³⁻ was by ion exchange.

The XRD reflections are indexed using a hexagonal cell with rhombohedral symmetry (R-3m), commonly used for description of the LDH structure, and the lattice XRD parameters can be calculated. The refined cell parameter $a$ is a function of the metal-metal distance in the layers, while the parameter $c$ is the interlayer distance regulated by the size and charge of the anion placed between the layers. LDH with different types of anions in the interlayer can be identified through the interlayer distance. According to a 3R polytypism for the Cu/Mg/Fe-LDH and from the positions of the XRD peaks, the lattice parameters $a$ and $c$ have been calculated. The parameters $a$ and $c$ of the LDH before and after adsorption of As(V) showed that the metal-metal distance in the layer of this LDH almost did not change after adsorption, while the interlayer distance has changed from 2.337 nm to 2.318 nm (Table 1). This result indicated that the adsorption of As(V) on LDH was by ion exchange process.

The XPS analyses of the LDH material before and after As(V) adsorption were conducted. The relative amounts of Cu, Mg, Fe, C, O and As atoms in terms of atom% on the surface of LDH before and after As(V) adsorption are summarized in Table 3. The remarkable percentage of As after As(V) adsorption signifies the As(V) binding to the LDH. The decreased percentage of C after As(V) adsorption demonstrates the successful exchange of carbonate with As(V) ions.

The binding energy value of Cu, Mg, Fe and O in LDH before and after As(V) adsorption are shown in Fig. 9. The results showed that the XPS spectra of Mg 2p and Fe 2p of LDH before and after arsenate adsorption showed insignificant change, indicating that Mg and Fe atoms might not take in the arsenate sorption (Fig. 9a and b). In comparison with Mg 2p and Fe 2p, the binding energy value of Cu in LDH (934.38 eV) showed a significant increase spectra intensity after arsenate adsorption and a spectra shift to 933.61 eV, showing that the strong interactions between As(V) and Cu atoms. The O 1s spectra of LDH before and after As(V) adsorption were slightly different, implying the alteration of oxygen constituents of LDH after As(V) adsorption.

Based on the results that the active group at Cu surface appeared to be important for the adsorption of As(V), the possible inner-sphere As(V) complexes can be postulated to form at the Cu²⁺ center in the LDH, resulting from As(V) interaction with Cu related functional groups. The ligand exchange process of As(V) with the OH group of Cu²⁺ in LDH could be hypothesized by the following form:

\[
\text{Cu}^{2+} + \text{H}_{2}\text{AsO}_4^- \rightarrow \text{Cu}^{2+} + \text{H}_2\text{AsO}_4\text{O}^-. 
\]

It could be deduced that the main mechanism controlling the adsorption of arsenate onto Cu/Mg/Fe -LDH included the ion exchange and the ligand exchange process with the layer OH group which caused inner- sphere arsenate complexes.

### 2.6 Effect of coexisting ions on the As(V) removal

When competing anions coexisted with As(V) in the aqueous solutions, the adsorption of As(V) on the Cu/Mg/Fe-LDH was primarily affected by the type and concentration of competing anions. The effect of several competing anions on the adsorption of As(V) is shown in Fig. 10. Regardless of the type of competing anions, increasing the concentration of a coexisting competing anion resulted in decrease in As(V) adsorption on the Cu/Mg/Fe-LDH. This is due to competition between the coexisting anions and As(V) for the positively-charged sites on the external and internal surfaces of the LDH.

Furthermore, the type of co-existing anions determines the extent of selectivity of the LDH toward arsenate. The effect of competing anions on the arsenate adsorption...
Fig. 9 XPS spectra of Mg 2p (a), Fe 2p (b), Cu 2p (c) and O 1s (d) for LDH before and after As(V) adsorption.

was in the order of \( \text{HPO}_4^{2-} > \text{CO}_3^{2-} > \text{SO}_4^{2-} > \text{NO}_3^- \). This order of competing anion effect was consistent with those observed for As(V) adsorption by uncalcined and calcined Mg/Al LDH-CO$_3$ (Yang et al., 2005). As shown in several previous studies, LDH has a greater affinity toward anions with a higher ionic charge density (Dutta and Puri, 1989; Bontchev et al., 2003; Yang et al., 2006). Thus, the presence of a competing anion with a higher ionic charge density has a greater negative impact upon the adsorption of a target anion (e.g., As(V)) by LDH.

2.7 Desorption experiments

Desorption is an important feature for repeated uses of a material with economic benefits. Desorption of As(V) adsorbed on the Cu/Mg/Fe–LDH was subsequently examined. It has been found that effects of various competitive anions on the adsorption of As(V) decreased in the order of \( \text{HPO}_4^{2-} > \text{CO}_3^{2-} > \text{SO}_4^{2-} > \text{NO}_3^- \). Generally, the anion better suited stereochemically for inclusion into the interlayer of LDH has a greater ability to cause the release of interlayer anions already present in the LDH (Goswamee el al., 1998). So in the desorption experiment, the sodium salt of \( \text{HPO}_4^{2-} \) was used as the desorption solution. The results show that with the increasing concentration of \( \text{HPO}_4^{2-} \) (10, 100, 1000 mg/L), the desorption rate increased (22.6%, 44.6%, 49.6%, respectively). The recycle experiments of adsorption-desorption were conducted using Na$_2$HPO$_4$ as the desorption solution. Results showed that after three recycles of adsorption-desorption experiments, the As(V) adsorption capacity remained higher than 8 mg/g.

Fig. 10 Effect of coexisting ions on adsorption of As(V). Initial As(V) concentration 2 mg/L, pH 6.0, temperature 298 K, adsorbent dosage 0.2 g/L, adsorption time 24 hr.
3 Conclusions

A mesoporous trimetal material Cu/Mg/Fe-LDH with carbonate intercalation was synthesized using a co-precipitation method, and used to remove As(V) from aqueous solutions. The Cu/Mg/Fe-LDH showed good adsorption ability for As(V) and it was able to reduce the As(V) concentration down to a final level of < 10 μg/L under the optimal conditions. The adsorption amount of As(V) by the Cu/Mg/Fe-LDH was dependent on initial solution pH. The results indicated that the Langmuir adsorption isotherm can excellently describe the adsorption of As(V), and the calculated adsorption capacity was 15.60 mg of As(V). The adsorption isotherm can excellently describe the adsorption of As(V) by the Cu/Mg/Fe-LDH under the optimal conditions. The adsorption amount of As(V) by the Cu/Mg/Fe-LDH was dependent on initial solution pH. The results indicated that the Langmuir adsorption isotherm can excellently describe the adsorption of As(V), and the calculated adsorption capacity was 15.60 mg of As(V). The coexisting ions had different effects on the adsorption of As(V), which was in the order of HPO₄²⁻ > CO₃²⁻ > SO₄²⁻ > NO₃⁻. The results showed the synthesized Cu/Mg/Fe-LDH a potential adsorbent for the treatment of arsenic polluted waters. However, as for the efficient reuse of these LDH materials after adsorption, more investigations are needed.

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References


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