Article

Decontamination of Arsenic in Actual Water Samples by Calcium Containing Layered Double Hydroxides from a Convenient Synthesis Method

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Abstract: A series of calcium-containing layered double hydroxides (LDHs) and calcined product (CLDH) were synthesized using a comparative simple synthesis method (without using organic solvents and with a shortened reaction time) and applied in the adsorption of arsenic in water. The adsorption performance of arsenate on these LDHs and CLDH were studied using batch tests. The effects of various factors during the adsorption process, such as pH of the solution, dosage of materials, coexisting ions, contact time, and initial arsenate concentration, were evaluated. The maximum adsorption capacity of arsenate on three materials (CaFe-CLDH, CaFe-Cl-LDH, CaFe-NO₃-LDH) were 156.0 mg·g⁻¹, 150.5 mg·g⁻¹, and 148.0 mg·g⁻¹, respectively. When the concentration of CaFe-CLDH was 0.5 g·L⁻¹, the concentration of arsenate was reduced from 5000 µg·L⁻¹ to 10 µg·L⁻¹ after adsorption. Moreover, when the CaFe-NO₃-LDH or CaFe-Cl-LDH dosage was 1.0 g·L⁻¹, a similar decontamination result could be achieved. The synthesized CaFe-CLDH was used to treat actual contaminated water samples from a river in a mining area north of Lengshuijiang City in Hunan Province, China. After treating using CaFe-CLDH, the residual arsenic concentration of actual water samples can fully meet the requirements for arsenic in the drinking water standards of the World Health Organization and China. This indicates that synthetic CaFe-CLDH has the potential to serve as an effective adsorbent for the removal of arsenic contamination.

Keywords: calcium; layered double hydroxides; arsenic; adsorption; actual water sample

1. Introduction

Arsenic pollution in water has always been a concern [1]. In many countries and regions, there are arsenic pollution problems in water environments. The concentration of arsenic in polluted areas is generally higher than 50 µg·L⁻¹, and in some areas the concentration of arsenic in water is above 1000 µg·L⁻¹ [2–6]. A variety of arsenic pollution control methods have been developed, such as filtration [7,8], phytoremediation [9,10], coagulation [11–13], membrane [14,15], ion exchange [16,17], and adsorption [18–20]. One of the most convenient methods to apply is adsorption [21,22].

Layered double hydroxides (LDHs) have a layered structure of anionic clay. The general formula is [M^{II}_{1-x}M^{III}_x(OH)₂]^{x+}(Aⁿ⁻)_{x/n}·mH₂O, where M^{II} and M^{III} are divalent and trivalent cations, respectively, and Aⁿ⁻ denotes the interlayer anion [23,24]. LDHs have been widely used for pollutant removal in water. They may be the most suitable adsorbents for the treatment of arsenic because the

LDHs synthesis process is relatively simple and cost effective. In recent years, many studies have focused on the synthesis of LDHs materials and used them for the purification of arsenic-polluted water [25,26]. However, in the process of using LDHs for the treatment of arsenic contamination in water, some of the harmful heavy metals in the material may dissolve (such as copper, manganese, aluminum, etc.); this may cause new contamination [27]. LDHs containing calcium and iron may be a better choice for removing arsenic from water. Some researchers have synthesized CaFe-LDHs, but the synthesis takes a long time, and the process uses ethanol, which is not a green synthetic method [28]. There are also complicated methods, such as using hot sodium hydroxide solution or grinding calcium hydroxide during synthesis [29,30]. Thus far, to the best of our knowledge, CaFe-LDHs materials have not been used to adsorb arsenic in water and to treat actual water samples.

In this study, we focused on the synthesis of CaFe-LDHs using convenient synthesis methods (without using organic solvents and shortening the reaction time) and used them for the treatment of arsenate pollution in actual water samples from a river. The adsorption of arsenate on a series of CaFe-LDHs was studied using batch adsorption tests. The effects on the adsorption by various factors, including initial pH of the solution, dosage of material, coexisting ions, contact time, and initial pollutants concentration, were evaluated. The synthesized materials have been used to treat actual contaminated water samples from a river in a mining area north of Lengshuijiang City in Hunan Province, China. The possible mechanisms of adsorption are also discussed.

2. Materials and Methods

2.1. Chemicals

The chemicals used in the synthesis experiments were of analytical grade and purchased from Sinopharm Group Reagent Co., Ltd., Shanghai, China. Arsenate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$) was purchased from Sigma Aldrich with a purity higher than 98%. A stock solution of $1000 \text{ mg} \cdot \text{L}^{-1}$ As (V) was prepared with Milli-Q water ($18.2 \text{ M}\Omega \text{ cm}$ at 298 K). The working solutions were obtained by diluting the stock solutions with de-ionized water.

2.2. Synthesis of Materials

CaFe-LDHs were synthesized using a co-precipitation method [24,28,31]. First, $0.05 \text{ mol Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $0.025 \text{ mol Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in 100 mL of Milli-Q water to obtain solution I. 0.1 mol NaNO_3 and 0.2 mol of NaOH was dissolved in 100 mL of Milli-Q water to obtain solution II. Then solution I and solution II were simultaneously dropped into stirred three-necked flasks containing 50 mL of Milli-Q water with nitrogen protection. The pH value was maintained around 13. After completion of the reaction, the mixture was stirred for 30 min , then suspensions were placed in a 353-K oven and aged for 24 h . Centrifugal separation and washing were carried out next. The precipitate was washed repeatedly with de-ionized water until the pH of the supernatant was neutral. The obtained material was then dried at 353 K and ground into a powder. The product was named CaFe- NO_3 -LDH.

CaFe- CO_3 -LDH was also prepared using the same method as above by using Na_2CO_3 instead of NaNO_3 . CaFe- CO_3 -LDH were calcined at 773 K in a muffle furnace for 4 h . After cooling, the product was obtained and named CaFe-CLDH.

CaFe-Cl-LDH was prepared using the same method as CaFe- NO_3 -LDH using the corresponding chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, NaCl) instead of nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, NaNO_3).

2.3. Characterization and Analysis

The aqueous arsenate concentration was determined by an inductively coupled plasma emission spectrometer (ICP)—Agilent (ICP-720 ES, Agilent Technologies, Santa Clara, CA, USA)—and atomic fluorescence spectrometry (AFS) (FP6-A, PERSEE). The materials were characterized with CuK α radiation operated at a voltage of 40 kV , and a current of 40 mA , using an X-ray diffractometer (D8

Advance, Bruker, Beijing, China) [32,33] and a specific surface area analyzer (Autosorb-iQ, Quanta Chrome Instruments, Boynton Beach, FL, USA). The Fourier transfer infrared (FTIR) spectrum was recorded using an FTIR instrument (Nicolet 6700, Nicolet, Nicolet Madison, WI, USA) in the wave number range of 400–4000 cm^{-1} . Samples were mixed with oven dried spectroscopic grade potassium bromide. 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 (BJH) method, which was applied to the desorption data. Scanning electron microscopy was performed using a CM200FEG (PHILIPS) and S-4800 (HITACHI). The water samples from the river in the north mining area of Lengshuijiang City were analyzed using inductively coupled plasma mass (ICP-MS) (Agilent Technologies), ICP and AFS. ICP was used to accurately determine the concentration of arsenic and other metals in the water samples (concentration range: 0.05–100 $\text{mg}\cdot\text{L}^{-1}$), while ICP-MS was used to accurately determine the concentration of arsenic and other metals in water samples (concentration range: 0.1–50 $\mu\text{g}\cdot\text{L}^{-1}$). AFS was used to check whether the concentration of arsenic after adsorption is lower than the limit specified by the World Health Organization (WHO) drinking water standard (concentration range: 0–10 $\mu\text{g}\cdot\text{L}^{-1}$) [34].

2.4. Batch Adsorption Experiments

Batch adsorption experiments were carried out using a conical flask as the adsorption reaction vessel and placed in a constant-temperature shaking incubator at 298 K with 150 rpm [35]. After reaction, the supernatants were collected and filtered with an 0.22 μm needle filter before analysis of the residual arsenate. All experiments were repeated twice. In the adsorption isothermal experiment, the initial pH values of working solutions were adjusted to 6.0. The dosage of materials was 0.2 $\text{g}\cdot\text{L}^{-1}$. The concentration range of arsenate was from 1 $\text{mg}\cdot\text{L}^{-1}$ to 100 $\text{mg}\cdot\text{L}^{-1}$. The adsorption reaction lasted for 24 h to achieve equilibrium. The concentration of arsenic was 10 $\text{mg}\cdot\text{L}^{-1}$, initial pH was adjusted to 6.0, and the dosage of materials was 0.2 $\text{g}\cdot\text{L}^{-1}$ in the test of adsorption kinetics [36]. In order to study the effects of coexisting ions on arsenic adsorption, the initial concentration of arsenate was set to 5 $\text{mg}\cdot\text{L}^{-1}$ and a certain concentration of anionic sodium salt (NaCl , NaNO_3 , Na_2CO_3 , Na_2SO_4 , Na_2HPO_4) was added to the arsenate solution. The pH of the solution was 6.0 and the dosage of adsorbents was 0.2 $\text{g}\cdot\text{L}^{-1}$. The initial concentration was set for 5 $\text{mg}\cdot\text{L}^{-1}$ in the experiments of dosage effect. The pH of the system was adjusted to 6.0. The dosage of adsorbents was set from 0.1 $\text{g}\cdot\text{L}^{-1}$ to 1.0 $\text{g}\cdot\text{L}^{-1}$. In the evaluation of pH effect on the adsorption of arsenic, the initial arsenic concentration was 5 $\text{mg}\cdot\text{L}^{-1}$. The pH range was from 3 to 10 and the dosage was 0.2 $\text{g}\cdot\text{L}^{-1}$.

3. Results and Discussion

3.1. Characterization

3.1.1. X-ray Diffraction (XRD)

The XRD patterns of $\text{CaFe-NO}_3\text{-LDH}$, CaFe-Cl-LDH , and CaFe-CLDH are shown in Figure 1a. It can be seen from Figure 1a that $\text{CaFe-NO}_3\text{-LDH}$ and CaFe-Cl-LDH show a series of characteristic diffraction peaks: (003), (006), (030), (033). The d (003) of $\text{CaFe-NO}_3\text{-LDH}$ was 0.7836 nm and d (003) of CaFe-Cl-LDH was 0.7677 nm, which were consistent with other studies. CaFe-CLDH exhibited a standard broad peak, which is the characteristic peak of the CLDH oxide.

Figure 1. (a) XRD patterns of CaFe-NO₃-LDH, CaFe-Cl-LDH and CaFe-CLDH. (b) Fourier Transfer Infrared (FTIR) spectra of CaFe-NO₃-LDH, CaFe-Cl-LDH and CaFe-CLDH.

3.1.2. FTIR Analysis

The infrared spectra of the synthesized materials are shown in Figure 1b. It can be seen from Figure 1b that CaFe-NO₃-LDH and CaFe-Cl-LDH had the characteristic peaks of the infrared spectra of typical LDHs. The peaks appearing near 3600 cm⁻¹ correspond to the hydrogen–oxygen bond stretching vibration peaks (V_{O-H}) of the lattice water molecules and -OH. Because of the adsorption of water on the surface of hydrotalcite, there was a certain amount of water molecules in the interlayer. Therefore, the bending vibration peak (δ_{H-OH}) of the crystal water appears at about 1600 cm⁻¹. The peak around 1406 cm⁻¹ of CaFe-NO₃-LDH was the peaks of NO₃⁻ [37]. The CaFe-Cl-LDH FTIR spectra showed the peak (V_{O-H} at 1486 cm⁻¹) and the peaks of metal oxygen bond and the metal hydrogen-oxygen bond (V_{M-O} at 500 cm⁻¹ to 1000 cm⁻¹, where M is Ca or Fe) [37,38].

3.1.3. Analysis of Specific Surface Area and Pore Size Distribution

The N₂ adsorption/desorption isotherms of the materials are shown in Figure 2. It can be seen from Figure 2a–c that the adsorption isotherm of the three materials basically conforms to the adsorption isotherm of class IV in the IUPAC classification. The hysteresis loop is basically consistent with the H3 hysteresis loop type and is characteristic of the flaky structure material [39]. In addition, there is no balance in the adsorption isotherm in the case of high relative pressure, indicating that the N₂ adsorption process occurred in the pellet accumulation area. This also proved the material's layered structure. This is consistent with previous reports [40,41]. The surface area (multi-point BET method), total pore volume, and average pore size (the BJH method was used to calculate from desorption curve data) were calculated and the results are shown in Table 1. It can be seen that the specific surface area order is CaFe-NO₃-LDH > CaFe-CLDH > CaFe-Cl-LDH. The average pore diameters of materials are around 3 nm. These data suggest that the three materials are mesoporous materials.

Figure 2. (a) N₂ adsorption/desorption isotherms of CaFe-CLDH. (b) N₂ adsorption/desorption isotherms of CaFe-Cl-LDH. (c) N₂ adsorption/desorption isotherms of CaFe-NO₃-LDH. (d) Pore size distribution of three materials (Brunauer-Joyner-Hallenda, BJH method).

Table 1. The specific surface area of the synthetic material, the average pore size, and the total pore volume.

Materials	BET Surface Area (m ² ·g ⁻¹)	C-Value in BET Equation	Pore Volume (cm ³ ·g ⁻¹)	Average Pore Diameters (nm)
CaFe-CLDH	21.17	18.14	0.5109	3.709
CaFe-Cl-LDH	20.68	70.74	0.4122	3.135
CaFe-NO ₃ -LDH	43.31	100.3	0.3037	2.359

3.1.4. Morphological Analysis

The SEM images of CaFe-CLDH, CaFe-Cl-LDH, and CaFe-NO₃-LDH materials are shown in Figure S1. It can be seen that CaFe-CLDH, CaFe-Cl-LDH and CaFe-NO₃-LDH all show a flaky morphology. This is also consistent with the results of the surface analysis of the materials; that is, the three synthesized materials have a sheet-like structure.

3.2. Adsorption of Arsenic

3.2.1. Isotherms of Arsenic Adsorption

In order to understand the adsorption process of arsenate on CaFe-LDHs and the related CLDHs, isothermal adsorption experiments were carried out. The Langmuir and Freundlich models were used

to analyze the relative data obtained from the adsorption experiment for arsenate [42,43]. The fitting curves are shown in Figure 3. The parameters of the curves were calculated, as shown in Table 2.

Figure 3. (a) Isothermal study of adsorption of arsenic with CaFe-CLDH. (b) Isothermal study of adsorption of arsenic with CaFe-Cl-LDH. (c) Isothermal study of adsorption of arsenic with CaFe-NO₃-LDH (Experimental condition: initial concentration range of arsenate was from 1 mg·L⁻¹ to 100 mg·L⁻¹, materials dosage = 0.2 g·L⁻¹, initial pH = 6.0).

The Freundlich adsorption isotherm model is in the following form:

$$Q_e = K_F C_e^{\frac{1}{n}} \quad (1)$$

where Q_e ($\text{mg} \cdot \text{g}^{-1}$) is the equilibrium adsorption capacity, K_F ($\text{L} \cdot \text{mg}^{-1}$) is the Freundlich constant, and $1/n$ is the heterogeneity factor.

The Langmuir model:

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

where C_e ($\text{mg} \cdot \text{L}^{-1}$) is the equilibrium concentration, Q_m ($\text{mg} \cdot \text{g}^{-1}$) is the maximum and equilibrium adsorption capacity, and K_L ($\text{L} \cdot \text{mg}^{-1}$) is the Langmuir adsorption constant.

The adsorptions of arsenate on the three materials were more consistent with the Freundlich adsorption isotherm equation than the Langmuir model. The Freundlich isotherm model is based on multi-layer adsorption of adsorbate on a multiphase surface and is suitable for adsorption data within a limited concentration range [44].

Table 2. Fitting curve parameters of arsenate adsorption isothermal equation.

Materials	Langmuir			Freundlich		
	Q_m ($\text{mg} \cdot \text{g}^{-1}$)	K_L ($\text{L} \cdot \text{mg}^{-1}$)	R^2	K_F ($\text{mg} \cdot \text{g}^{-1}$) ($\text{L} \cdot \text{mg}^{-1}$) $^{-1/n}$	n	R^2
CaFe-CLDH	156.0	0.05848	0.9626	24.31	2.514	0.9920
CaFe-Cl-LDH	150.5	0.03509	0.8241	19.57	2.504	0.9424
CaFe-NO ₃ -LDH	148.0	0.04894	0.9448	17.64	2.245	0.9524

The comparison results of the maximum adsorption capacities of various adsorbents for arsenate adsorption are shown in Table 3. It was found that CaFe-LDHs in this study have a high adsorption capacity for arsenate, which makes them possible efficient adsorbents for arsenate removal from aqueous solutions.

Table 3. Comparison of adsorption capacity for arsenate onto CaFe-LDHs with other reported adsorbents.

Adsorbents	Concentration Range ($\text{mg} \cdot \text{L}^{-1}$)	pH	Adsorption Capacity ($\text{mg} \cdot \text{g}^{-1}$)	Reference
Leonardite char	1–80	7.0	8.4	[45]
Pyrite Ash	0.01–0.5	7.0	0.295	[46]
UltraCarb	20–22	6.0	51.3	[47]
CeO ₂ –ZrO ₂ nanospheres	0.5–60	6.9	145.35	[48]
Mg-Fe-Cl-LDH	3.75–562.5	6.0	129.5	[49]
Zn-Al-SO ₄ -LDH	900	9.0	74.9	[50]
CaFe-CLDH	1–100	6.0	156.0	This study
CaFe-Cl-LDH	1–100	6.0	150.5	This study
CaFe-NO ₃ -LDH	1–100	6.0	148.0	This study

3.2.2. Kinetics of Arsenic Adsorption

In order to study the kinetic process of the adsorption of arsenate by CaFe-CLDH, CaFe-Cl-LDH, and CaFe-NO₃-LDH, the adsorption capacity variations with time were investigated. The pseudo-first order kinetic model and pseudo-second order kinetic model were used to fit the relevant data of the arsenate adsorption kinetics experiment [51]. The pseudo-first order kinetic model equation follows:

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \quad (3)$$

The pseudo-second order kinetic model equation follows:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \quad (4)$$

Q_e ($\text{mg}\cdot\text{g}^{-1}$) and Q_t ($\text{mg}\cdot\text{g}^{-1}$) are the adsorption amounts of the adsorbents at equilibrium and at time t respectively; K_1 (min^{-1}) and K_2 [$\text{g}\cdot(\text{mg}\cdot\text{min})^{-1}$] are the adsorption rate constants. The resulting fitting curves are shown in Figure 4, and the obtained fitting parameters are shown in Table 4.

As shown in Figure 4, the time required for arsenic to adsorb to equilibrium in material CaFe-NO₃-LDH was the shortest, followed by CaFe-Cl-LDH, and arsenic took the longest time to adsorb to equilibrium with CaFe-CLDH. The reason may be that the CaFe-CLDH adsorbs arsenate and undergoes structural remodeling that requires a longer equilibrium time.

As shown in Table 4, the correlation coefficients of the three materials with the pseudo-second order kinetic equation model are larger than those of the pseudo-first order kinetic equation. This suggests that the pseudo-second order kinetic model can better reflect the adsorption process of arsenate on the three materials. The correlation coefficients of the three materials using the pseudo-second order kinetic equation model were larger than those obtained by fitting the pseudo-first order kinetic equation. This indicates that the pseudo-second order kinetic equation model can better reflect the dynamic adsorption of arsenate by the three materials. This is also consistent with the conclusions obtained from many previous studies: the adsorption of arsenic by solid materials generally conforms to pseudo-secondary kinetics [35,52]. It could indicate that the process controlling the rate may be a chemical sorption involving LDHs and arsenate [53,54]. In addition, the adsorption rate constants K_2 of CaFe-NO₃-LDH were larger than that of CaFe-CLDH and CaFe-Cl-LDH also indicating that the adsorption of arsenate in CaFe-NO₃-LDH was faster.

Figure 4. Cont.

Figure 4. Kinetic fitting curve of arsenic adsorption on the three materials: (a) CaFe-CLDH; (b) CaFe-Cl-LDH; (c) CaFe-NO₃-LDH (Experimental condition: initial concentration of arsenate was 10 mg·L⁻¹, materials dosage = 0.2 g·L⁻¹, initial pH = 6.0).

Table 4. Fitting curve parameters of arsenic adsorption kinetic equation.

Materials	Pseudo First-Order			Pseudo Second-Order		
	Q_e (mg·g ⁻¹)	K_1 (min ⁻¹)	R^2	Q_e (mg·g ⁻¹)	K_2 (g·mg ⁻¹ ·min ⁻¹)	R^2
CaFe-CLDH	25.89	0.0461	0.8044	27.84	0.00226	0.9077
CaFe-Cl-LDH	16.50	0.0539	0.9378	17.30	0.00517	0.9856
CaFe-NO ₃ -LDH	16.43	0.1054	0.9428	17.23	0.00948	0.9832

3.2.3. Effect of pH on Arsenic Adsorption

The effects of initial solution pH on arsenate adsorption are shown in Figure 5a. It can be seen from Figure 5a that the effect of pH on the adsorption of arsenate by CaFe-CLDH was not significant in the initial pH range from 3 to 10. With the increase in pH, the adsorption capacity decreased. This is

similar to the previously reported adsorption behavior of arsenate on ferrihydrite: As the pH increases, the adsorption capacity for arsenate decreases [55]. This may be related to the electrostatic repulsion of arsenate and the surface occupation of active sites on the materials.

Figure 5. (a) Effect of pH on arsenic adsorption (Experimental condition: initial concentration of arsenate was 5 mg·L⁻¹, materials dosage = 0.2 g·L⁻¹). (b) Effect of dosage on arsenic adsorption (Experimental condition: initial concentration of arsenate was 5 mg·L⁻¹, initial pH = 6.0).

3.2.4. Effect of Materials Dosage on Arsenic Adsorption

The effect of the adsorbent dosage on the removal efficiency of arsenic was evaluated by gradually increasing the dosage of the adsorbent in the experiment. The experimental results are shown in Figure 5b.

It can be seen from Figure 5b that increasing the amount of adsorbent will increase the removal rate of arsenate. When the CaFe-NO₃-LDH or CaFe-Cl-LDH dosage was 1.0 g·L⁻¹, the removal rate reached 99.9%; the remaining arsenic concentration was below 10 µg·L⁻¹. Moreover, when the concentration of CaFe-CLDH was 0.5 g·L⁻¹, the same result could be achieved. The above situation can meet the concentration of arsenic limit requirements of the World Health Organization, EPA, and China's drinking water standards.

3.2.5. Effects of Anions on Arsenic Adsorption

The presence of various anions in the natural water may affect the adsorption of arsenate on the adsorbent, so several common anions in water were selected to study their effect on the adsorption of arsenic. The ions, including PO₄³⁻, SO₄²⁻, CO₃²⁻, NO₃⁻, and Cl⁻, were selected as the coexisting ions. The effects of excess anions on the adsorption of arsenate on materials were investigated. The experimental results were shown in Figure 6. The high concentration of HPO₄²⁻ had a very significant inhibitory effect on the adsorption of arsenate, while the inhibitory effects of SO₄²⁻, Cl⁻, and NO₃⁻ were not obvious. In general, the inhibitory effect of coexisting ions on arsenate adsorption was HPO₄²⁻ > CO₃²⁻ > SO₄²⁻ > Cl⁻ > NO₃⁻.

Figure 6. Effect of coexisting anions on arsenic removal by materials in water: (a) CaFe-CLDH; (b) CaFe-Cl-LDH; (c) CaFe-NO₃-LDH (Experimental condition: initial concentration of arsenate was 5 mg·L⁻¹, materials dosage = 0.2 g·L⁻¹, initial pH = 6.0).

3.2.6. Adsorption and Removal of Arsenic in Actual Water Samples

The actual water samples were collected from the river of the North Mining Area, Lengshuijiang City in Hunan Province, China. The elemental analyses in actual water samples are shown in Table 5. The pH values of the water samples were 7.12 and 7.62, respectively. Arsenic in the water sample exists in the form of arsenate. The concentrations of arsenic were $0.03 \text{ mg}\cdot\text{L}^{-1}$ and $1.11 \text{ mg}\cdot\text{L}^{-1}$ respectively. The CaFe-CLDH was chosen as the adsorbent. After adsorption by $1 \text{ g}\cdot\text{L}^{-1}$ CaFe-CLDH, the amount of the remaining arsenic concentration was $1.7 \text{ }\mu\text{g}\cdot\text{L}^{-1}$ and $9.2 \text{ }\mu\text{g}\cdot\text{L}^{-1}$, respectively. This is fully able to meet the requirements for the concentrations of arsenic in drinking water standards of the World Health Organization, EPA and China.

Table 5. Elemental analysis in actual water samples ($\text{mg}\cdot\text{L}^{-1}$).

Sample	As	Ba	Mg	Fe	Ca	K	Cu	Na	Al	P	Sb
I	0.03	0.03	9.24	0.54	6.89	1.9	0.01	10.62	0.47	0	0.18
II	1.11	0.04	7.69	0	6.64	9.8	0.01	36.09	0.21	0.02	0.1

XRD of Ca-Fe-CLDH material after adsorption of As (V) is shown in Figure 7a. It can be found that the XRD pattern showed a series of characteristic diffraction peaks of LDHs. This is similar to the characterization result of arsenic adsorption onto LDHs calcined products in previous reports [56,57]. The SEM image in Figure 7b also shows the significant appearance of the lamellar structure of LDHs. This indicated that the structure of LDHs had been rebuilt after adsorption.

Figure 7. (a) XRD pattern of CaFe-CLDH after adsorption of arsenate. (b) SEM image pattern of CaFe-CLDH after adsorption arsenate.

4. Conclusions

A series of calcium-containing layered double hydroxides were successfully synthesized using a comparative simple synthesis method and were then characterized. The effects of various factors during the adsorption process, such as pH of the solution, dosage of materials, coexisting ions, contact time, and initial arsenate concentration, were evaluated. The maximum adsorption capacity of arsenate on the three synthesized materials (CaFe-CLDH, CaFe-Cl-LDH, and CaFe-NO₃-LDH) were $156.0 \text{ mg}\cdot\text{g}^{-1}$, $150.5 \text{ mg}\cdot\text{g}^{-1}$ and $148.0 \text{ mg}\cdot\text{g}^{-1}$, respectively. When the concentration of CaFe-CLDH was $0.5 \text{ g}\cdot\text{L}^{-1}$ the concentration of arsenate was reduced from $5000 \text{ }\mu\text{g}\cdot\text{L}^{-1}$ to $10 \text{ }\mu\text{g}\cdot\text{L}^{-1}$ after adsorption. When CaFe-CLDH was applied in the decontamination of arsenic in actual water samples, it can fully meet the requirements for the concentrations of arsenic in drinking water standards of the

World Health Organization, EPA and China. The synthesized CaFe-CLDH is potentially an effective adsorbent for the removal of arsenic contamination.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4441/10/9/1150/s1>, Figure S1: SEM images of materials.

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