



Removal of arsenic from water by Friedel's salt (FS: $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$)

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ABSTRACT

Low levels of arsenic can be effectively removed from water by adsorption onto various materials and searching for low-cost, high-efficiency new adsorbents has been a hot topic in recent years. In the present study, the performance of Friedel's salt (FS: $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$), a layered double hydroxide (LDHs), as an adsorbent for arsenic removal from aqueous solution was investigated. Friedel's salt was synthesized at lower temperature (50°C) compared to traditional autoclave methods by reaction of calcium chloride with sodium aluminate. Kinetic study revealed that adsorption of arsenate by Friedel's salt was fast in the first 12 h and equilibrium was achieved within 48 h. The adsorption kinetics are well described by second-order Lagerren equation. The adsorption capacity of the synthesized sorbent for arsenate at pH 4 and 7 calculated from Langmuir adsorption isotherms was 11.85 and 7.80 mg/g, respectively. Phosphate and silicate markedly decreased the removal of arsenate, especially at higher pH, but sulfate was found to suppress arsenate adsorption at lower pH and the adverse effect was disappeared at $\text{pH} \geq 6$. Common metal cations (Ca^{2+} , Mg^{2+}) enhanced arsenate adsorption. The results suggest that Friedel's salt is a potential cost-effective adsorbent for arsenate removal in water treatment.

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1. Introduction

Arsenic is a primary concern of water contamination due to its high toxicity and carcinogenicity and is regarded as the first priority issue among the toxic substances [1]. Millions of people in developing countries, e.g. Bangladesh, Vietnam and China are suffering serious health problems such as cancer, skin lesions, metabolic and cardiac disorders due to chronic exposure to arsenic contaminated drinking water [2]. The maximum contaminant level (MCL) for arsenic in public drinking water in Europe, China and the United States is $10\ \mu\text{g/L}$, which means that some arsenic removal processes have to be adopted by public water system in order to meet the lately released drinking water standard.

Various technologies are currently available to remove arsenic from aqueous solution, such as ion exchange [3], coagulation (coprecipitation) [4], reverse osmosis [5], bioremediation [6], and adsorption [7,8]. Among these methods, adsorption technique using various adsorbents (elemental iron, iron (hydr)oxides, modified active carbons, silicotriphosphate molecular sieve, active alumina and aluminosilicate clay materials) has been widely investigated [7–13], all showing some advantages and disadvantages on performance, cost-effectiveness and easiness of implementation.

Hence, investigation of new adsorbents with high effectiveness and low cost in order to meet large numbers of demands from industrial and civil community is attracting increasing attentions. To this end, layer double hydroxide (LDHs), especially, Friedel's salt (FS: $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$) may be one of the potential candidates.

Layer double hydroxides (LDHs) are a group of anionic clay minerals consisting of cationic brucite layers and exchangeable interlayer anions. These compounds can be nominally expressed with a chemical formula $[\text{M}_{1-x}^{2+}\text{M}_x^{3+}(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n}\cdot m\text{H}_2\text{O}$, where M^{2+} and M^{3+} are divalent and trivalent metal cations, respectively, with an ionic radius similar to that of M^{2+} ; A^{n-} is an n -valent exchangeable anion (inorganic or organic) and x typically ranges from 0.17 to 0.33 [14]. Most of LDHs have relatively weak interlayer bonding and, as a consequence, exhibit excellent ability to capture inorganic anions by both surface adsorption and anion exchange [15]. Various types of LDHs with easily exchangeable anions, such as chloride, nitrate and carbonate-LDHs and their corresponding calcined product have been explored as adsorbents to remove arsenic contaminants in recent years [16–23].

Friedel's salt was first observed in the work of Friedel, who studied the reactivity of lime with aluminum chloride. This compound is formed in cements such as Portland cement which contains large amounts of tricalcium aluminate [24] and belongs to the layer double hydroxide (LDHs) family. Due to its ion exchange characteristic, FS has received considerable attention in recent years by various groups. For example, Dai et al. examined the adsorption behaviors

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of FS for Cr (VI) from aqueous solution at different concentrations and various initial pHs [25]. Recently, Wu et al. found that Friedel phase can rapidly adsorb large amounts of selenate from aqueous solutions [26]. The FS was usually synthesized using autoclaves at elevated temperatures. Most recently, FS was prepared using calcium chloride generated from soda ash industry at low temperature and found to have desilication capacity in sodium aluminate solution [27]. To the best of our knowledge, there are no published studies on the adsorption behavior of arsenic on Friedel's salt from aqueous solution.

The objective of this study was to test the performance of Friedel's salt as an adsorbent for arsenic removal from water. The effects of various parameters such as pH and common ions on arsenic removal were investigated.

2. Experimental

All chemicals were of analytical grade and used without further purification. Distilled water was used for all experiments. All glassware was cleaned by soaking in 5% HNO₃ and rinsed three times with distilled water. Arsenate and arsenite stock solution was prepared from Na₃AsO₄·12H₂O and NaAsO₂, respectively. The container of arsenite stock solution was purged with N₂ and sealed tightly to prevent from oxidation of As(III).

2.1. Synthesis of Friedel's salt

Friedel's salt was synthesized by precipitation at ambient pressure. The preparation experiments were conducted by pre-heating 0.5 M CaCl₂ (300 mL) to a desired temperature (50 °C) and 0.25 M NaAlO₂ with equal volume was added using a peristaltic pump at a rate of 5 mL/min and the mixture was stirred at 300 rpm. After the mixture was reacted for 1 h, the white precipitate was collected by filtration, washed three times with distilled water to remove residual substances and dried in a vacuum oven at 50 °C for 10 h.

2.2. Characterization of Friedel's salt

The structure and morphology of the synthesized samples were examined by using powder X-ray diffraction (XRD) and scanning electron microscopy (SEM). The powder X-ray diffraction patterns were recorded on a diffractometer (X'Pert PRO MPD, PANalytical, The Netherlands) using Cu K α radiation, operating at 40 kV/30 mA. A scanning rate of 0.02°/s was applied to record the patterns in the 2 θ angle range from 10° to 90°. The morphology of the synthesized sample was examined by scanning electron microscopy (SEM, JEOL-JSM-6700F). The FTIR spectrum was obtained on a Shimadzu IR Prestige-21 spectrometer with the resolution of 4 cm⁻¹. The KBr/sample discs were prepared by mixing 1% of samples in KBr.

2.3. Arsenic adsorption kinetics

0.1 g Friedel's salt adsorbent was added to the conical flasks containing 500 mL of 2 mg/L arsenic solution. The initial pH of the solution was adjusted to 7 ± 0.2 with 1 mol/L HNO₃ or 1 mol/L NaOH and maintained constant throughout the adsorption process. The mixture was shaken for 72 h at 25 °C. At regular intervals an aliquot of supernatant was sampled and filtered through 0.22- μ m membrane filter (Millipore) for the analysis of aqueous arsenic concentration.

2.4. Arsenic adsorption isotherms

In the tests of adsorption isotherms, 0.2 g/L of Friedel's salt was used. To obtain adsorption isotherms, a series of arsenate solutions

with initial arsenic concentration from 0.4 to 4.1 mg/L were prepared. The pH of As(V) solution was preadjusted to 4 and 7 prior to adsorption tests. 100 mL of As(V) solution and 0.02 g of Friedel's salt were added into a 250-mL conical flask and the mixture was equilibrated at 25 °C for 48 h on a reciprocating platform shaker. The slurries were maintained at pH 4 ± 0.2 and pH 7 ± 0.2 by addition of 0.1 N HCl or NaOH. The solution was filtered through 0.22- μ m membrane filter for the concentration analysis of aqueous arsenic.

2.5. Arsenic adsorption envelopes

The adsorption envelopes were obtained by equilibrating 0.02 g of Friedel's salt with 100 mL of 2 mg/L arsenic solution for 48 h at pH 3–10, 25 °C. For As(III), the conical flasks were covered with aluminum foil to prevent from light irradiation and purged with N₂ before capping and during pH adjustment. Each experiment was run in duplicate and the mean value was reported.

2.6. Effect of coexisting ions

0.02 g of Friedel's salt was added to 100 mL of 2 mg/L arsenic solutions containing additional cations (calcium and magnesium) or anions (phosphate, silicate and sulfate). The slurry was adjusted to various pHs ranging from 3 to 10 and the molar ratio of arsenic to the added ions was 1:10. The mixtures were mildly agitated for 48 h at 25 °C and the concentration of arsenic remaining in solution was analyzed.

2.7. Determination of the concentration of As, Al, Ca

The concentration of arsenic in solution was determined on an atomic fluorescence spectrophotometer (AFS-2202E, Haiguang Corp., Beijing) coupled with a hydride generator. The detection limit of the instrument for arsenic was 0.1 μ g/L. The concentration of aluminum and calcium in solution was determined on inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (Perkin Elmer Optima 3000) with the detection limit of 0.2 and 0.02 mg/L, respectively.

3. Results and discussion

3.1. Characterization of the adsorbent

The SEM images of the synthesized Friedel's salt are shown in Fig. 1. Typical flat hexagonal (or pseudohexagonal) crystal morphology was observed. Some aggregation and small non-uniform growths were also present in this compound. The XRD patterns of the synthesized Friedel's salt were sharp and consistent with the literature values (JCPDS 78-2051) (see Fig. 2). The infrared spectrum of the synthesized Friedel's salt was also presented in Fig. 2. The features at 528 cm⁻¹ and 789 cm⁻¹ are ascribed to the bending and stretching vibration of Al–OH [26]. The peak at 1624 cm⁻¹ was due to the H–O–H bending vibration of the interlayer water molecule (ν_2 H₂O). The stretching vibration of lattice water and structural OH groups (ν_{OH}) in the Friedel's salt were also reflected by the strong overlapping bands at 3473 and 3630 cm⁻¹, respectively. The band at 1420 cm⁻¹ was attributed to CO₃²⁻ due to incorporation of CO₂ during synthesis of the compound.

3.2. Adsorption kinetics

As shown in Fig. 3, the kinetics of arsenic adsorption by Friedel's salt included two steps: a fast initial sorption followed by a much slower sorption process. At pH 7, approximately 66.2% of arsenic was removed from As(V) solution in the first 12 h and adsorption equilibrium was reached within 48 h. Thus, the equilibration time

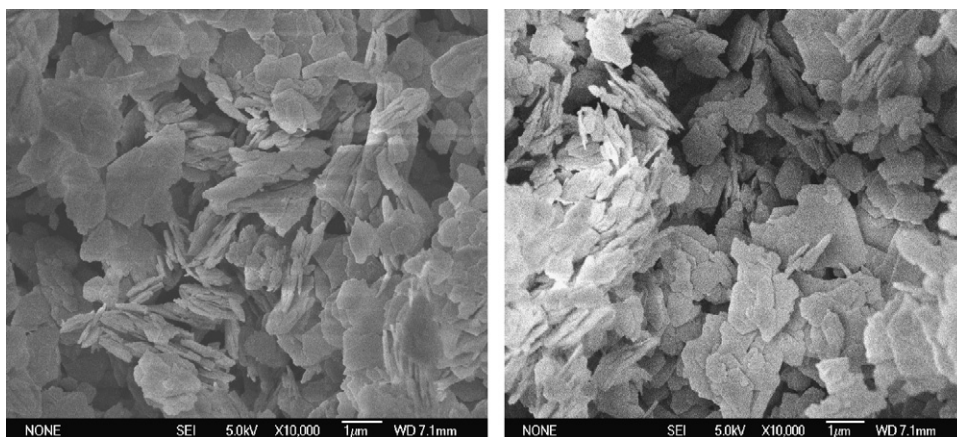


Fig. 1. SEM microimages of the synthesized Friedel's salt.

of 48 h was applied in the determination of adsorption isotherms and envelopes. In a previous study on the application of uncalcined MgAl-CO₃-LDHs for arsenic removal from water, it took 48–72 h to reach equilibrium [17]. In comparison, Lazaridis et al. reported that it needed only 8 h to reach equilibrium when the same mineral was used as adsorbent for the removal of arsenic and the fast kinetics was ascribed by the authors to the positive influence of potassium nitrate used for regulating the solution ionic strength [16]. Gener-

ally, a fast initial oxyanion adsorption followed by a slower process to reach equilibrium was the characteristic of oxyanion adsorption kinetics using various forms of LDHs as adsorbents [15]. Similar phenomenon was observed here for the adsorption of arsenate on Friedel's salt.

The kinetics of adsorption reaction was well described by second-order Lageren equation:

$$\frac{dQ_t}{dt} = k_2(Q_e - Q_t)^2 \quad (1)$$

where Q_e (mg/g) is the amount of arsenate adsorbed on Friedel's salt at equilibrium, Q_t (mg/g) is the amount of arsenate adsorbed at time t , k_2 (g/mg h) is the adsorption rate constant. Eq. (1) can be simplified by using initial condition and boundary condition ($t=0$, $Q_t=0$; $t=t$, $Q_t=Q_e$) as follows:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (2)$$

According to Eq. (2), the rate constant can be obtained as $k_2=0.13$ g/mg h.

3.3. Adsorption envelopes

The adsorption envelopes of arsenite and arsenate on Friedel's salt at pH 3–10 are illustrated in Fig. 4. Apparently, arsenate

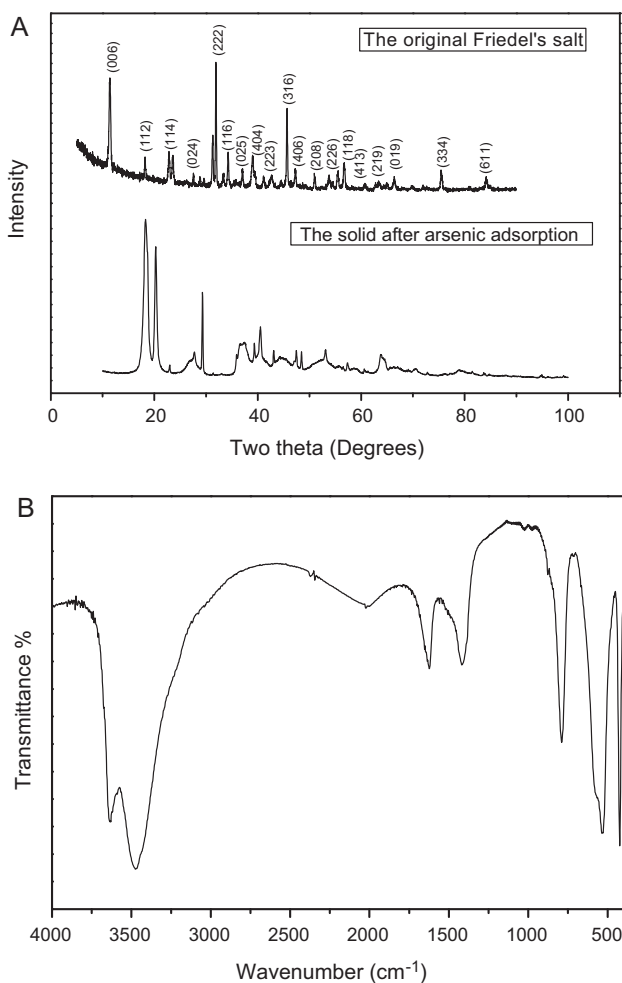


Fig. 2. (A) XRD patterns of the Friedel's salt prepared at 50 °C and the solid after adsorption of arsenate at pH 7 and (B) FTIR spectrum of the prepared Friedel's salt.

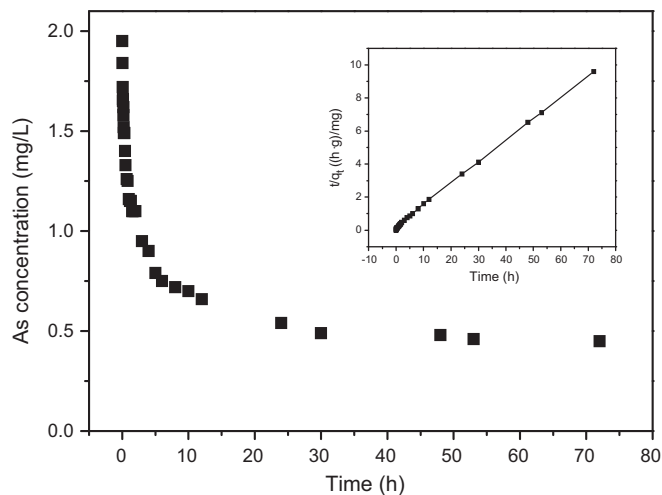


Fig. 3. The kinetics of arsenic adsorption by Friedel's salt. Reaction conditions: 2.0 mg/L As(V), 0.2 g/L Friedel's salt, pH 7, 25 °C. Inset shows modeling of the kinetics by second-order Lageren equation.

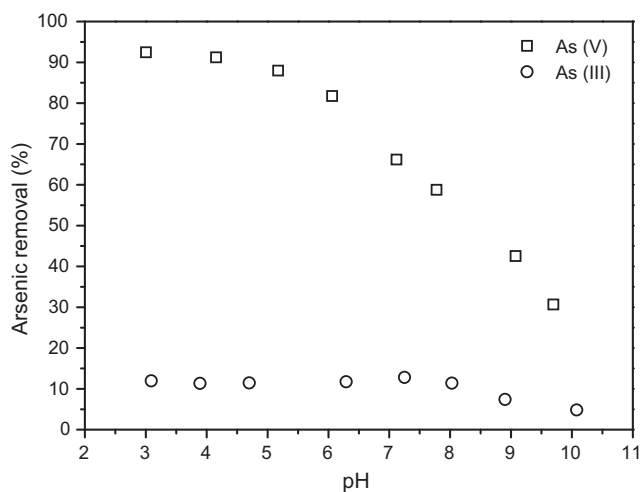


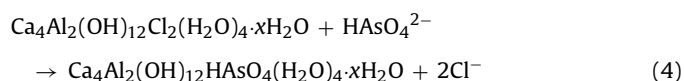
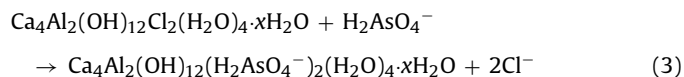
Fig. 4. Adsorption envelopes of As(V) and As(III) on Friedel's salt at initial arsenic concentration of 2 mg/L, the solid/liquid ratio of 0.2 g/L and equilibration time of 48 h.

removal efficiency is strongly dependent on media pH, while arsenite removal appeared not to be significantly affected by pH. The percentage of arsenate removal by Friedel's salt went down all the way from 92% to <30% when pH increasing from 3 to 10, whereas the removal of arsenite appears unchanged at ~12% at pH 3–8 and decreased at pH ≥ 9. It was also reported in previous work that adsorption of arsenate on ferrihydrite and nano-sized zero-valent iron decreased from mildly acidic to alkaline media, while adsorption of arsenite increased in acidic solution but decreased in alkaline solution [28,29]. Compared to iron-based adsorbents, the removal efficiency of arsenite by Friedel's salt was much lower than that of arsenate at all pH. Similar results were also found by Yang et al. who reported that uncalcined MgAl–CO₃–LDH adsorbed almost no arsenite [17]. The possible reason for low adsorption capacity of Friedel's salt for arsenite is that its major chemical compositions are aluminum and calcium. It is commonly observed in water treatment literatures that aluminum oxides and oxyhydroxides or aluminosilicate minerals are ineffective for the removal of As(III) from potable water but can remove As(V) efficiently [30,31].

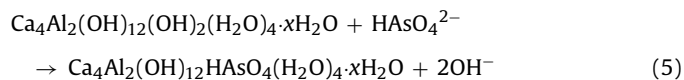
The pH dependent behavior of arsenic adsorption by Friedel's salt is the coeffect of several competing factors controlling the adsorption reaction. It was proposed that other types of LDHs can uptake contaminants from aqueous medium by three different mechanisms: (1) surface adsorption, (2) interlayer anion exchange, and (3) intercalation by reconstruction of the structure of the calcined LDHs [15]. Grover et al. suggested that the underlying mechanism for arsenate removal by hydrocalcumite-type LDH appears to be anion exchange as well as partial dissolution–precipitation [22]. Dai et al. reported that the removal and fixation of chromate from aqueous solution by Friedel's salt involves the adsorption/exchange process [25]. Since arsenate and chromate were both oxyanions with varying aqueous species at different pH, they probably show similar adsorption mechanism by Friedel's salt. Oxyanions migration to the surface of the adsorbent is the prerequisite of the adsorption reaction and largely controlled by electrostatic attraction or repulsion of the aqueous arsenate or arsenite species with the surface of the adsorbent [32]. Hence, pH of zero point charge (pH_{ZPC}) of the adsorbent and the speciation of aqueous arsenate and arsenite are governing factors.

The degree of protonation of arsenate and arsenite anions in aqueous solution is a function of pH. The dissociation constants of aqueous arsenate are pK_{a1} = 2.3, pK_{a2} = 6.8, pK_{a3} = 11.6, resulting in arsenate species varying from H₂AsO₄[−], HAsO₄^{2−}, to AsO₄^{3−} when pH increases from acidic region to alkaline region [31]. It is well

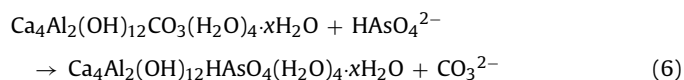
known that solid surface is positively charged at pH below pH_{ZPC} and negatively charged at pH above pH_{ZPC}, resulting in increased electrostatic attraction or repulsion with anionic arsenic species, hence leading to more or less readily adsorption. The pH_{ZPC} for the uncalcined LDH was reported to be in the range 6.8–8.9 [33], below which the surface of the adsorbent is positively charged and normally beneficial for the adsorption of the negatively charged anionic species. The surface of the adsorbent becomes less positively charged when pH increased hence shows less attraction towards anionic arsenate species. Therefore, at higher pH range, the adsorption of arsenate decreased significantly. The adverse effect of pH on arsenate adsorption at higher pH range may be further compounded by the increasing competitive effect of OH[−] adsorption on Friedel's salt. By referring to the mechanism proposed by Dai et al. and Wu et al. for chromate and selenate adsorption on Friedel's salt [25,26], arsenate adsorption may be schematically depicted by following reactions:



When the pH was increased to 10, the following two reactions may also be involved. Firstly, the freshly formed OH[−] could probably be intercalated into the interlayer spacing by replacing the original interlayer ion (Cl[−] in Friedel's salt) prior to arsenate adsorption.



Secondly, the solution can readily adsorb CO₂ from air and transfer to CO₃^{2−} and trigger the following exchange of HAsO₄^{2−} with the original carbonate hydrocalumite to happen:



The mechanism of arsenate adsorption on Friedel's salt may be different at lower pH and higher pH. After contacting with lower-pH arsenate solution, the adsorbent has been partly transformed to aluminum oxides (see Fig. 2). In this case, the bidentate binuclear interaction mode of arsenate anions with aluminum oxide may also be involved.

3.4. Adsorption isotherms

Fig. 5 shows the adsorption isotherms of arsenate by Friedel's salt at pH 4 and 7. Langmuir and Freundlich models are usually used to describe adsorption isotherms of compounds from liquid onto solid. Langmuir model assumes monolayer adsorption onto homogeneous surface with a finite number of identical sites, while the Freundlich model is empirical in nature. The results of arsenate adsorption were found to fit well with both Freundlich and Langmuir isotherm models ($r^2 > 0.95$) and the adsorption constants evaluated from the isotherms are listed in Table 1.

The adsorption capacity of Friedel's salt for arsenate calculated from the isotherms obtained at arsenic equilibrium concentration of <2 mg/L (Fig. 6) was 11.85 mg/g (pH 4) and 7.80 mg/g (pH 7), respectively. This is higher than the adsorption capacity of some reported adsorbents: activated carbon (3.1 mg/g) [9], nano-iron (hydr)oxide impregnated granulated activated carbon (0.263 mg/g) [34] and iron-containing ordered mesoporous carbon (7.0 mg/g)

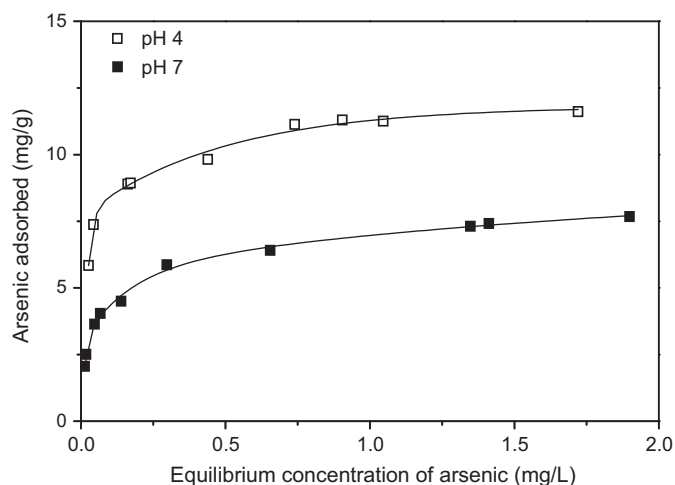


Fig. 5. Adsorption isotherms of As(V) by Friedel's salt at pH 4 or 7, the solid/liquid ratio of 0.2 g/L, 25 °C and equilibration time of 48 h.

Table 1

Langmuir and Freundlich adsorption isotherm parameters of arsenate on Friedel's salt at pH 4 and 7, respectively.

pH	Langmuir model: $q_{eq} = \frac{bQ_{max}C_{eq}}{1+bC_{eq}}$			Freundlich model: $q_{eq} = KC_{eq}^{1/n}$		
	<i>b</i>	<i>Q</i> _{max} (mg/g)	<i>r</i> ²	<i>K</i>	<i>n</i>	<i>r</i> ²
4	20.59	11.85	0.999	11.31	6.460	0.953
7	13.78	7.800	0.998	7.071	4.045	0.964

[35]. While for other common types of adsorbents, activated alumina has a comparable arsenate adsorption capacity of 15.9 mg/g at pH 5.2 while bead cellulose loaded with iron oxyhydroxide has a higher capacity as 33.2 mg/g at pH 7 [7,12].

It has been reported that the capacities of other forms of LDHs for arsenate adsorption range from 4.5 mg/g to 615 mg/g [15], however, it should be noticed that the relatively higher arsenate adsorption capacities such as 615 mg/g and 87.5 mg/g were obtained using calcined forms of LDHs as adsorbents. It has been observed in previous studies that arsenate adsorption by calcined LDHs was considerably higher than the adsorption by uncalcined LDHs [16]. As for the uncalcined form of LDHs which was the case in our investigation, Liu et al. reported that arsenate adsorption

Table 2

The concentration of aluminum and calcium released at various equilibrium concentration of arsenate after adsorption by Friedel's salt at pH 4 and 7, respectively.

pH 4			pH 7		
A _{seq} (mg/L)	Ca (mg/L)	Al (mg/L)	A _{seq} (mg/L)	Ca (mg/L)	Al (mg/L)
0.026	5.19	b.d.	0.013	5.69	b.d.
0.043	5.14	b.d.	0.018	5.52	b.d.
0.162	5.55	b.d.	0.047	5.84	b.d.
0.172	5.34	b.d.	0.067	5.50	b.d.
0.439	5.47	b.d.	0.139	5.22	b.d.
0.740	5.45	b.d.	0.297	5.31	b.d.
0.904	5.67	b.d.	0.655	5.57	b.d.
1.046	5.88	b.d.	1.348	5.24	b.d.
1.721	5.62	b.d.	1.412	5.25	b.d.

b.d.: below detection limit.

capacity was 24.2 mg/g at pH 5 for LiAl–Cl–LDHs at initial arsenate concentration of 150 mg/L and solid/liquid ratio of 2.5 g/L [18]. Lazaridis et al. found arsenate adsorption capacity of 15.8 mg/g and 32.6 mg/g by MgAl–CO₃–LDHs at neutral pH value, ion strength of 0.001 and 0.1 respectively [16]. These results as well as our data indicated that different chemical composition or types of anions present in the interlayers of LDHs as well as using different experimental procedures (different initial arsenate concentration, adsorption pH, ionic strength as well as solid liquid ratio) may have an effect on arsenate adsorption capacity.

The stability of an adsorbent is one of the most important considerations in its practical applications. If metals in the brucite-like sheets are released in the solution, it would be important that the amount of metals keeps below the levels that are harmful, or otherwise to choose cations with low toxicity [15]. In fact, few works report adsorbent stability when using other type of LDHs or iron-based adsorbents for removal of contaminant from water. Ferreira et al. found that the amount of magnesium ions released from the Mg–Fe/Al–LDHs increased with decreasing pH during removal of boron from water [36]. Yang et al. observed significant dissolution of aluminum and magnesium from the LDHs during removal arsenic and selenate contaminants [17]. In our investigation, it was observed that during the adsorption of arsenate, little aluminum was released from the adsorbent especially at neutral pH. The concentration of aluminum in water after adsorption was below the detection limit (i.e. <0.2 mg/L), which meets the drinking water standard for aluminum in some countries (e.g. 0.2 mg/L in China). Calcium release was remained at a relative stable level (5.1–5.8 mg/L) irrespective of the amount of arsenate uptake (Table 2). The structure of the adsorbent after adsorption of arsenate was characterized by XRD and the result was presented in Fig. 2. As can be observed, the structure of Friedel's salt was altered after contacting with arsenate solution. The XRD patterns were dominated by aluminum oxides features, while the features of some Ca-related compounds which constitute the relatively unactive adsorption site of the adsorbent disappeared [26]. Similar results have also been reported by Wu et al. who found that at lower pH, the framework 'Ca(OH)₂' was partially dissolved [26].

3.5. Effect of coexisting ions

Drinking water or industrial effluent usually contains various anions and cations which may negatively or positively influence the adsorption of arsenic. The effects of some common anions (PO₄³⁻, SiO₄³⁻, SO₄²⁻) and cations (Ca²⁺, Mg²⁺) on arsenate adsorption by Friedel's salt were investigated (see Figs. 6 and 7). The removal of arsenate was adversely affected in the presence of phosphate, silicate and sulfate. Among the oxyanions considered in this work, phosphate showed most adverse effect on arsenate removal across the whole pH range. The suppressing effect of phosphate

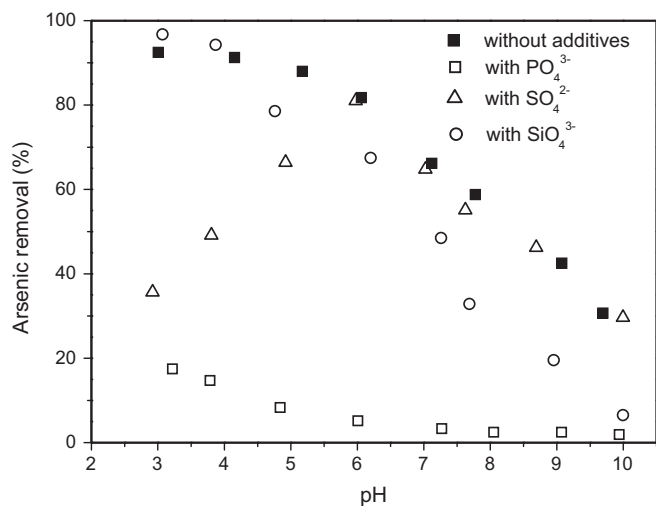


Fig. 6. Effect of coexisting anions on arsenate removal by Friedel's salt at pH 3–10. Initial arsenate concentration was 2 mg/L and the solid/liquid ratio of 0.2 g/L; the molar ratio of As to coexisting anions was 1:10.

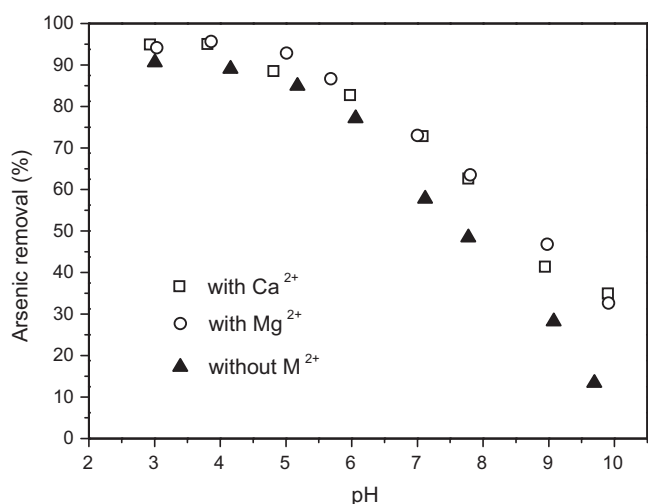


Fig. 7. Effect of coexisting cations on arsenate removal by Friedel's salt at pH 3–10. Initial arsenate concentration was 2 mg/L and the solid/liquid ratio of 0.2 g/L; the molar ratio of As to coexisting cations was 1:10.

and silicate on arsenate removal became more pronounced with increasing pH. Dadwhal et al. examined the adsorption isotherms of arsenic on MgAl–CO₃–LDH in the presence of various competing ions and found that sulfate and phosphate severely affected arsenic adsorption [37]. Violante et al. also demonstrated that arsenate adsorption on MgAl–CO₃–LDH was decreased in the presence of phosphate [20]. Arsenate, phosphate and silicate are specific adsorbing anions while sulfate ions can be sorbed both specifically and non-specifically. They would compete for similar binding sites, hence decreasing arsenate sorption. The detrimental effect of these anions on arsenate removal may reduce treatment efficiency of arsenate-contaminated water by Friedel's salt.

The effect of sulfate on arsenate removal by Friedel's salt is surprising. At pH < 5, arsenate removal was more significantly reduced by sulfate at lower pH, while at pH ≥ 6 the negative effect of sulfate was negligible. This indicates that for the treatment of arsenic-contaminated groundwater using Friedel's salt as adsorbent at environmental relevant pH, arsenate removal may not be reduced by sulfate. The removal of arsenate by most iron-containing adsorbents was not appreciably affected by sulfate [38]. High concentration of sulfate was found to even improve arsenate removal by zero-valent iron [39]. The reason for the significantly adverse effect of sulfate on arsenate adsorption on Friedel's salt at acidic pH is unknown.

Common divalent metal cations such as Mg²⁺ and Ca²⁺ were found to enhance the adsorption of arsenate on the synthesized adsorbent. The positive effect increased slightly with increasing pH. This is beneficial for the treatment arsenate contaminated groundwater that usually contains dissolved magnesium and calcium ions. The enhancing effect of metal cations on arsenate adsorption was reported for iron (hydr)oxides [29,40]. This is probably due to that the presence of metal cations in the solution shifted the surface of the adsorbent to more positively charged nature, which in turn enabled the adsorbent to show higher affinity for arsenate anions.

4. Conclusions

Friedel's salt with good crystallinity was prepared from sodium aluminate solution using calcium chloride at 50 °C, ambient pressure and its performance for arsenic removal from water was investigated by batch adsorption experiments. The results showed that the synthesized adsorbent was effective for the removal of arsenate with relatively fast kinetics. The adsorbent showed higher

removal efficiency for arsenate than arsenite across wide pH range from acidic to alkaline media. The adsorption capacity for arsenate at pH 4 and 7 was 11.85 and 7.80 mg/g, respectively. Arsenic removal was markedly decreased in the presence of phosphate or silicate, however, sulfate was found to suppress arsenate adsorption at pH < 6 and its effect was negligible at pH > 6. The presence of common metal cations (Ca²⁺, Mg²⁺) in water enhanced arsenate removal.

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References

- [1] S.L. Lo, H.T. Jeng, C.H. Lai, Characteristics and adsorption properties of iron coated sand, *Water Sci. Technol.* 35 (1997) 63–70.
- [2] A. Basu, J. Mahata, S. Gupta, A.K. Giri, Genetic toxicology of a paradoxical human carcinogen, arsenic: a review, *Mutation Res.* 488 (2001) 171–194.
- [3] J. Kim, M.M. Benjamin, Modeling a novel ion exchange process for arsenic and nitrate removal, *Water Res.* 38 (2004) 2053–2062.
- [4] A. Zouboulis, I. Katsoyiannis, Removal of arsenates from contaminated water by coagulation-direct filtration, *Sep. Sci. Technol.* 37 (2002) 2859–2873.
- [5] R.Y. Ning, Arsenic removal by reverse osmosis, *Desalination* 143 (2002) 237–241.
- [6] T.M. Gihring, G.K. Druschel, R.B. McCleskey, R.J. Hamers, J.F. Banfield, Rapid arsenite oxidation by *thermus aquaticus* and *thermus thermophilus*: field and laboratory investigations, *Environ. Sci. Technol.* 35 (2001) 3857–3862.
- [7] X. Guo, F. Chen, Removal of arsenic by bead cellulose loaded with iron oxyhydroxide from groundwater, *Environ. Sci. Technol.* 39 (2005) 6808–6818.
- [8] X.H. Guan, J. Wang, C.C. Chusuei, Removal of arsenic from water using granular ferric hydroxide: macroscopic and microscopic studies, *J. Hazard. Mater.* 156 (2008) 178–185.
- [9] C.L. Chuang, M. Fan, M. Xu, R.C. Brown, S. Sung, B. Saha, C.P. Huang, Adsorption of As(V) by activated carbon prepared from oat hulls, *Chemosphere* 61 (2005) 478–483.
- [10] Z. Gu, J. Fang, B. Deng, Preparation and evaluation of GAC-based iron containing adsorbents for arsenic removal, *Environ. Sci. Technol.* 39 (2005) 3833–3843.
- [11] D. Chandra, N.K. Mal, A. Bhaumik, Novel mesoporous silicotinophosphate molecular sieve with high anion exchange capacity, *J. Mol. Catal. A: Chem.* 247 (2006) 216–221.
- [12] T.F. Lin, J.K. Wu, Adsorption of arsenite and arsenate within activated alumina grains: equilibrium and kinetics, *Water Res.* 35 (2001) 2049–2057.
- [13] B.A. Manning, S. Goldberg, Adsorption and stability of arsenic(III) at the clay mineral–water interface, *Environ. Sci. Technol.* 31 (1997) 2005–2011.
- [14] T. Kwon, G.A. Tsigdinos, T.J. Pinnavaia, Pillaring of layered double hydroxides (LDH's) by polyoxometalate anions, *J. Am. Chem. Soc.* 110 (1988) 3653–3654.
- [15] K.H. Goh, T.T. Lim, Z. Dong, Application of layered double hydroxides for removal of oxyanions: a review, *Water Res.* 42 (2008) 1343–1368.
- [16] N.K. Lazaridis, A. Hourzemanoglou, K.A. Matis, Flotation of metal-loaded clay anion exchangers. Part II: the case of arsenates, *Chemosphere* 47 (2002) 319–324.
- [17] L. Yang, Z. Shahrivari, P.K.T. Liu, M. Sahimi, T.T. Tsotsis, Removal of trace levels of arsenic and selenium from aqueous solutions by calcined and uncalcined layered double hydroxides (LDH), *Ind. Eng. Chem. Res.* 44 (2005) 6804–6815.
- [18] Y.T. Liu, M.K. Wang, T.Y. Chen, P.N. Chiang, P.M. Huang, J.F. Lee, Arsenate sorption on lithium/aluminum layered double hydroxide intercalated by chloride and on gibbsite: sorption isotherms, envelopes, and spectroscopic studies, *Environ. Sci. Technol.* 40 (2006) 7784–7789.
- [19] G.P. Gillman, A simple technology for arsenic removal from drinking water using hydrotalcite, *Sci. Total Environ.* 366 (2006) 926–931.
- [20] A. Violante, M. Pucci, V. Cozzolino, J. Zhu, M. Pigna, Sorption/desorption of arsenate on/from Mg–Al layered double hydroxides: influence of phosphate, *J. Colloid Interface Sci.* 333 (2009) 63–70.
- [21] K. Grover, S. Komarneni, H. Katsuki, Uptake of arsenite by synthetic layered double hydroxides, *Water Res.* 43 (2009) 3884–3890.
- [22] K. Grover, S. Komarneni, H. Katsuki, Synthetic hydrotalcite-type and hydrocalumite-type layered double hydroxides for arsenate uptake, *Appl. Clay Sci.* 48 (2010) 631–637.
- [23] A. Bhaumik, S. Samanta, N.K. Mal, Efficient removal of arsenic from polluted ground water by using a layered double hydroxide exchanger, *Indian J. Chem. A.* 44 (2005) 1406–1409.
- [24] A.K. Suryavanshi, J.D. Scantlebury, S.B. Lyon, Mechanism of Friedel's salt formation in cements rich in tricalcium aluminate, *Cement Concrete Res.* 26 (1996) 717–727.
- [25] Y. Dai, G. Qian, Y. Gao, Y. Chi, Y. Xu, J. Zhou, Q. Liu, Z.P. Xu, S. Qiao, Effective removal and fixation of Cr(VI) from aqueous solution with Friedel's salt, *J. Hazard. Mater.* 170 (2009) 1086–1092.

- [26] Y. Wu, Y. Chi, H. Bai, G. Qian, Y. Gao, J. Zhou, Y. Xu, Q. Liu, Z.P. Xu, S. Qiao, Effective removal of selenate from aqueous solutions by the Friedel phase, *J. Hazard. Mater.* 176 (2010) 193–198.
- [27] J. Ma, Z. Li, Y. Zhang, G.P. Demopoulos, Desilication of sodium aluminate solution by Friedel's salt (FS: $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$), *Hydrometallurgy* 99 (2009) 225–230.
- [28] K.P. Raven, A. Jain, R.H. Loeppert, Arsenite and arsenate adsorption on ferrihydrite: kinetics, equilibrium, and adsorption envelopes, *Environ. Sci. Technol.* 32 (1998) 344–349.
- [29] H.J. Zhu, Y.F. Jia, X. Wu, H. Wang, Removal of arsenic from water by supported nano zero-valent iron on activated carbon, *J. Hazard. Mater.* 172 (2009) 1591–1596.
- [30] Y.J. Arai, E.J. Elzinga, D.L. Sparks, X-ray absorption spectroscopic investigation of arsenite and arsenate adsorption at the aluminum oxide–water interface, *J. Colloid Interface Sci.* 235 (2001) 80–88.
- [31] S. Goldberg, C.T. Johnston, Mechanisms of arsenic adsorption on amorphous oxides evaluated using macroscopic measurements, vibrational spectroscopy, and surface complexation modeling, *J. Colloid Interface Sci.* 234 (2001) 204–216.
- [32] A. Jain, K.P. Raven, R.H. Loeppert, Arsenite and arsenate adsorption on ferrihydrite: surface charge reduction and net OH^- release stoichiometry, *Environ. Sci. Technol.* 33 (1999) 1179–1184.
- [33] D.P. Das, J. Das, K. Parida, Physicochemical characterization and adsorption behavior of calcined Zn/Al hydrotalcite-like compounds (HTLc) towards removal of fluoride from aqueous solution, *J. Colloid Interface Sci.* 261 (2003) 213–220.
- [34] K.D. Hristovski, P.K. Westerhoff, T. Möller, P. Sylvester, Effect of synthesis conditions on nano-iron (hydr)oxide impregnated granulated activated carbon, *Chem. Eng. J.* 146 (2009) 237–243.
- [35] Z. Gu, B. Deng, J. Yang, Synthesis and evaluation of iron-containing ordered mesoporous carbon (FeOMC) for arsenic adsorption, *Microporous Mesoporous Mater.* 102 (2007) 265–273.
- [36] O.P. Ferreira, S.G. Moraes, N. Durán, L. Cornejo, O.L. Alves, Evaluation of boron removal from water by hydrotalcite-like compounds, *Chemosphere* 62 (2006) 80–88.
- [37] M. Dadwhal, M. Sahimi, T.T. Tsotsis, Adsorption isotherms of arsenic on conditioned layered double hydroxides in the presence of various competing ions, *Ind. Eng. Chem. Res.* 50 (2011) 2220–2226.
- [38] H.J. Shipley, S.Y. Yean, A.T. Kan, M.B. Tomson, Adsorption kinetics model for arsenic adsorption to magnetite nanoparticles, *Environ. Sci. Pollut. Res.* 17 (2010) 1053–1062.
- [39] H. Sun, L. Wang, R. Zhang, J. Sui, G. Xu, Treatment of groundwater polluted by arsenic compounds by zero valent iron, *J. Hazard. Mater.* 129 (2006) 297–303.
- [40] Y. Jia, G.P. Demopoulos, Adsorption of arsenate onto ferrihydrite from aqueous solution: influence of media (sulfate vs. nitrate), added gypsum, and pH alteration, *Environ. Sci. Technol.* 39 (2005) 9523–9527.