Arsenic removal from aqueous solution using ferrous based red mud sludge

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ABSTRACT

Ferrous based red mud sludge (FRS) which combined the iron–arsenic co-precipitation and the high arsenic adsorption features was developed aimed at low arsenic water treatment in rural areas. Arsenic removal studies shown that FRS in dosage of 0.2 or 0.3 g/l can be used effectively to remove arsenic from aqueous solutions when initial As(V) concentration was 0.2 or 0.3 mg/l. Meanwhile, turbidity of supernatant in disturbing water was lower than 2 NTU after 24 h. The pH range (4.5–8.0) for FRS in effective arsenic removal was applicable in natural circumstance. Phosphate can greatly reduce the arsenic removal efficiency while the presence of carbonate had no significant effect on arsenic removal. Arsenic fractionation experiments showed that amorphous hydrous oxide-bound arsenic was the major components. When aqueous pH was decreased from 8.0 to 4.5, arsenic in FRS was not obviously released. The high arsenic uptake capability, good settlement performance and cost-effective characteristic of FRS make it potentially attractive material for the arsenic removal in rural areas.

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1. Introduction

Arsenic is a geogenic water menace affecting millions of people all over the world and is regarded as the largest mass poisoning in history. Permanent arsenic intake leads to chronic intoxication, and prolonged arsenic exposure can damage the central nervous system, liver, skin and results in the appearance of diverse types of cancer, such as hyperkeratosis, lung and skin cancer [1].

For the past few years, unexpected arsenic leakage to natural water has taken place frequently in China. In September 2008, high accumulations of arsenic caused severe water pollution in Yangzonghai Lake, which is 45 km east of Yiliang County, Kunming Prefecture. Water arsenic concentration in this lake was above 0.12 mg/l while the state standard in China is below 0.05 mg/l. Considering the huge water volume (0.6 billion cubic meters) and broad water surface (31.9 km^2) affected by arsenic leakage, high efficiency, easy operated and cost-effective arsenic removal techniques were needed.

Worldwide awareness of the arsenic crisis has motivated researchers to develop various techniques for removing aqueous arsenic. At present, many approaches such as adsorption, ion exchange, reverse osmosis, nanofiltration, coagulation (co-precipitation), membrane distillation, biological methods and photo catalytic oxidation are increasingly being used for the removal of arsenic from water body [2–5]. Coagulation (co-precipitation) and adsorption processes are most promising for aqueous arsenic removal because of the low cost and high efficiency, and are widely used in the developing world.

Presently, low-cost adsorption materials are popular for arsenic removal from natural water [6,7]. Agricultural products, industrial by-products/wastes, soils and clay minerals were investigated for arsenic removal. Red mud (RM) is a by-product during alkaline-leaching of bauxite in Bayer process. About 1–2 tons of RM residues are produced for a ton of alumina [8]. At present, about 10–20 million tons of caustic RM must be disposed of annually in China [9] and such residue has accumulated over years and causes a serious environmental problem due to its high alkalinity and large amount. Researches focused on the application of RM in wastewater treatment. RM has been found effective to remove arsenic from aqueous solution [10,11]. However, the direct application of RM in rural areas is limited by its high alkaline, therefore, proper modification to RM was considered [12]. For example, iron based sorbents and impregnated adsorbents were found effective in removing arsenic from aqueous environment [13–15]. Zhang et al. [9] prepared ferric modified RM as adsorbent in arsenic removal, and the arsenic adsorption capacity was high.

Meanwhile, most previous studies focused on ferric based absorbents or ferric–arsenic co-precipitation for arsenic removal [13–15]. Recent studies have mentioned the possibility of using ferrous in aqueous arsenic removal [16,17]. Addition of ferrous leads to a better arsenic removal efficiency than ferric [16]. Iron–arsenic co-precipitation and arsenic absorption on iron (hydro)oxides were used to explain the arsenic removal phenomena.

According to the information available, the possibility of associated ferrous and RM in arsenic removal was not reported.

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Table 1
Chemical compositions of the RM.

Constituent	% w/w
SiO_2	20.08
Fe_2O_3	24.66
Al_2O_3	6.06
$CaO + MgO$	24.80
Na_2O	6.04
K_2O	0.45
TiO_2	4.3
LOI[a]	16.45

[a] Loss on ignition.

Furthermore, ferrous based materials were cost-effective compared to ferric in China [$FeCl_2$: 600–800 yuan/t (about 88–118 dollars/t) compared to $FeCl_3$: 3000–3300 yuan/t (about 441–485 dollars/t)]. Therefore, the main objectives of this research were: (1) To prepare a cost-effective material with high arsenic removal efficiency and great settlement performance by mixing $FeCl_2$ and RM. (2) To evaluate the effects of $FeCl_2$ based RM Sludge (FRS) in aqueous arsenic removal, and the stability of pollutants in sludge. (3) To explore the interaction mechanism between FRS and arsenic.

2. Materials and methods

2.1. Materials and reagents

RM provided by Shandong Branch, Aluminum Corporation of China, was sieved through a 40 mesh screen and without any further treatment. The average chemical composition of RM was listed in Table 1, RM is mainly consisted of Ca, Si, Fe and Al oxides. The single-point N_2–BET method indicated that the specific surface area of a typical RM sample was about $14.76\,m^2\,g^{-1}$ [18].

All the reagents used were analytical grade and used as received. $Na_2HAsO_4\cdot7H_2O$ salt (Merck 6284) was dissolved in deionized water for 50 mg/l As(V) stock solution. As_2O_3 was dissolved in deionized water for 50 mg/l As(III) stock solution. These stock solutions were diluted to prepare As(V) or As(III) bearing water of specified As(V) or As(III) concentrations with tap water. The main cations and anions of the tap water are shown in Table 2.

Solutions of KBH_4, thiourea, sscorbic acid, NaOH, and HCl were prepared by dissolving the adequate quantities of the compound in deionized water. The KBH_4, thiourea and ascorbic acid solutions were prepared before use.

2.2. Preparation of FRS materials

2 g $FeCl_2\cdot4H_2O$ was dissolved in 10 ml deionized water, RM was added quantitatively in ferrous solution. The pH improved by the addition of RM (Table 3). The FRS was prepared before use and without any further treatment.

2.3. Arsenic removal experiments

Low arsenic water (500 ml) was mixed with a given amount of FRS, RM or $FeCl_2$ in flasks by stirring at 100 rpm for 20 min, mixtures were then stirred at 20 rpm at room temperature for 24 h. After that, the suspensions were filtered through 0.45 μm PVDF membrane filter and filtrates were analyzed for arsenic concentration. Aqueous

Table 3
The pH of FRS in different amounts of red mud added (different amounts of red mud was added in 10 ml 1 M $FeCl_2$ solution).

Red mud dosage (g)	The pH of slurry
0	2.52 ± 0.1
5.0	6.57 ± 0.1
6.0	6.73 ± 0.1
7.0	6.98 ± 0.1
7.69	7.17 ± 0.1

pH values were adjusted with either acid (1 M or 0.1 M HCl) or base (1 M or 0.1 M NaOH) solutions. Aqueous pH values were measured during the arsenic removal process, meanwhile, arsenic and iron concentrations were measured in the suspensions.

After FRS, RM or $FeCl_2$ were added to low arsenic water, 20 ml of the suspension was transferred to a tube for turbidity measurement in different time. Turbidity as a function of settling time was obtained from this measurement, which could provide information on settling performance and settling rate of FRS, RM and $FeCl_2$.

Different amounts of Na_2HPO_4, Na_2SiO_4 or $NaHCO_3$ (0.1, 0.5, 1 or 10 mM) were added to assess the effects of co-existing anions on arsenic removal. For arsenic fraction test, 50 ml plastic centrifuge tube contained 1 g FRS and 45 ml arsenic solution were shaken at room temperature in a rotary shaker for 24 h. Immediately after the loading step, the FRS samples containing arsenic were chemically fractionated using the five-step sequential extraction procedure for arsenic proposed by Wenzel et al. [19] (Table 4).

2.4. Methods of analysis

Arsenic was analyzed on Atomic Fluorescence Spectrometer (AF-610A). The micrograph and microanalysis of the samples were determined using a 30 kV HITACHI S-3000N scanning electron microscope (SEM). Iron concentration is analyzed on Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, Prodigy). Turbidity of suspension was determined by using a HACH 2100N IS Turbidimeter.

The experiments were performed in duplicate and the mean values were considered. In order to ascertain the reproducibility of results, a group of experiments were repeated a number of times and the results were found to vary within 5%. The blank experiments showed no detectable As(V) or iron adsorbed on the walls of the flask.

3. Results and discussion

3.1. Arsenic removal by ferrous-modified red mud, un-modified red mud or ferric modified red mud

Kinetics experiments for As(V) and As(III) removal by FRS were shown in Fig. 1. It is shown that 24 h is enough for arsenic removal by FRS. Aqueous arsenic concentration changed a little after 8 h since FRS added.

Comparison of ferrous and ferric based RM materials in arsenic removal was studied and the results were shown in Fig. 2. 2×10^{-4} mol/l iron (ferrous or ferric) and 7.7×10^{-2} g/l RM were added in arsenic water, meanwhile, research done before had shown that Cl anion has little effect on As(V) removal [20]. Arsenic removal efficiency for ferrous based red mud was higher than ferric based red mud ($91.7 \pm 2.3\%$ compared to $81.2 \pm 3.9\%$) when the

Table 2
Main cations and anions of the tap water.

pH	HCO_3^-	Cl^-	NO_3^-	SO_4^{2-}	HPO_4^2	Mg^{2+}	Na^+	K^+	Ca^{2+}
7.3	103.2	19.5	3.5	65.3	<0.01	12.7	12.5	1.9	115.4

Table 4
Sequential extraction procedure for arsenic.

Fraction	Extractant	Extraction conditions	SSR[a]	Wash step
1	$(NH_4)_2SO_4$ (0.05 M)[b]	4 h shaking, 20 °C	1:25	
2	$(NH_4)H_2PO_4$ (0.05 M)	16 h shaking, 20 °C	1:25	
3	NH_4-oxalate buffer (0.2 M);pH 3.25[c]	4 h shaking in the dark, 20 °C	1:25	NH_4-oxalate (0.2 M); pH 3.25 SSR 1:12.5; 10 min shaking in the dark
4	NH_4-oxalate buffer (0.2 M); +axcorbic acid (0.1 M) pH 3.25	30 min in a water basin at 96 ± 3 °C in the light	1:25	NH_4-oxalate (0.2 M); pH 3.25 SSR 1:12.5; 10 min shaking in the dark
5	HNO_3/H_2O_2	Microwave digestion	1:50[b]	

[a] SSR: soil solution ratio.
[b] After the digestion.

initial As(V) concentrations were varied in the range of 0.16–1.4 mg/l. An amount of 0.4 g/l ferrous based red mud or ferric based red mud were enough for efficient arsenic removal when initial As(V) concentrations were 0.5 mg/l or 0.2 mg/l respectively.

Comparison of un-modified red mud and ferrous-modified red mud in arsenic removal was also studied in Fig. 2. The absorption capacity of red mud is about 0.55–0.60 mg/g which is consistence with other work done before [11]. Arsenic removal efficiency was much lower without the addition of ferrous. Meanwhile, the usage of un-modified RM in water treatment is limited by its high alkalinity.

pH is not the major factor for the discrepancy in arsenic removal efficiency (shown in Fig. 3 the final pH is about 8.2 ± 0.1).
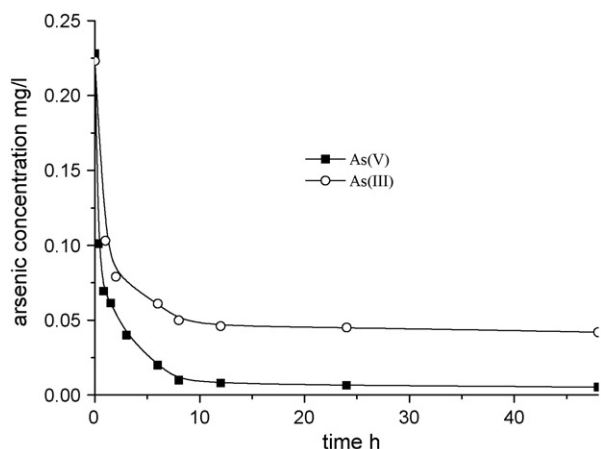

Fig. 1. kinetics experiments for As(V) or As(III) removal (0.4 g/l FRS was added in As(V) or As(III) bearing water).
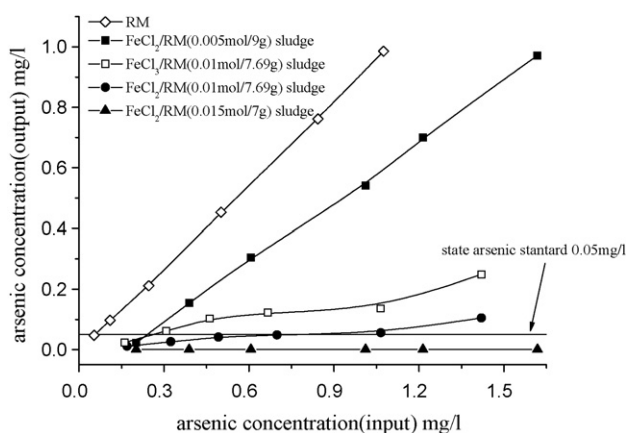

Fig. 2. As(V) concentrations of input or output arsenic water (red mud, ferric based red mud or ferrous based red mud were added).

Aqueous pH increased during arsenic removal process after FRS, red mud, ferric based red mud or $FeCl_2$ were added, the pH was influenced by ferrous oxidation, arsenic absorption on iron hydroxides or iron–arsenic co-precipitation process. However, the final pH after the addition of different reagents was almost the same (8.1–8.3), therefore, pH is not the major factor affects on the comparison of different reagents in arsenic removal efficiency.

The effects of Fe^{2+} concentration in ferrous based RM on arsenic removal were investigated in Fig. 2. Arsenic removal efficiency increased by $FeCl_2$ content increased from 10% to 30% in ferrous based RM. However, when $FeCl_2$ content increased from 20% to 30%, the pH of ferrous based red mud decreased from 7.2 ± 0.1 to 6.4 ± 0.1. For practical consideration, neutral ferrous based red mud was used in this work.

3.2. Effects of dosages of FRS on arsenic removal

Effects of FRS dosages on As(III) and As(V) removal were shown in Fig. 4. The As(III) and As(V) removal efficiency both increased with increasing FRS dosage. There may be two reasons: (1) greater availability exchangeable sites or surface area at high amounts of red mud and iron hydroxide and (2) greater amounts of free iron in iron–arsenic co-precipitation process. As(V) removal efficiency was higher than As(III) when FRS used. However, 0.6 g/l FRS was effective to reduce aqueous arsenic concentration from 0.23 mg/l to 0.05 mg/l. Ferrous–As(III) co-oxidation process can contribute to the As(III) removal.

3.3. Variation of turbidity in overlying water

The variation of turbidity in overlying water as a function of elapsed time of As(V) removal experiment is shown in Fig. 5. It can be seen that elapsed time had much effect on the turbidity in overlying water. Turbidity of overlying water was 96.1, 98.2 or 61.3
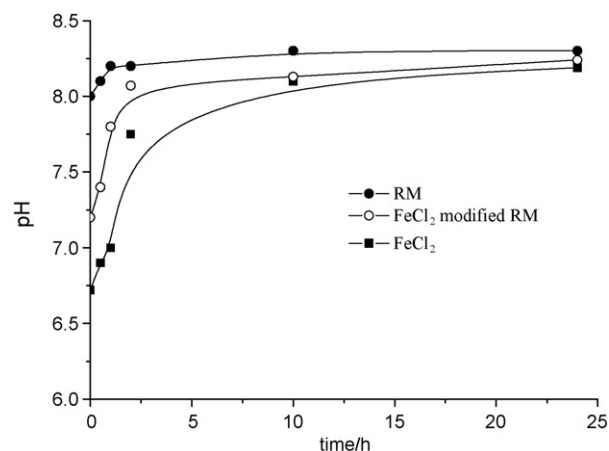

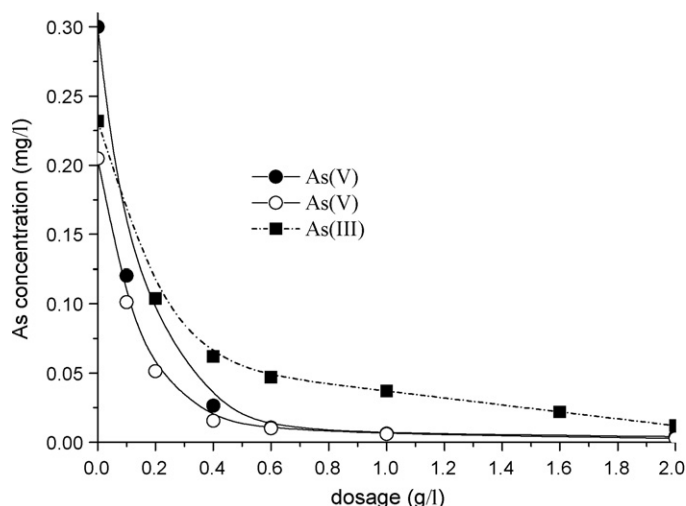**Fig. 3.** Kinetics of pH during the arsenic removal process.

Fig. 4. Effects of dosages of FRS on As(V) and As(III) removal.

Fig. 6. Effects of pH on arsenic removal by FRS, FeCl$_2$ or red mud.

NTU with the addition of FRS, red mud or FeCl$_2$ after 20 min mixture. Stirring condition of 20 rpm/min was performed to simulate natural disturbance in following 24 h. The turbidity of overlying water was 1.9, 23 or 61 NTU with the addition of FRS, red mud or FeCl$_2$ after 24 h. Meanwhile, the Water Quality Standard for Drinking Water Sources (CJ 3020-93) guide line value of turbidity was lower than 3.0 NTU. After combined ferrous and red mud, settling performance was better than red mud or ferrous used only. Flocculants of iron oxide was too cheap to settle down when only FeCl$_2$ was added, meanwhile, small particles of red mud is hard to settle down when only red mud used. By combining ferrous and red mud, small red mud particles aggregated through the flocculation process, thus enhanced the settlement performance of FRS. FRS precipitated with arsenic in 24 h under simulated agitating circumstance, therefore, further treatment such as filtration or coagulation was unnecessary.

3.4. Effects of pH on arsenic removal

The pH is one of the most important parameters controlling As(V) removal from water body. For pentavalent arsenic, the corresponding stable species and pH values are: H$_3$AsO$_4$ (pH 0.0–2.0), H$_2$AsO$_4^-$ (pH 2.0–7.0), HAsO$_4^{2-}$ (pH 7.0–12.0) and AsO$_4^{3-}$ (pH
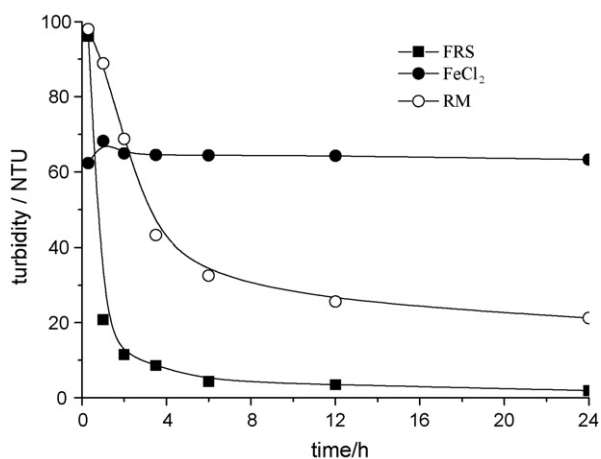

Fig. 5. Variation of turbidity in overlying water as a function of elapsed time of arsenic removal experiment (0.4 mg/l FRS was added, initial As(V) concentration was 0.2 mg/l).
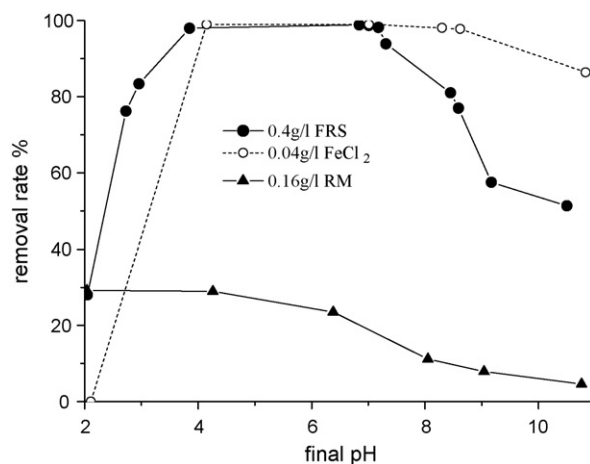
12.0–14.0) [3]. Therefore, different solution pH determined different As(V) removal efficiency. In order to investigate the optimum pH conditions for PFS usage, different pH conditions were adjusted with HCl or NaOH (Fig. 6). Arsenic removal efficiency of As(V) was decreased when pH < 4.0 or pH > 8.0. In the pH range of 4.0–7.0, arsenic removal efficiency of As(V) could reach above 95%. It was noted that As(V) was removed most effectively in the pH range of 2.0–3.5 when only RM was used [11], meanwhile, acid circumstance (pH < 5) was believed effective in As(V) removal by coagulation with ferric ions [21].When pH was lower than 4.0, oxidation and hydroxide of ferrous was inhibited (FeCl$_2$ used only in arsenic removal in Fig. 6), therefore, arsenic removal efficiency of FRS was decreased when pH was lower than 4.0. Meanwhile, adsorption intensity of As(V) in red mud was improved to 0.256 mg/g by RM when pH was 2.5. This adsorbed capacity of red mud was comparable to studies done before [11]: As(V) adsorption intensity was 0.375 mg/g when initial As(V) concentrations were 0.13 mg/l.

3.5. Effects of anion concentrations on As(V) removal

Natural inorganic anions are not only ubiquitous in natural waters but also highly reactive toward both metals and surfaces. So its potential influences on arsenic sorption and mobility are great. The presence of those anions which can compete with arsenic anions for the adsorptive sites will affect the removal of arsenic [22]. Thus, three anions (CO$_3^{2-}$, SiO$_3^{2-}$, PO$_4^{3-}$) whose molecular structures are similar to that of arsenic were selected to assess the effects of co-existing anions on arsenic removal, and the results are shown in Fig. 7. Phosphate caused the greatest percentage decrease in arsenic removal rate among the three anions and the CO$_3^{2-}$ had less effect on the arsenic removal. This result is in agreement with previous studies [23,24]. This high interfering effect of phosphate in the arsenic removal can be explained by the chemical similarity between them. Phosphate element and arsenic element are located in the same main group, and the molecular structure of phosphate ion is very similar to that of arsenic ion. CO$_3^{2-}$ was less adversely effects on arsenic removal compared this work to Zhang et al. [9] (arsenic removal efficiency reduced by 4–6% compared to 20–22% when 1 mM CO$_3^{2-}$/HCO$_3^-$ was added). The reasons may be as follows: (1) arsenic removal mechanism is different. Absorption is the only process for arsenic removal in the study of Zhang et.al., however, absorption and co-precipitation combined in this work. (2) Free iron. There is free iron when FeCl$_2$ based RM (our work) was added in arsenic water, however, the free iron was not mentioned
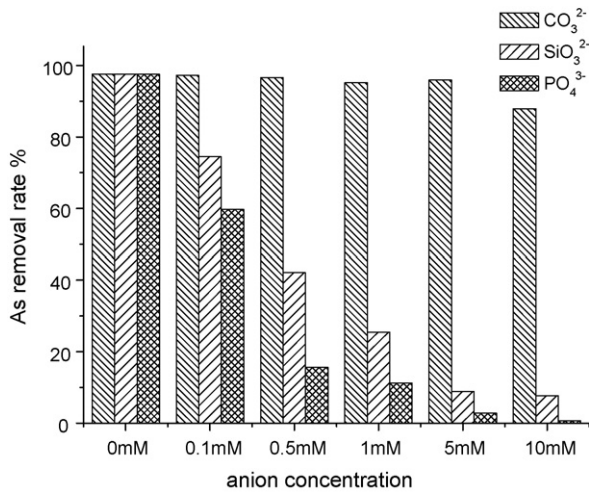
Fig. 7. Effects of co-existing anions on arsenate removal at fixed initial arsenic concentration (0.2 mg/l).

Fig. 9. The result of SEM-EDS analysis of FRS after As(V) removal. In inset are shown general views of selected areas (SEM magnification: 1800×).

in other works. (3) Green rust formation. In the ferrous oxidation process, it is possible that $[Fe_{(1-x)}^{II}Fe_x^{III}(OH)_2]^{x+}[CO_3^{2-}]$ formed. Therefore, the effect of competitive absorption of CO_3^{2-} on arsenic absorption is weakened. (4) Tap water used. The combination of Ca^{2+} and CO_3^{2-} may also reduce the adverse effect of CO_3^{2-} on arsenic removal.

3.6. Arsenic fractionation

These operationally defined fractions can represent non-specifically-bound, specifically-bound, amorphous hydrous oxide-bound, crystalline hydrous oxide-bound and the residual. Arsenic fractionation has been studied in the sewage sludge shown in Fig. 8. Similarly, the percentage of non-specifically-bound arsenic adsorption by RM or FRS was very little (the exchangeable forms are <1%, w/w). The specifically-bound arsenic comprised 14.5% in RM or 16.4% in FRS sewage sludge. It was possible that arsenic combined to iron do not contribute to specifically-bound fraction. The percentage of amorphous hydrous oxide-bound arsenic is remarkable higher compared FRS (61.1%) sewage sludge to RM (32.3%), this result is consistent with researches done before [25] that arsenic is specifically adsorbed on to iron oxides. Meanwhile, the crystalline hydrous oxide-bound arsenic in FRS is very little.
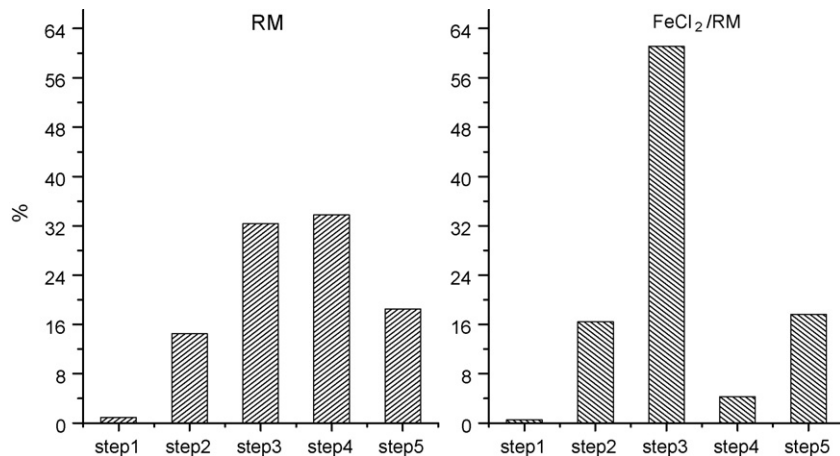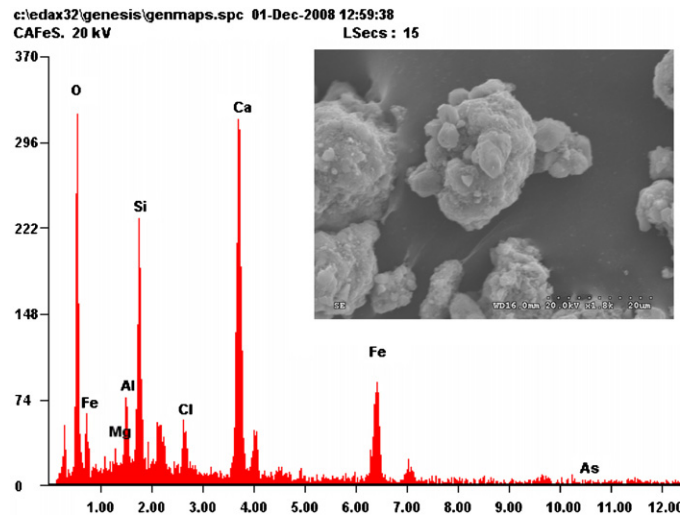
3.7. SEM-EDX analysis of FRS after As(V) removal

The morphology and surface elements distribution of FRS after adsorbed arsenic were studied by a SEM combined to an EDAX KEVEX level 4. The image obtained for the FRS showed that there were many small particles laid on the surface of RM, such small particles possibly generated by free $FeCl_2$ precipitation process. The EDS analysis (Fig. 9) revealed that Fe and O were abundant on the surface and the oxidation of Fe^{2+} may contribute to the high content of O.

Fe(II) and Fe(III) redox fundamental equation was invited to discuss the mechanism after FRS was added in low arsenic polluted water:

$$4Fe^{2+} + O_2 + 4H^+ = 4Fe^{3+} + 2H_2O \tag{1}$$
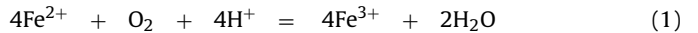
The Fe(II) and Fe(III) redox kinetics follow the equations [26]:

$$\frac{-d[Fe(II)]}{dt} = k[Fe(II)][OH^-]^2 P_{O_2} \tag{2}$$

where [Fe(II)] is the ferrous concentrations (mol/l), t is the time(min), [OH$^-$] is the OH$^-$ concentrations (mol/l), k is rate constant ($k = 8.0(\pm 2.5) \times 10^{13}$ L^2/min, atm, mol^2(20 °C)) and P_{O_2} is the partial pressure of oxygen.

Fig. 8. Distribution (% of total arsenic extracted) of sorbed arsenic(V) on RM and FeCl$_2$/RM sludge as a function of arsenic surface concentration.
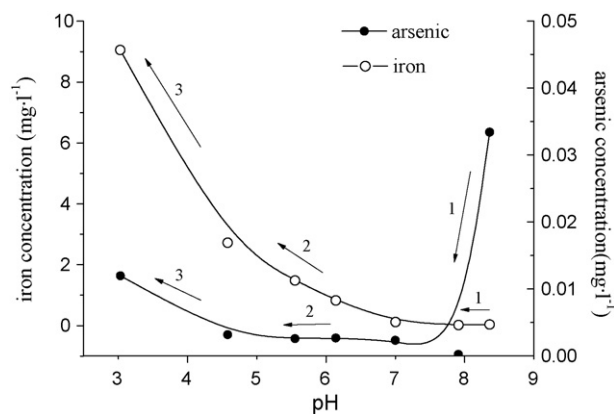
Fig. 10. Release of arsenic and iron in FRS, pH was measured after 24 h equilibrium.

Furthermore, Eq. (2) can be converted to Eq. (3):

$$\frac{-d[Fe(II)]}{dt} = \frac{k_H[O_2(aq)]}{[H^+]^2}[Fe(II)] \tag{3}$$

where [H⁺] is the concentrations of H⁺, $k_H = 3 \times 10^{-12}$ mol/(L min) (20 °C). After FRS was added, $[O_2(aq)]$ in the tap water is assumed to be 8.32 mg/l (2.6×10^{-4} mol/l) and the pH value was in the range of 7.2–8.0 after FRS was added. The initial ferrous concentrations were 2×10^{-4} mol/l and the oxidation rate of ferrous was about 3.12×10^{-3} mol/l min by Eq. (3), therefore, all ferrous added in the low arsenic polluted tap water was theoretically oxidized to ferric in several minute.

3.8. Release of arsenic and iron from FRS in acid water

The desorption process of arsenic and iron in acid circumstance were also studied by stepwise addition of HCl. The acidification process can divided into three stages shown in Fig. 10. In the 1st stage (8.0 < pH < 9.0), arsenic concentrations in aqueous solution decreased and iron concentrations had not changed. This result was consistent with Section 3.3 that optimum pH conditions of FRS for arsenic removal was lower than 8.0. In the 2nd stage (4.5 < pH < 8), with more amount of addition of HCl, absorbed arsenic was not significantly desorbed while iron concentrations increased from 0.04 to 2.72 mg/l. In the 3rd stage (3 < pH < 4.5), arsenic and iron concentrations both increased. When pH value was 3.0, concentrations of arsenic and iron were 0.12 and 9.05 mg/l, respectively. There may be two possibilities for the differences between iron release and arsenic release. (1) Iron with no arsenic absorbed released, there is 24.3% Fe₂O₃ in red mud which may dissolve when HCl was added. (2) Iron with arsenic absorbed released, however, parts of released arsenic was absorbed again.

Ferrous may be oxidized to ferric in a short period in this experiment, the interaction of arsenic and iron in this transformation process (within 1 min) may be complex. It is reported that green rust (GR) will appear in the aerobic circumstance which was known as layered double hydroxides (LDH), in which $[Fe_{(1-x)}^{II}Fe_x^{III}(OH)_2]^{x+}$ layers alternate with interlayers made of anions (such as CO_3^{2-}, SO_4^{2-} or Cl^-). Arsenic can take part in the formation of GR, or which can be effectively adsorbed on the surface of GR [27]. Meanwhile, it is possible that transition materials like GR will not appear and instantaneous transformation from ferrous to ferric was happened. Importantly, there is no evidence to suggest the formation of the more mobile As(III) species after the addition of ferrous [28]. After the formation of ferric, the coagulation and adsorption process will contribute to arsenic removal, and it is commonly regarded that arsenate is adsorbed via surface complex formation on ferrihydrite [29].

It is believed that the nature of As(V) adsorption in RM is chemical and the adsorption arsenic types is spontaneous, and the positive values of entropy change suggest some structural changes in adsorbate and adsorbent [11]. The iron can be adsorbed on the surface of RM, thus strengthening the arsenic adsorption capacity [9]. The setting performance of FRS is pretty good, small RM particles may be accelerating the setting process by acting as the crystal nucleus.

4. Conclusion

Ferrous based red mud which combined high arsenic removal efficiency and great settlement performance can be used as a cost-effective material for arsenic removal based on iron–arsenic co-precipitation and arsenic absorption. Arsenic was removed within 24 h after FRS was added and further treatment was not needed. Arsenic in FRS was considered steady and hardly released to natural circumstance. FRS can be easily produced and used, raw materials of FRS were easy transported and preserved. All these features made FRS as a candidate for aqueous arsenic removal in rural areas.

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