Removal of inorganic arsenic from aqueous solution by Fe-modified ceramsite: batch studies and remediation trials

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ABSTRACT

During sediment remediation, adsorbent addition is an effective technology for the removal of contaminants but the cost is often high. In this study, a low-cost adsorbent, ceramsite, made from contaminated riverbed sediment was synthesized. The Fe-modified ceramsite (FMC) was used as adsorbent to remove arsenate from aqueous solutions and reduce the inorganic arsenic release from contaminated sediments. Kinetic studies showed that chemisorption mainly governed the adsorption process while batch studies yielded the theoretical adsorption capacity for arsenate of 10.63 mg/g at pH = 7 condition. Co-existing anions and pH have no significant impact on the adsorption process. In the regeneration studies, 91, 86, and 80% of the adsorption capacity were recovered in 3 cycles. In-situ remediation trials revealed that the addition of the adsorbent to sediment surface significantly reduced the release of inorganic arsenic into aqueous system, with a reduction efficiency of 86%. Furthermore, the species of the arsenic in the surface layer was significantly inactivated from an active state to a stable state. These findings highlight the application of the FMC as a facile and cost-effective adsorbent for containment of arsenic in solutions and sediments, demonstrating that they are highly applicable for practical cases.

Key words | Fe-modified ceramsite, inorganic arsenic, sediment remediation

HIGHLIGHTS

- Contaminated sediment was used as the support for the iron oxides.
- FMC was used as an adsorbent and remediator.

INTRODUCTION

The presence of arsenic in river water and riverbed sediments is a significant issue worldwide; it is estimated that 226 million people are drinking from unsafe water resources containing arsenic (Rodríguez-Lado et al. 2015; Iriel et al. 2019). The exposure to arsenic via drinking water will lead to potential toxicity and carcinogenic effects (Liu et al. 2015). To minimize the risk of the arsenic, the maximum contaminant level (MCL) established by the World Health Organization (WHO) is lowered to 0.01 mg/L for drinking water (Wei et al. 2019). However, the arsenic pollution in aqueous solutions and riverbed sediments is still not solved.

The arsenic, when presenting in aqueous solutions, can be generally subdivided into organic forms and inorganic forms. Compared with organic arsenic, inorganic arsenic is more toxic to humans. Hence, the removal of inorganic arsenic from environmental water sources is of great significance for public health (Ren et al. 2020). Owing to extensive mining activities, the arsenic levels in river water and sediments near the mining zone increased dramatically (Kaartinen et al. 2017). For example, arsenic pollution in Jie River, Yantai, has become a matter of concern considering the gold mining industry in Shandong Province, China.
The total arsenic content in the Jie River reached 0.091 mg/L and the downstream concentration is higher than upstream (with no additional arsenic discharge into the river being observed) (Ma et al. 2020). This indicates that the origin of arsenic is not from outside the river but from the river sediments. Adsorption technology happens to be a more applicable technology under this situation than other technologies because it can remove the excessive arsenic in the water bodies and reduce arsenic release from the sediments simultaneously.

To date, the metal oxides have been thoroughly studied for arsenic adsorption because the metal oxides can form hydroxides, which combine with arsenic ions (Xu et al. 2019). The theoretical adsorption capacity and adsorption mechanism of the synthesized adsorbents such as magnetite nanoparticles, zirconium oxide nanoparticles, and copper oxide nanoparticles have been fully investigated in previous researches (Shipley et al. 2010; Cui et al. 2012; Goswami et al. 2012). Nonetheless, the application of these synthesized adsorbents remained stagnant; one of the most important reasons that hinders their application is the high cost of these adsorbents. To lower the cost, more cost-effective support is needed. As we all know, to achieve a more applicable adsorbent that can be applied in a fixed bed column or directly on the riverbed, most of the metal oxides are immobilized on a support or a matrix (Wei et al. 2019). Ceramsite has been proved to be a promising and considerable support due to its low cost and stable structural strength. However, the common raw material of ceramsite, clay, is being exhausted in the earth (Zou et al. 2009). The riverbed sediment, which has a similar chemical composition to clay, was found to be a perfect substitution in fabricating ceramsite (Yin et al. 2020). In this research, the arsenic-contaminated riverbed was chosen to be the raw material of the ceramsite and the iron was immobilized on the ceramsite to improve the adsorption capacity.

When preparing ceramsite with sediment, the calcination progress stabilized the arsenic inside the raw materials, the leaching test of the ceramsite used in this framework was less than 3 μg/L, which supports the application of this raw material. The objectives of this research were to: (1) study the adsorption capacity of the Fe-modified ceramsite adsorbent (FMC), (2) evaluate the factors that impact on the adsorption behavior of FMC, and (3) investigate the feasibility of using FMC as a sediment remediation material, and its mechanism. The obtained FMC successfully removed the arsenic from the aqueous solutions and contained the arsenic in CRS (contaminated riverbed sediment). To a certain extent, it realized the purpose of ‘use the waste to treat the waste’.

MATERIALS AND METHODS

Materials and instruments

The raw materials of the ceramsite used in this study were collected from an arsenic-polluted river sediment, Jie River (Yantai, China). The chemical compositions of the sediments are shown in Table S1 in Supplementary Information. The pH of all solutions was measured by a pH meter (model Orion Star™ A211, Thermo Fisher). The stock arsenic solution (1,000 μg/L) was prepared from a high concentration standard arsenic solution (Sinopharm Chemical Reagent, 100 mg/L). The adsorption experiments were conducted in a constant temperature shaker. An atomic fluorescence spectrometer (SHIMADZU) was used to determine the arsenic concentration of all solutions. The chemical reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. The FMC was characterized by X-ray fluorescence spectroscopy (XRF-1800, SHIMADZU) and X-ray diffraction (XRD, Rigaku) using Cu radiation (45 kV, 40 mA).

Preparation of adsorbents

After air drying for 5 days, the sediments were ground and sieved by a 100-mesh sieve to be mixed homogeneously. Then, the sediment powders were mixed with deionized water to pelletize by hand with particle sizes of 8–10 mm. After pelleting, the raw pellets were moved to a high-temperature muffle furnace for sintering. The sintering procedure is as follow: the heating of samples started at 20 °C with a ramp rate of 10 °C/min and sintered at 1,200 °C for 30 min, then naturally cooled to 20 °C in the furnace. The obtained ceramsite was ground and sieved by a 60-mesh sieve for future iron loading. The FMC was prepared by single one-step synthesis: the ceramsite powders were mixed with dissolved ferric chloride (10 g ferric chloride dissolved with 50 ml ethyl alcohol) at a temperature of 60 °C for 4 h. The 1 M NaOH was added dropwise after mixing. Subsequently, the mixed solution was filtered and the FMC was rinsed with deionized water several times. The adsorbents were dried at 80 °C for 24 h and stored in the desiccator for further analyses.

Experiment methods and statistical analysis

The leaching behavior of the ceramsite was according to the widely accepted Toxicity Characteristics Leaching Procedure method (TCLP 1992, Environmental Protection
Agency, United States). The total arsenic content was measured using microwave digestion; briefly, 0.1 g sample was added into the PTFE digestion jar with 3 ml 65% nitric acid, 1.5 ml 35% hydrogen peroxide, and 1 ml 40% hydrogen fluoride for digestion. The arsenic fraction investigation was followed by the method reported by Shiowatana (Shiowatana et al. 2003). Unless otherwise stated, the static adsorption experiments were all carried out at 25 °C with 50 ml of arsenic solutions with stirring speed at 240 rpm for 2 h, the pH was adjusted to 7 with 0.1 M HCl or 0.1 M NaOH. After equilibrium, the 50 ml mixed solution was filtered through a 0.45 μm membrane and the arsenic concentration was detected by atomic fluorescence spectrometer. The amount of the arsenic absorbed: \( q_e \) (mg/g) and the removal efficiency of arsenic: \( R \) (%) were calculated by Equations (1) and (2):

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

\[
R = \left( \frac{C_0 - C_e}{C_0} \right) \times 100\%
\]

where \( C_0 \) is the initial arsenic concentration (mg/L), \( C_e \) is the arsenic concentration at equilibrium time (mg/L), \( a \) is the dosage amount (g/L).

**Kinetic study**

For adsorption kinetic fitting, 1 g of FMC was added into a 1 L flask with 1,000 ml arsenic solution; after different time intervals (from 1 to 120 min), the samples were taken and tested. The experimental data were fitted with the pseudo-first-order kinetic, pseudo-second-order kinetic, and intra-particle diffusion model.

The pseudo-first-order was proposed by Lagergren and the equation is expressed as follows (Robati et al. 2016):

\[
\ln (q_e - q_t) = \ln q_e - K_1t
\]

The pseudo-second-order kinetic equation is shown as follows:

\[
\frac{t}{q_t} = \frac{1}{K_2q_m^2} + \frac{t}{q_e}
\]

The initial adsorption rate is given by (Dabrowski 2001):

\[
h = k_2q_e^2
\]

The mathematical equation of the intra-particle diffusion model is given by:

\[
q_t = kt^{1/2} + C
\]

where \( K_t \) (min \(^{-1}\)) and \( K_2 \) (g mg \(^{-1}\) min \(^{-1}\)) are the equilibrium rate constants. Pseudo-first-order kinetic suggests that physical interaction is the dominant step, while the pseudo-second-order kinetic suggests that the rate controlling step for the adsorption is a chemical interaction (Cheng et al. 2018; Hsini et al. 2021), and the number of activated sites, along with the amount of the activated arsenic ions present in the aqueous solution, all determine the adsorption kinetics (Mashhadi et al. 2016; Hsini et al. 2020a). The slope of the plots between \( q_t \) vs \( t^{1/2} \) is \( k \) and the intercept value is \( C \).

**Isotherm study**

For adsorption isotherm studies, 0.05 g of FMC was accurately added into a 100 ml flask with 50 ml arsenic solution, the initial concentrations ranged from 0.5 to 20 mg/L and the temperature was set at 25, 35, and 45 °C. The experimental data were fitted with the Langmuir isotherm, Freundlich isotherm, and thermodynamic equations. The Langmuir and Freundlich isotherms are two common isotherms, with the Langmuir isotherm based on a monolayer adsorption mechanism and the Freundlich isotherm based on the multilayer adsorption condition (Zhu et al. 2016). The linear forms of the two isotherms can be modeled as follows:

Langmuir isotherm equation: \( q_e = q_m \frac{k_L C_e}{1 + k_L C_e} \) (7)

Freundlich isotherm equation: \( q_e = k_F \cdot C_e^\alpha \) (8)

where \( K_L \) is the Langmuir constant (L/mg), \( q_{\text{max}} \) represents the theoretical adsorption capacity (mg/g). \( K_F \) is the Freundlich constant (mg/g). Also, the dimensionless factor \( R_L \) is defined by the equation (Tangde et al. 2017):

\[
R_L = \frac{1}{1 + K_L C_0}
\]

The \( R_L \) value represents whether the adsorption process is favorable or unfavorable under certain concentrations. If \( 0 < R_L < 1 \), the adsorption is favorable under this initial concentration, otherwise, it is unfavorable. If \( R_L = 0 \), the
adsorption is irreversible, and $R_L = 1$ indicates linear adsorption (Shao et al. 2019).

The thermodynamic equation is as follows:

$$
\Delta G^0 = -RT \ln \frac{q_e}{C_c}
$$

(10)

The $\Delta G^0$ is related to free energy change (kJ mol$^{-1}$). Where $T$ is the solution temperature (K), $R$ is the ideal gas constant (0.008514 kJ mol$^{-1}$ K$^{-1}$). The $\Delta H^0$ (standard enthalpy) (kJ mol$^{-1}$) and $\Delta S^0$ (standard entropy) (kJ mol$^{-1}$ K$^{-1}$) can be evaluated from the linearized van't Hoff equation (the intercept and the slope, respectively), which is given by:

$$
\Delta G^0 = \Delta H^0 - T \Delta S^0
$$

(11)

**Effect of adsorbent dosage**

For the effect of the adsorbent dosage on the arsenic adsorption, different dosages (0.5, 1, 2, 3, 5, and 10 g/L) were applied with 5 mg L$^{-1}$ initial arsenic concentration.

**Effect of pH**

To determine the effect of pH, different pH levels (1, 3, 5, 7, 9, 11, and 13) were adjusted for 5 mg L$^{-1}$ initial arsenic concentration. The pH$_{pzc}$ was the pH point of zero charge; that is, the pH condition in which the charge of the surface is zero. It was determined in this research by the potentiometric mass titration method (Koh et al. 2020). Briefly, 100 ml 0.01 M KNO$_3$ were added into a flask with 0.1 g FMC. The pH of the KNO$_3$ solution was adjusted to 2–10 by 0.1 M HCl and 0.1 M NaOH. The mixed solution was stirred for 2 h to reach equilibrium and the final pH was measured. The change of the pH values (initial pH-final pH) was designated as $\Delta$pH, which was plotted against initial pH, the point where the curve intersects the X-axis was the point of zero charge (Zhu et al. 2010).

**Application study**

To investigate the real application of FMC for the removal of arsenic, the effect of co-existing anions and recyclability was conducted. The effect of common co-existing anions such as Cl$^-$, F$^-$, PO$_4^{3-}$, SO$_4^{2-}$, HCO$_3^-$ were studied by adding 10 mg/L co-existing anions into 5 mg/L arsenic solution. Five cycles of regeneration and reuse were conducted using 10 g/L adsorbent dosage in 10 ppm arsenic solutions, after one cycle, the adsorbents were filtered and rinsed using 0.1 M NaOH for 30 min. The desorbed adsorbents were added with arsenic solutions again for the next cycle.

**Sediment remediation incubation**

The sediment remediation in this study was conducted according to the method described by Lin et al. (2019). Briefly, 5 cm height of dry arsenic-contaminated sediments were placed into a brown reagent bottle, then 0, 3, 5, and 10 g of FMC were introduced to the surface of the sediments. After that, deionized water was slowly added into the bottles to avoid disturbance until the water level reached the mouth of the bottle. To prevent the oxidation of the sediment, sodium sulfite was added to eliminate the dissolved oxygen. The bottles were kept in a thermostatic incubator with a temperature of 25 ºC and a shaking speed of 40 rpm. The four brown reagent bottles were referred to as SR-X, where X stands for the added mass of the FMC (X = 3, 5, 10). A total of 1 mL of water samples of the overlying water in different bottles were collected daily and of which the arsenic concentration, pH, and the DO were tested. After incubation, the water was discarded carefully to avoid any disturbance. The surface was first disposed to avoid the influence of the FMC, then the surface layer of the sediments was collected for further speciation analysis.

**Statistical analysis**

All the measurements were triplicated, and the mean values were present in this study. The standard deviations of all data in batch experiments were below 8%. Statistical analysis was performed by using GraphPad Prism 8.

**RESULTS AND DISCUSSION**

**Characterization of FMC**

From the SEM images of the ceramsite and FMC, the natural ceramsite shows a smooth surface while the FMC has a more rugged surface, which may be caused by the attachment of the iron oxide to the surface (Figure 1). The SEM result confirms that the Fe modification onto ceramsite was successful. The BET surface of the ceramsite and the FMC was 0.55 and 1.33 m$^2$/g, which was in agreement with the SEM results that the added iron on the surface of the ceramsite significantly improves the surface area. The XRD patterns of the
ceramsite and FMC are shown in Figure S1 in Supplementary Information, the crystalline species were identified using Highscore Plus, which showed the ceramsite was composed of 76% silicon oxide, 13% calcium carbonate, and 11% aluminum oxide. After modification, 12% iron oxide was detected, confirming the successful Fe loading. Figure 2 shows FTIR patterns of ceramsite and FMC. The adsorption band at 1,425 cm\(^{-1}\) in ceramsite was not observed in FMC, which could be due to the modification with Fe (Lin et al. 2019).

**Adsorption kinetics**

The adsorption of the arsenic onto the FMC largely depends on the reaction time. Less adsorption time favors the feasibility of the adsorbents (Wang et al. 2016). The adsorption of arsenic onto FMC and ceramsite is depicted in Figure 3; it is observed that the FMC showed better arsenic adsorption capacity while ceramsite did not show an effective adsorption curve. To evaluate the adsorption rate in the adsorption progress, adsorption kinetics were applied by Equation (3). The calculated parameters were given in Table 1. As from the table, the data plot poorly fitted the pseudo-first-order model with lower regression coefficients except for the 1 mgAs L\(^{-1}\) initial solution. Moreover, the calculated theoretical adsorption capacities from the pseudo-first-order were different from the experimental values; therefore, the pseudo-first-order can not be used to explain the adsorption behavior of arsenic onto FMC and ceramsite. On the contrary, as from Table 1, the pseudo-second-order dominated the adsorption progress with high values of the regression coefficients. For FMC, the experimental adsorption capacities under different initial arsenic concentrations were close to the calculated values. The rate constant \(K_2\) of the pseudo-second-order kinetic decreased with higher initial arsenic concentration, indicating that the adsorption behavior was more rapid in low concentration arsenic solutions.
which were beneficial to treat low-contaminated arsenic wastewater/water. The initial adsorption rate increased with higher initial arsenic concentrations, which may be due to more arsenic ions being present in the aqueous solutions. For ceramsite, the adsorption fitted the pseudo-second-order well; however, concerning its low adsorption capacity, the application of ceramsite as an arsenic adsorbent was not feasible. Thus, only FMC was further investigated.

The fitting results of intra-particle diffusion model are shown in Figure S2 (e-f). The three fitted lines indicated that the whole time range could not be fitted only by one line, which implied that the adsorption of arsenic onto FMC could be controlled by three processes: surface adsorption, intra-particle diffusion, and final equilibrium (Zhou et al. 2014). With higher initial arsenic concentration, the slope of the first line increased, showing that a higher initial concentration could accelerate the surface adsorption. Meanwhile, the slopes of three lines follow the order of first > second > third, suggesting a slower adsorption rate occurred in intra-particle diffusion and final equilibrium (Yang et al. 2018). Moreover, the intra-particle diffusion was not the only rate-limiting step due to the fitted line not passing the origin (Khatri et al. 2020).

Adsorption isotherm and thermodynamic

The fitting of the experimental data with different isotherms can improve the understanding of adsorption behavior and favor practical applications (Chaudhry et al. 2017). In this study, the thermodynamic parameters in arsenic adsorption were calculated to ascertain the nature and feasibility of the adsorption process (Kumar & Jiang 2016).

### Langmuir and Freundlich isotherms

To optimize the adsorption process for arsenic removal, it is vital to analyze the adsorption behavior using modeling of different adsorption isotherms (Figure S3). The results are given in Table 2, which shows that the data fitted better with the Freundlich isotherm, especially under high temperature, indicating that the adsorption of the arsenic onto the adsorbent was a multilayer process. The theoretical maximum adsorption capacity inferred from Langmuir under 25 °C is 10.63 mg/g, which was the common adsorption capacity compared with other adsorbents (Table 3). However, the raw materials in this research are hazardous wastes, which lowered the cost of FMC, thus the adsorbent in this study exhibited a challenging adsorption capacity and promising future application. The estimated adsorption capacities increased with the increasing temperatures, which demonstrated that the adsorption of arsenic onto ceramsite adsorbent was an endothermic process; however, after 35 °C, the temperature had slight improvement on the adsorption capacity. The RL values are depicted in Table 4, all values were less than unity, suggesting that the adsorption was favorable under each initial arsenic concentration tested in this study.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>C0 (mg/L)</th>
<th>qe (mg/g)</th>
<th>Pseudo-first-order constant</th>
<th>Pseudo-second-order constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>FMC</td>
<td>1</td>
<td>0.55</td>
<td>0.34 0.06 0.9870</td>
<td>0.57 0.48 0.16 0.9997</td>
</tr>
<tr>
<td>Ceramsite</td>
<td>0.09</td>
<td>0.04</td>
<td>0.04 0.8217</td>
<td>0.25 3.53 0.22 0.9994</td>
</tr>
<tr>
<td>FMC</td>
<td>2</td>
<td>0.96</td>
<td>0.56 0.04 0.9678</td>
<td>0.99 0.36 0.35 0.9998</td>
</tr>
<tr>
<td>Ceramsite</td>
<td>0.18</td>
<td>0.10</td>
<td>0.04 0.9146</td>
<td>0.18 1.33 0.04 0.9995</td>
</tr>
<tr>
<td>FMC</td>
<td>5</td>
<td>1.99</td>
<td>0.88 0.04 0.8368</td>
<td>2.02 0.17 0.69 0.9993</td>
</tr>
<tr>
<td>Ceramsite</td>
<td>0.77</td>
<td>0.17</td>
<td>0.04 0.9273</td>
<td>0.33 0.75 0.08 0.9989</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>qmax (mg/g)</th>
<th>KL (L/mg)</th>
<th>R²</th>
<th>q0 (mg/g)</th>
<th>k2 (g/mg-min)</th>
<th>h (mg/g-min)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>10.63</td>
<td>2.22 × 10⁻¹</td>
<td>0.9791</td>
<td>1.25</td>
<td>1.43</td>
<td>1.35</td>
<td>0.9782</td>
</tr>
<tr>
<td>35</td>
<td>16.45</td>
<td>1.57 × 10⁻¹</td>
<td>0.9518</td>
<td>1.35</td>
<td>1.32</td>
<td>1.35</td>
<td>0.9964</td>
</tr>
<tr>
<td>45</td>
<td>16.81</td>
<td>1.59 × 10⁻¹</td>
<td>0.9150</td>
<td>1.35</td>
<td>1.35</td>
<td>1.35</td>
<td>0.9905</td>
</tr>
</tbody>
</table>
Thermodynamics of adsorption

The adsorption data under different temperatures were used to determine the thermodynamic parameters such as free energy change ($\Delta G^0$), standard enthalpy ($\Delta H^0$), and standard entropy ($\Delta S^0$) (Liu et al. 2018; Naga Babu et al. 2019). The calculated thermodynamic parameters $\Delta G^0$ were $-0.99$, $-1.57$, and $-1.84$ kJ mol$^{-1}$ under 298.15, 308.15, and 318.15 K, respectively. Additionally, the $\Delta H^0$ and $\Delta S^0$ were $11.52$ kJ mol$^{-1}$ and $0.042$ kJ mol$^{-1}$ K$^{-1}$, respectively. The negative values of Gibbs free energy implied that the adsorption behavior of arsenic onto adsorbent was spontaneous (Tangde et al. 2017), whereas the positive value of $\Delta H^0$ indicated that the endothermic nature of the arsenic adsorption process was in accordance with the isotherm results (Liu et al. 2015). Moreover, the randomness would increase at the solid-liquid interface of the ceramsite adsorbent due to the positive $\Delta S^0$ (Yang et al. 2018).

Influence factors

Effect of adsorbent dosage

The effect of dosage is depicted in Figure 4; it is observed that the arsenic removal rate increased from 22.08% to 91.07% with increasing adsorbent dosage (Pholosi et al. 2019); this can be attributed to increased active sites and greater surface area present in the solutions (Rahman et al. 2020). Meanwhile, the adsorption capacity ($q_e$, mg/g) decreased with increased adsorbent dosage. It drops from 8.32 to $1.82$ mg/g. This is because the arsenic concentration in the solution was constant (20 mg/L), while by increasing the dosage, most of the arsenic can be adsorbed and a lot of the active sites remained unsaturated, leading to a decrease in estimated capacity. Besides, the aggregation among the adsorbent molecules increased via intramolecular interaction, which resulted in lower capacities (Lingamdinne et al. 2016).

Effect of pH

The pH of the aqueous solution was the most dominant factor influencing the adsorption behavior because the surface charge changes under different pH conditions.
(Lingamdinne et al. 2016). Also, the pH change in the solution will change the species of the arsenic (Rahman et al. 2020). There are four different forms of arsenic (V) present in aqueous solution in different pH condition: H$_3$AsO$_4$ (pH < 2.2), H$_2$AsO$_4$ (2.2 < pH < 6.98), HAsO$_4^{2-}$ (6.98 < pH < 11.5), and AsO$_4^{3-}$ (11.5 < pH) (Rahman et al. 2020).

The effect of the pH on the arsenic adsorption behavior, along with the determination of the point of zero charge of pH was studied (Figure 5). The point of zero charge was where the blue curve intersected the line ($\Delta$ pH = 0) at pH = 6.4. At this point, the surface will not acquire any H$^+$ or OH$^-$ ions from solution. When the solution pH was lower than pH$_{pzc}$, the surface of the ceramsite adsorbent will be positively charged, which will accelerate the arsenic adsorption. However, if the solution pH > pH$_{pzc}$, the surface will be charged negatively and influence the adsorption of arsenic adversely (Dong et al. 2019). As from Figure 5, the amount of the adsorbed arsenic increased from 2.275 to 2.995 mg/g from pH = 1 to pH = 7; this revealed the FMC can be used as a functional adsorbent under low pH or neutralized conditions. The forms of the arsenic under this situation were mostly H$_3$AsO$_4$ and H$_2$AsO$_4$ while the surface of the adsorbent was charged with protons, the electrostatic attraction between the positive-charged surface and the negative forms of arsenic promoted the amount of arsenic adsorbed (Koh et al. 2020). More importantly, low pH conditions will favor the hydrolysis of the hydroxyl (Fe-OH), which will participate in arsenic adsorption by ligand exchange. However, on the contrary, with the pH increases above 7, the predominant form of the arsenic turned into more negatively charged HAsO$_4^{2-}$ and AsO$_4^{3-}$ while the surface of the adsorbent was also negatively charged after a pH of 6.4; this led to a greater repulsion between the adsorbate and adsorbent, which deteriorated the arsenic adsorption behavior. The adsorption capacity decreased to 1.446 mg/g at a pH of 13 with 51.72% decrease in adsorption capacity compared with at a pH of 7. Nevertheless, the design condition for FMC is natural water bodies, which normally lie in pH range of 6–8. Therefore, the adsorbent had a great adsorption performance under the design conditions, which favored its future application in natural water bodies.

**Effect of co-existing anions**

In real cases, contaminated water contains not only arsenate but also other co-existing anions, which will compete for the active sites and interfere with the arsenate adsorption. Interfering anions that normally exist in natural water such as chloride, fluorine, phosphate, sulfate, and bicarbonate were studied and are presented in Figure 6. From the diagram, when the concentration of the co-existing anions was 20 mg/L, the chloride and fluorine were found to have a negligible impact on the arsenic adsorption behavior due to the space charge effect and smaller molecular size (Xia et al. 2020). Compared with the small monovalent anions, the bicarbonate had a relatively stronger adverse influence, which may owe to the large bulk of the anion. Moreover, the divalent anions present in the solutions had a greater influence on arsenic adsorption, especially phosphate. The phosphate shared similar chemical structures with arsenate while both of them formed inner-sphere complexes with the OH$^-$ group of the iron oxides (Nikić et al. 2019; Hsini et al. 2020b). Another previous study reported that the phosphate and the arsenate were all tetrahedral anions. When both of them existed in the solution, phosphate will compete for the active sites on the adsorbent, resulting in a pronounced adverse effect (Sigdel et al. 2019).
As expected, the inhibition of the co-existing anions will become greater with a higher initial concentration of the anions. But only under 50 mg/L of phosphate and sulfate presence will significantly deteriorate the arsenic adsorption (lower than 50%).

Regeneration

The regeneration of the adsorbent was vital for future practical applications and economics. Five cycles of regeneration were investigated using the alkaline solution as a desorbing agent (Sigdel et al. 2016). The initial arsenic concentration was selected as 10 mg/L, which is the highest concentration in normal arsenic-polluted water bodies. Figure 7 presents the regeneration cycles of the adsorbent. It was noteworthy that a significant amount of the arsenic was adsorbed from the solution even after 3 cycles. The regenerated adsorbent achieved 80% adsorption capacity compared to the pristine adsorbent. Beyond three cycles, the adsorption capacity of the regenerated adsorbent decreased below 60%, showing the desorption of the adsorbent after 3 cycles was not sufficient. Therefore, it can be concluded that the iron-loaded ceramsite adsorbent can be used at least 4 times without replacing the adsorbent, and thus offers a cheap adsorbent for water bodies with low concentrations of arsenic. In this study, the desorbing agent was 0.1 M NaOH according to other researches (Sima et al. 2018), but it was still worthwhile to try other different agents to investigate the recyclability of the adsorbent.

In-situ remediation

To better explore the application of the FMC, the adsorbents were introduced to the sediment surface to control the arsenic release from the sediments. The arsenic concentration of overlying water with simulating time is given in Figure 8. It was observed that the arsenic concentrations decreased predominantly with more introduced FMC, demonstrating that the addition of the FMC can significantly adsorb the arsenic released from the sediment. According to the calculation, the controlling efficiencies of arsenic release from sediment by SR-3, SR-5, and SR-10 were found to be 28.74%, 42.63%, and 85.07% at day 10 and 30.95%, 54.48%, and 86.51% at day 26. With the incubation continued, the arsenic concentration of the overlying water rose exponentially (release period: day 1–10) followed by a relatively stable plateau (stable period: day 11–26), which is quite different from other researches (Liu et al. 2017; Zhan et al. 2019). The possible reason is the difference between the experiment conditions; the incubation bottles were placed on a thermostatic incubator with a speed of 40 rpm in this study, which will promote its arsenic release. Moreover, the unexpectedly good result from SR-10 could be partially ascribed to the FMC capping effect: when 10 g of FMC was introduced to the sediment surface, compared to 3 and 5 g, an integrated adsorbent layer was formed at the sediment surface, which will block the arsenic from leaching. The average arsenic concentrations of the overlying water under release period and stable period are given in Figure S4. It is evident that more addition of FMC will dramatically reduced the arsenic released from sediment. The addition of the FMC significantly adsorbed at least 33.89% arsenic present in overlying water during the sediment initial release period (SR-3). Furthermore, the released...
arsenic from SR-10 was significantly lower than SR-3 and SR-5, which should be ascribed to the capping effect.

Except for the adsorption and capping effect, the introduction of FMC changed the arsenic fractions in the surface sediments. As suggested by previous works (Shiowatana et al. 2001b), total arsenic concentration can not be indicative of the real arsenic toxicity. To be specific, the arsenic is present in five bonding fractions in solid phases, from easily leachable to strongly fixed. The water-soluble species (FS1) is the most labile fraction of all five As species that will release to the overlying water readily (Garau et al. 2011). From Figure 9, compared to the total arsenic concentration, the water-soluble arsenic concentration was relatively low and decreased with the addition of FMC. The water-soluble species concentration of SR-10 significantly decreased by 51.14% compared to the control group. The FS2, FS3, and FS4 are related to surface-adsorbed, Fe/Al associated, and acid-extractable species. The surface-adsorbed species can be considered as exchangeable arsenic, which can be extracted by anion exchange; the addition of FMC did not change this arsenic fraction, indicating that the anion exchange was not involved in the FMC remediation. Fe/Al associated and acid-extractable species are related to the arsenic adsorbed at surfaces of amorphous and Fe/Al oxides or oxy-hydroxides. In this study, the addition of FMC did not change the total amount of FS3 and FS4 significantly. This results could be due to a stable ability to retain arsenic by Fe/Al and other oxy-hydroxides inside the pristine sediment.

Finally, an increase in residual species (FS5) was observed, indicating the arsenic species were strongly retained by the sediment. A significant difference was observed in SR-10, compared with the control group; the residual concentration increased by 66.35% (from 10.81 mg/kg to 17.99 mg/kg). The proportion of residual arsenic was increased from 21.47% (control group) to 36.77% (SR-10), indicating a promising arsenic species remediation was performed.

CONCLUSION

The CRS was used for the fabrication of the ceramsite; it showed a negligible arsenic leaching (4 μg/L). The characterization of the FMC confirmed that the ceramsite was successfully modified by Fe, which significantly improved its arsenic adsorption capacity. Through batch experiments, the nature and capability of the FMC were fully studied. The adsorption was governed by chemisorption, its adsorption process was spontaneous and endothermic. The adsorption capacity inferred from the Langmuir isotherm was 10.63 mg/g under 25 °C. The adsorption capacity showed stable values under acidic and neutral conditions while decreasing with increasing pH under alkaline conditions. The presence of different anions of 20 mg/L has no significant adverse effect on the arsenic adsorption; meanwhile, the adsorbent can be easily regenerated without greatly deteriorating its adsorption capacity. In remediation trials, the addition of FMC reduced the arsenic concentration of the overlying water by at least 53.89%; meanwhile, the SR-10 group showed a significant potential, which transferred the arsenic species at the surface layer from an active state to a stable state, resulting in less arsenic leaching from the surface layer. In summary, FMC showed high arsenic adsorption capacity and can act as a facile and cost-effective adsorbent for adsorption and sediment amendment in a future field test.

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DECLARATION OF INTEREST STATEMENT

The authors declare that there is no conflict of interest regarding the publication of this paper.
DATA AVAILABILITY STATEMENT

Data cannot be made publicly available; readers should contact the corresponding author for details.

REFERENCES


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