Chemical Engineering Journal 198-199 (2012) 440–448

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Arsenate adsorption from water using a novel fabricated copper ferrite

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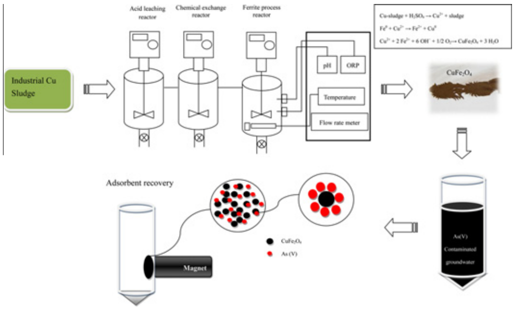
HIGHLIGHTS

- A novel technology for fabricating $CuFe_2O_4$ was developed from industrial Cu sludge.
- The fabricated $CuFe_2O_4$ was effective in removing As(V) from contaminated water.
- The adsorbent can be rapidly recovered by a magnet because of its paramagnetism.
- As *K*-edge XANES showed the adsorbed As(V) was not reduced to more toxic As(III).
- Desorption rate is in an order of $H_3PO_4 > Na_3PO_4 > H_2SO_4 > Na_2SO_4 > HCl > HNO_3$.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 15 March 2012
Received in revised form 31 May 2012
Accepted 3 June 2012
Available online 12 June 2012

Keywords:
Adsorption
Arsenate
Industrial sludge
Copper ferrite
As *K*-edge XANES

ABSTRACT

A novel fabricated copper ferrite was investigated for its As(V) removal in this study. The adsorption of As(V) by this recycled copper ferrite exhibited an L-shaped nonlinear isotherm, suggesting limited binding sites on the adsorbent surface. The As *K*-edge XANES indicated that the adsorbed As(V) on copper ferrite was not reduced to more toxic As(III) by Fe^{2+} in the structure. The maximum As adsorption capacity of the copper ferrite was 45.66 mg g^{-1} at pH 3.7 and decreased with pH due to enhanced electrostatic repulsion between As(V) and the adsorbent surface. Desorption of As(V) using six different acid and salt solutions revealed that the desorption rate decreased in the order of $H_3PO_4 > Na_3PO_4 > H_2SO_4 > Na_2SO_4 > HCl > HNO_3$. These results suggest that the recycled copper ferrite without surface modification is an effective adsorbent for removing As(V) from water, confirmed by effective removal of As(V) from contaminated groundwater. Furthermore, the novel fabricated copper ferrite can be used to recover rapidly in 20 s using a magnet. The information obtained in this work shows great potential for developing a cost-effective adsorbent for immobilization of arsenate using the recycled copper ferrite.

1. Introduction

Arsenic (As) contamination is threatening water supplies in many developing countries [1–3]. The anthropogenic sources of As include the waste and wastewater of various industries utilizing As and the materials used in agricultural production, such as herbicide and wood preservative [1,4]. In addition to man-made pollutants, elevated levels of As in surface waters and groundwater also occur naturally in certain areas of the world as a result of leaching from As-bearing minerals [2,3]. Because As is highly carcinogenic after long-term or high-dose exposure, the occurrence of As in water supplies can pose a deleterious impact on public health. Therefore, developing techniques to remove As from contaminated water is an important task for healthy living in a society.

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1385-8947/$ - see front matter © 2012 Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.cej.2012.06.006

The common treatment techniques for removing As from contaminated waters include precipitation [5–7], oxidation [8–10], coagulation [11–14], adsorption [15–18], ion-exchange [19–21], and membrane filtration [22–26]. The adsorption method is considered more advantageous over others because of its removal effectiveness, treatment cost, and ease in equipment handling. Commercial adsorbents such as activated carbons are effective for arsenic removal from water [27–29]. However, the high cost makes it less competition in market. Mohan and Pittman [1] has summarized some interesting literatures of low-cost adsorbents for arsenic removal. In other words, adsorbents were regarded as low-cost if they only need less pre-treatment procedures, or were either waste materials or by-products from the other industrial factories [30–33].

This study demonstrates the arsenate removal by using copper ferrite, which is recycled from the sludge in printed circuit board (PCB) industry. The copper ferrite, a magnetic Cu–Fe oxide, contains Cu^{2+} and Fe^{3+} in the spinel structure. It was reported that synthesized copper ferrite was effective for arsenic removal from solution due to Cu^{2+} and Fe^{3+} have strong affinity toward inorganic arsenic [34]. If the copper ferrite can be obtained or recycled from industrial sludge, then the adsorbent price could be decreased dramatically. Our earlier investigation has successfully recycled copper powder from PCB sludge by combination of acid leaching and chemical exchange [35]. After these two combinations of technologies, ferrite process has been conducted not only to make sure the supernatant but also the sludge can meet the environmental rules. The sludge generated from ferrite process hence is regarded as a general industrial waste due to its stability in environment. If there are no other resourced uses for the sludge, it could be disposed to the sanitary landfills.

The authors attempt to resource this sludge as an adsorbent and test its adsorption feasibility of arsenate in solutions. The adsorbent characterization including particle size, crystalline phases, surface area, point of zero charge (pH_{pzc}), and saturation magnetization were studied systematically. Furthermore, As *K*-edge XANES spectra were used to understand the transformation of different As phases on copper ferrite. The information obtained in this work shows a great potential for developing a cost-effective adsorbent for immobilization of arsenate using recycled copper ferrite.

2. Material and methods

2.1. Recycled copper ferrite

A green low-cost adsorbent, copper ferrite, was manufactured from PCB sludge by combination of acid leaching, chemical exchange, and ferrite process. Literature [35] has reported detailed procedure for preparation of copper powder or copper ferrite. Briefly, acid leaching was conducted with 500 g of the industrial sludge as 10 L diluted sulfuric acid was added for extracting copper from solid to solution. Fe powder was used as sacrificed metal to substitute Cu^{2+} by chemical exchange in liquid. To ensure the supernatant qualify fulfill the effluent standards, ferrite process was performed after chemical exchange. A green low-cost adsorbent, copper ferrite, was manufactured after the ferrite process. The main corresponding reaction of acid leaching, chemical exchange, and ferrite process is described as Eqs. (1)–(3), respectively.

$$\text{Cu-sludge} + H_2SO_4 \rightarrow Cu^{2+} + \text{sludge} \quad (1)$$

$$Fe^0 + Cu^{2+} \rightarrow Fe^{2+} + Cu^0 \quad (2)$$

$$Cu^{2+} + 2Fe^{2+} + 6OH^- + 1/2O_2 \rightarrow CuFe_2O_4 + 3H_2O \quad (3)$$

If one wants to obtain a large number of $CuFe_2O_4$, Eq. (2) may not be able to perform in this combination system. In other words, the $CuFe_2O_4$ could be manufactured by using acid leaching and then followed by ferrite process.

The manufactured green low-cost adsorbent was collected using a magnetic separation method by taking advantage of its magnetism. The copper ferrite product was then washed with de-ionized water several times until pH of the solution reached near 7. The solid was then dried at 50 °C for 24 h in an oven and stored for further tests.

2.2. Characterization of copper ferrite

The XRD spectrum is used for determining the crystallographic identity of the produced material and phase purity. The recycled copper ferrite was characterized using XRD (D8 Advance, Bruker, Germany) with a graphite monochromatic copper radiation over the 2θ range of 10–80°. The BET surface area was determined using an ASAP 2010 analyzer (Micromeritics, USA) and N_2 adsorption at 77 K. The surface morphology and particle size were examined by scanning electron microscopy (JSM-6330, Japan). The saturation magnetization of the recycled copper ferrite was measured using a Superconducting Quantum Interference Device (MPMS-XL7, Quantum Design, USA) at 27 °C.

The isoelectric point, also referred as PZC (point of zero charge), is the pH at which the particles in suspension have net charge of zero and no mobility in the electric field. The determination of PZC in this study was carried out according to the procedures described by Smiciklas et al. [36]. Briefly, aliquots of 0.1 M KNO_3 were prepared in a series of flasks and the pHs of the aliquots were adjusted to values ranging from 2 to 12 using 0.1 M KOH or HCl solution. The ferrite samples were then added into each of the flasks to have a solid-to-solution ratio of 1:200 (w/w). The suspensions were allowed to equilibrate for 24 h in a shaker thermostated at 27 ± 1 °C. Then, the suspensions were magnetically separated from the aqueous phase by using a magnet with 4000 Gauss and the pH values (pH_f) of the residual solutions were measured using pH meter. For each sample, the values of the final pH (pH_f) were plotted against the values of the corresponding initial pH (pH_i). The experimental pH_f at the stable values was defined as PZC for the sample.

2.3. As(V) adsorption

Stock solutions of As(V) ($1000\ mg\ L^{-1}$) were prepared by dissolving sodium arsenate ($NaH_2AsO_4{\cdot}7H_2O$) (Merck, Darmstadt, Germany) in de-ionized water. Working solutions for experiments were freshly prepared from the stock solution. All experiments were performed in triplicate in 15 mL centrifuge tubes under 30 rpm shaking at 27 ± 1 °C. An initial As(V) concentration of $10\ mg\ L^{-1}$ and 10 mL As(V) solution was used for every experiment unless specially stated.

As(V) adsorption experiments were conducted using a batch method. To investigate the effect of pH on As(V) adsorption of copper ferrite, the pH of As(V) solutions were controlled at 2.3 ± 0.1, 3.7 ± 0.1, 5.4 ± 0.1, 7.1 ± 0.1, 8.9 ± 0.1, 9.8 ± 0.1, 11.2 ± 0.1, 12.4 ± 0.1 by adding NaOH or HNO_3 solution under the conditions of As(V) concentration $80\ mg\ L^{-1}$ and copper ferrite 0.02 g. Different adsorbent dosages (0.0025 g, 0.005 g, 0.01 g, 0.02 g) were used to determine the required dosage that fulfills the regulation concentration of $10\ \mu g\ L^{-1}$ under the conditions of pH 3.7 and initial As(V) concentration of $100\ mg\ L^{-1}$. The As(V) adsorption isotherms of copper ferrite were also recorded in batch experiments to estimate arsenic uptake under the conditions of $CuFe_2O_4 = 0.001$ g and pH 3.7, 7.1, and 11.2.

The solid and liquid phases were magnetically separated using a magnet with 4000 Gauss. The As concentrations in the filtrate were determined by ICP-MS (Element XR, Thermal Scientific, Germany). The adsorbed amount of As(V) on the copper ferrite was determined using the differences between the initial and equilibrium As concentrations. The detection limit of As, Fe, and Cu is 2.3 μg L^{-1}, 5.6 μg L^{-1} and 4.1 μg L^{-1}, respectively. The relative standard deviation (RSD) of three replicate analyses was normally lower than 3%.

2.4. As K-edge XANES analysis

The As *K*-edge X-ray absorption near edge structure (XANES) spectra were recorded with a Beamline 01C1 at the National Synchrotron Radiation Research Center (NSRRC) in fluorescent mode for powdered samples. Energy calibration was conducted using the first inflection point of the As *K*-edge (11867.0 eV) absorption spectra of As metal foil. The scans for each sample were averaged, followed by background removal and normalization. The XANES spectra of As metal foil As(0), As_2O_3 As(III), and H_3AsO_4 As(V) compounds were also obtained to serve as the reference standards.

2.5. As(V) desorption

Desorption experiments were conducted using six different 0.1 M acid and salt solutions (HNO_3, HCl, H_2SO_4, Na_2SO_4, H_3PO_4, Na_3PO_4). Copper ferrite was firstly reacted with 10 mg L^{-1} As(V) solution at pH 3.7. Subsequently, the copper ferrite samples were washed with de-ionized water several times to remove excessive salts and the acid or salt solution was added into the samples to initiate the desorption process. The desorption experiments were conducted under the conditions of $CuFe_2O_4$ dosage 0.05 g, desorption reagent 10 mL, desorption time 30 min. The solid/solution ratio (W/V) used here was 5 g L^{-1}. The initial working pH for 0.1 M HNO_3, 0.1 M HCl, 0.1 M H_2SO_4, 0.1 M H_3PO_4, 0.1 M Na_3PO_4, and 0.1 M Na_2SO_4 was 1.47, 1.45, 1.41, 1.69, 11.97, and 10.87, respectively. The suspensions were shaken for 30 min and the copper ferrite solids were then separated from the solutions using a magnet. The desorption efficiency was calculated from the amount of As released into the solutions.

3. Results and discussion

3.1. Characterization of adsorbent

Fig. 1a displays SEM of the recycled copper ferrite, showing that the primary particle size ranged from 20 to 120 nm. The XRD pattern of this material showed diffraction peaks at *d*-spacings of 4.790, 2.960, 2.517, 2.100, 1.613, 1.479, 1.272, 1.087, and 0.964 Å (Fig. 1b), which matched well with $CuFe_2O_4$ (JCPDS File Number 00-025-0283). No other crystalline phases were detected in the XRD pattern. The BET surface area, pore volume, and average pore diameter of the adsorbent were determined to be 48.3 m^2 g^{-1}, 0.08 cm^3 g^{-1}, and 13.57 Å respectively. The point of zero charge (PZC) of the recycled copper ferrite was around 7.3, determined based on procedures described in Smiciklas et al. [36]. This is consistent with the value measured by Nasrallah et al. in 2011 [37].

The saturation magnetization of recycled copper ferrite was determined to be 62.52 emu g^{-1} (Fig. 2). No remnant was detected in the sample, confirming that this recycled copper ferrite was superparamagnetic. In the experiments, this magnetic nano-particle could be collected using a magnet within 20 s. When the external magnetic field was removed, the material could be well re-dispersed in the solution by shaking.

3.2. Effect of pH on As(V) adsorption

The pH is one of the most critical factors controlling the adsorption of adsorbate onto adsorbent. The As(V) adsorption kinetics on copper ferrite at pHs ranging from 2.3 to 12.4 are shown in Fig. 3. The amount of As(V) removed increased rapidly initially during the first 60 min. When the pHs was lower than 7, the As(V) removal reached close to 100% in 300 min, indicating a fast and complete removal of As(V) at these pHs. An increase in pH resulted in decrease in As(V) adsorption rate and a substantial reduction occurred at pH > 10. At pH 11.2 and 12.4, the As(V) removal was 54.02% and 15.65%, respectively, even after 1200 min. Thus, the recycled copper ferrite was more effective in removing As(V) at low pH.

The effect of pH on As(V) adsorption arose apparently from the charge properties of both As(V) and copper ferrite. Depending on the pH value in solution, arsenate ions existed as different ionic species [38,39]. On the other hand, the surface of adsorbent is subject to protonation/deprotonation, depending on the solution pH. As indicated by PZC (i.e. 7.3), the surface of copper ferrite is positively charged at pH < 7.3, which is beneficial for adsorbing the anionic As(V) species. This explains the high As uptake of the recycled copper ferrite in acidic conditions. An increase in pH resulted in buildup of negative charges on both adsorbent and adsorbate, leading to an enhanced electric repulsion between them. Consequently, dramatic reduction in As(V) adsorption was observed at high pH. Similar results were also reported by Zhang [40] and Yean [41].

As indicated in Fig. 3, the adsorption equilibrium was established within 300 min under selected conditions. The 300-min agitation time was therefore chosen for obtaining adsorption isotherms. Fig. 4 demonstrates the As(V) adsorption isotherms of copper ferrite at 27 °C and pH 3.7, 7.1 and 11.2. All the isotherms were L-shaped, suggesting the reaction is via surface adsorption with limited sites on copper ferrite surface available for As(V). As more sites were occupied by As(V), the copper ferrite surface became increasingly difficult for As(V) adsorption. With these characteristics, the adsorption isotherms were analyzed by the Freundlich and Langmuir models. Detailed parameters of the adsorption isotherm models for As on copper ferrite were summarized in Table 1 and the As(V) adsorption capacities were determined to be 45.66, 36.63 and 15.06 mg g^{-1} at pH 3.7, pH 7.1, and pH 11.2, respectively.

Table 2 presents As adsorption by recycled $CuFe_2O_4$ and other adsorbents. Experimental conditions in other studies were similar to the present work. Even though some experimental conditions, such as solution, adsorbent ratio and amount of adsorbent used varied largely in Table 2, the data show that As adsorption was favorable in all the cited studies [40,42–47]. From the table, it is apparent that recycled $CuFe_2O_4$ are very useful adsorbent for As(V) uptake from aqueous solution.

After As(V) is adsorbed on the surface, the Fe^{2+} sites in the copper ferrite structure may potentially reduce As(V) to As(III), the latter one is more toxic and highly mobile in the environment [38]. Especially, the reduction of As(V) occurs more likely at lower pH because decreasing pH can result in an increase in redox potential of the As(V)/As(III) couple. To investigate possibility of this unfavorable As(V) reduction on the copper ferrite surface, the oxidation state of As adsorbed at pH 3.7 was determined. Fig. 5 displays the As *K*-edge XANES spectra of As(V) adsorbed on the copper ferrite surface and the reference samples, As metal foil As(0), As_2O_3 As(III), and H_3AsO_4 As(V). The XANES spectrum of As(0), As(III) had an absorption edge at 11869.5 eV, 11871.0 eV, respectively, while As(V) was at 11874.5 eV. For the copper ferrite sample containing 3.6 mg g^{-1} As, the absorption edges all occurred near 11874.3 eV. Because we saw no apparent down-shift of the edge in the XANES

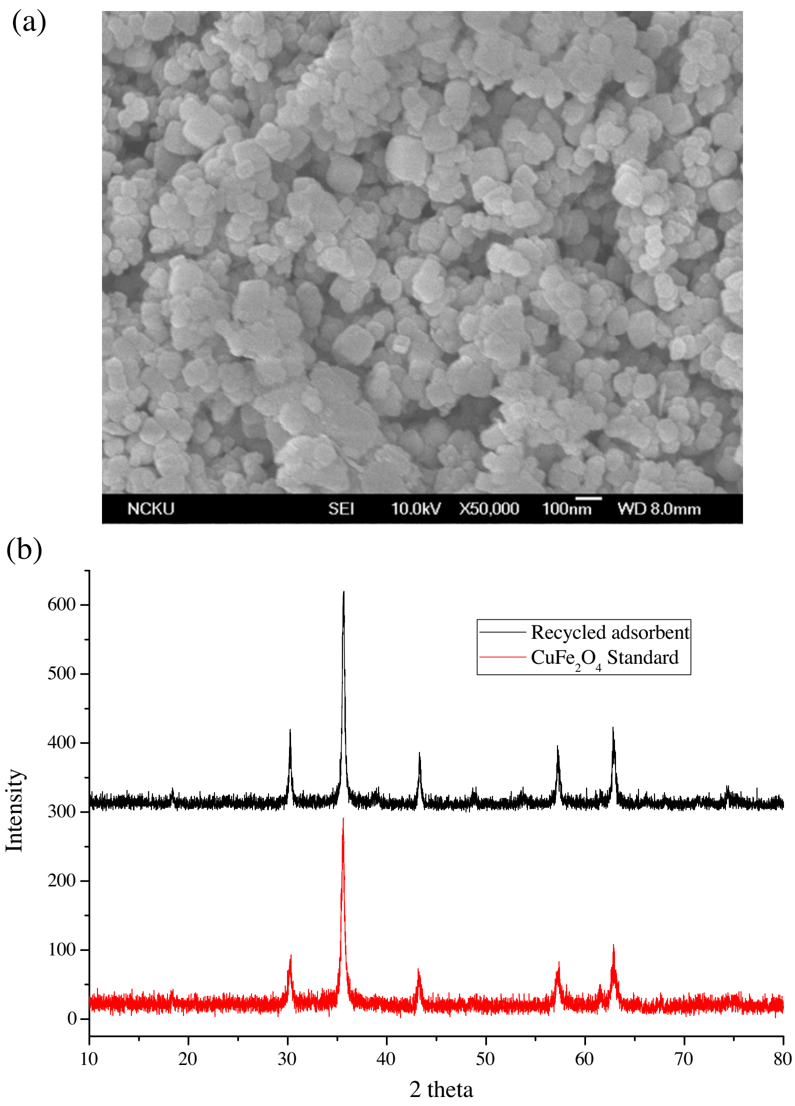

Fig. 1. (a) Scanning electron micrograph (SEM) and (b) X-ray diffraction pattern of the recycled copper ferrite.

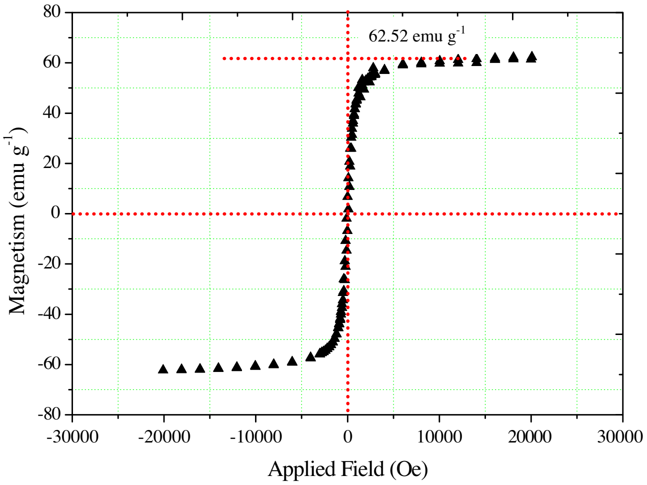

Fig. 2. Magnetization curve of the recycled copper ferrite as a function of magnetic field applied.

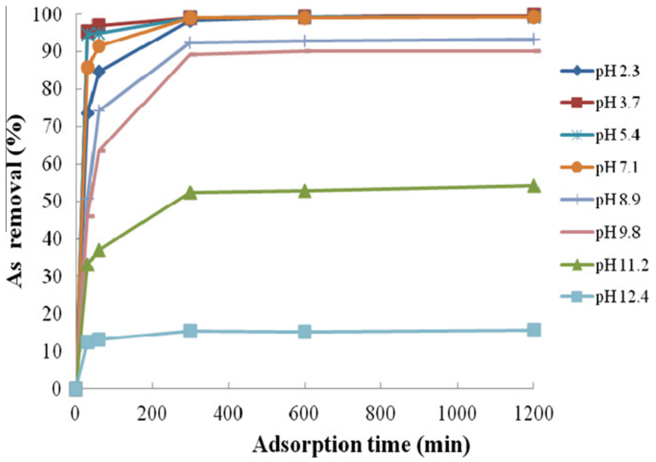

Fig. 3. Effect of pH on As(V) adsorption of the copper ferrite as a function of time at 27 °. Conditions: 80 mg L^{-1} initial As(V) concentration and 0.02 g copper ferrite.

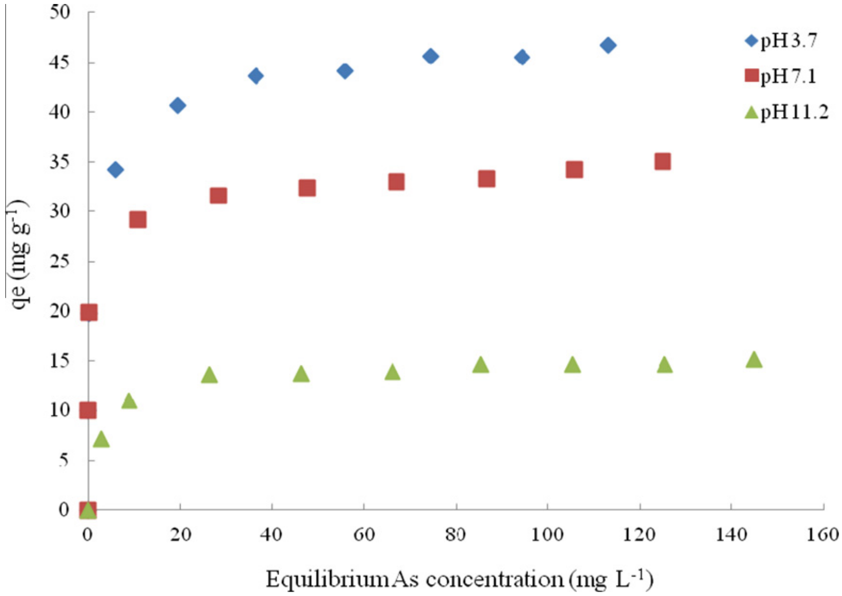

Fig. 4. As(V) adsorption isotherms of the copper ferrite at pH 3.7, 7.1 and 11.2. Conditions: $T = 27\ ^\circ C$, 10 mL solution volume, and 0.001 g $CuFe_2O_4$.

Table 1
Parameters of Freundlich and Langmuir adsorption isotherm models for As on the recycled copper ferrite.

	Freundlich			Langmuir		
	K_F	n	R^2	q_m	K_L	R^2
pH 3.7	39.85	32.79	0.9328	45.66	0.00025	0.9999
pH 7.1	22.85	10.88	0.9685	36.63	0.00381	0.9993
pH 11.2	10.70	14.56	0.9784	15.06	0.01056	0.9995

Note: K_F and n are Freundlich constants that are related to the adsorption capacity and adsorption intensity respectively. q_m is the maximum adsorption capacity (mg g^{-1}); K_L is the Langmuir constant.

Table 2
Comparison of the recycled $CuFe_2O_4$ with other adsorbents for As(V) adsorption at room temperature.

Adsorbents	pH	As(V) adsorption capacity (mg g^{-1})	References
$CoFe_2O_4$	3.0	73.80	[40]
$MnFe_2O_4$	3.0	90.40	[40]
Magnetic p(4-VP)-E nanoparticle	6.0	9.70	[42]
Magnetite–maghemite nanoparticles	5.0	3.71	[43]
Magnetite	6.1	1.65	[44]
Granular ferric hydroxide	7.6	0.16	[45]
Iron-oxide-coated sand	5.0	0.01	[46]
Iron-oxide-coated manganese sand	7.0	5.45	[47]
Recycled $CuFe_2O_4$	3.7	45.66	Present study

spectra for As(V) adsorbed on copper ferrite, we concluded that As(V) was the predominant oxidation state of As adsorbed on copper ferrite and no reduction of As(V) to As(III) occurred on the surface.

3.3. Effect of adsorbent dosage on As(V) adsorption

Examination of Fig. 3 suggests that the adsorbent dosage (i.e., 2 g L^{-1}) was ample for removing 80 mg L^{-1} As(V) at pH < 7, all As(V) removal in these pHs almost reached 100% after 300-min reaction. In order to find the optimum adsorption dosage, the amount of copper ferrite added to react with 80 mg L^{-1} As(V) solution was varied. As shown in Fig. 6, the increase in the adsorbent dosage had a positive effect on As(V) removal. For example, with adsorbent dosage of 0.25 g L^{-1}, the removal of As(V) was 10.5% after 300-min reaction at pH 3.7. As the adsorbent dosage was increased to 0.5 and 1.0 g L^{-1}, the As(V) removal after 300-min reaction were 25.0% and 45.7% respectively. A complete removal of As(V) was observed with adsorbent dosage of 2 g L^{-1}. Figs. S1 and S2 in the Supplementary Information section show that the extent of As(V) removal with the same adsorbent dosages generally decreased as the pH increased. At pH 7.1, a complete removal of As(V) could be achieved with adsorbent dosage of 2 g L^{-1} (Fig. S1). The removal rate significantly decreased as the pH was increased to 11.2 (Fig. S2) and, even with the highest adsorbent dosage, no complete removal of As(V) was achieved. As mentioned above, this negative effect of increasing solution pH is mainly due to increasing repulsion between the As(V) and copper ferrite surface at higher pH.

3.4. As(V) desorption

Desorption experiments were carried out to investigate the feasibility of regeneration of used copper ferrite for adsorbent after As(V) adsorption. Fig. 7a shows the effect of six kinds of acid or salt buffers on desorption efficiency of As(V) with 30 min desorption time. The recovery efficiencies of As(V) using different solutions were in the order of $H_3PO_4 > Na_3PO_4 > H_2SO_4 > Na_2SO_4 > HCl > HNO_3$, with the corresponding efficiency of 95.36%, 74.17%, 63.74%, 52.29%, 1.97% and 0.76%, respectively. Meanwhile, with the same anion in the desorption solutions (e.g., 0.4 M H_3PO_4 vs. Na_3PO_4), the As(V) recovery was more effective in acidic (i.e., 95.36%) than in alkaline conditions (i.e., 80.48%) (Fig. 7b). A similar trend was also found in the case of H_2SO_4 and Na_2SO_4.

Because phosphate exhibited the best As(V) recovery rate among all anions tested, the effect of phosphate concentration on As(V) recovery was further investigated. As the concentration of H_3PO_4 or Na_3PO_4 solution increased from 0.0125 M to 0.4 M, the amount of arsenic desorbed from copper ferrite increased significantly (Fig. 7b). The As desorption could reach equilibrium within

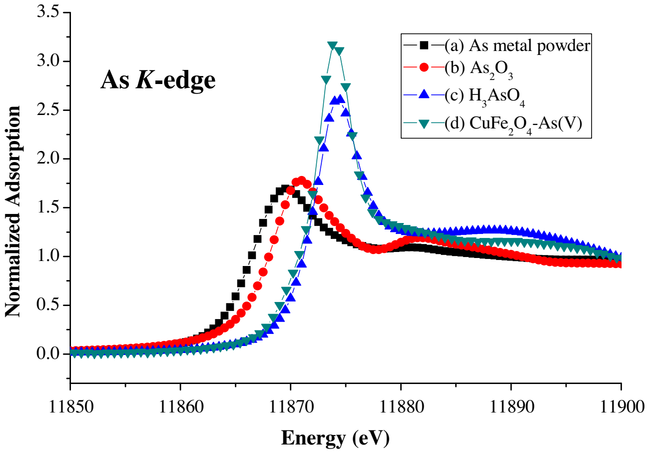

Fig. 5. The As *K*-edge XANES spectra of (a) As(0), (b) As(III), and (c) As(V) standards, and (d) As(V) adsorbed on $CuFe_2O_4$ surface with the adsorbed amounts of 3.6 mg g^{-1}.

30 min and the optimal As recovery rate could reach 95% and 80% with 0.4 M H_3PO_4 and Na_3PO_4 solutions, respectively. On the contrary, almost no As could be desorbed in <0.05 M Na_3PO_4 solution. This indicates that the strength of PO_4^{3-} at low concentrations was not sufficient to desorb As(V) from the copper ferrite surface under alkaline conditions. After the desorption experiments, the copper ferrite could be rapidly recovered from the solutions by a magnet. This could facilitate the recovery of the magnetic nano-adsorbents.

Generally speaking, the $CuFe_2O_4$ owns good acid-resisting characteristic because of its spinel structure [48]. However, Fe and Cu will be leached out if the pH is low enough. In our case, Fe and Cu was leached out 6.27% and 6.19%, respectively, under the extreme conditions of 0.4 M H_3PO_4, 0.05 g $CuFe_2O_4$ dosage, 10 mL desorption agent, and 30 min desorption time. Nevertheless, when the H_3PO_4concentration is lower than 0.1 M, the released Fe and Cu are all below 1% (see Table S1 in Supplementary material). Moreover, if the desorption time was shorten to 5 min, the desorption efficiency still could reach 90% and almost no Fe and Cu released.

The mechanisms of desorption could be divided in two types in this study. One is the change of electric charge on $CuFe_2O_4$ surface caused by pH variation while the other is the competition adsorption of ions in the systems.

The electric repulsion would hinder adsorption of anionic As(V) species at pH > PZC of copper ferrite (i.e. 7.3). This phenomenon is consistent with the observations of substantial decrease in As(V) adsorption at high pH (Fig. 4). This also could be interpreted as high As(V) removal at pH < 7.1 (Fig. 3). On the other hand, the reason for no desorption under 0.1 M HNO_3 and HCl could be attributed to strong affinity between positive charged copper ferrite and anionic As(V) species in acidic conditions. It was rather difficult for NO_3^- and Cl^- to desorb anionic As(V) species from the copper ferrite.

Fig. 7b shows that the desorption performance of H_3PO_4 is much better than Na_3PO_4. The working pH for 0.1 M H_3PO_4 and 0.1 M Na_3PO_4 was 1.69 and 11.97, respectively. If alkaline condition is unfavorable for As(V) adsorption, Na_3PO_4 should have better desorption performance. This dis-agrees with our observations. Ions concentration could be another potential factor for consideration due to competition adsorption. Fig. 7b shows that the desorption efficiency was increased with the concentration of desorption reagent. This phenomenon can be understood in terms of competition adsorption between H_3PO_4 species and As(V) species on the surface of copper ferrite. Fig. 7a reveals a similar trend for H_2SO_4 and Na_2SO_4, indicating strong H_2SO_4 species and As(V) species competition. Nevertheless, the H_2SO_4 competition efficiency is worse than H_3PO_4, as well as the desorption performance.

3.5. As removal from As-contaminated groundwater

To investigate the feasibility of the copper ferrite recycled in actual groundwater, five As contaminated groundwaters were sampled and used to test the As removal performance. The As concentrations are ranged from 31.6 to 89.3 μg L^{-1}, higher than the maximum contamination level of drinking water regulated by WHO (i.e. 10 μg L^{-1}). The As removal efficiency was tested by adding 0.005 g copper ferrite into 10 mL contaminated groundwater. The results demonstrated that the As removal efficiency could reach more than 94.9% (Table 3). The highest residual As concen-

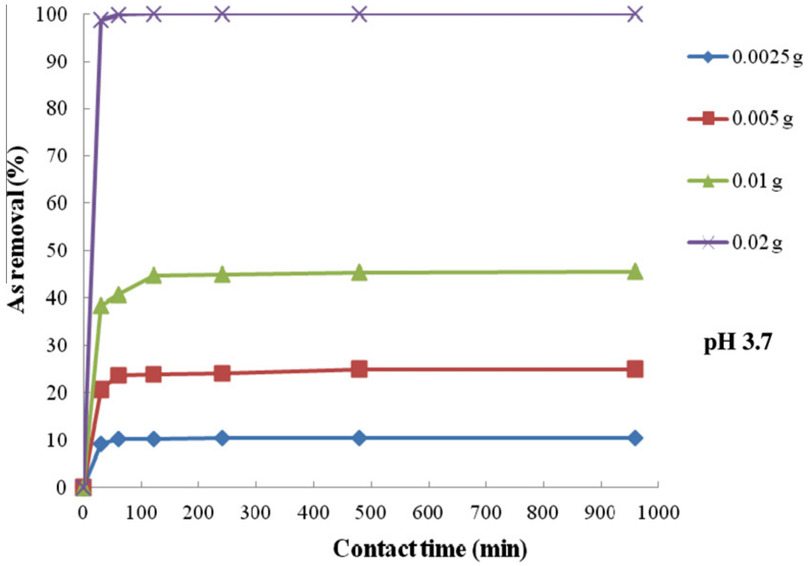

Fig. 6. Effect of adsorbent dosage on As(V) removal rates of the copper ferrite at pH 3.7. Conditions: *T* = 27 °C, 10 mL solution volume, and 100 mg L^{-1} initial As(V) concentration.

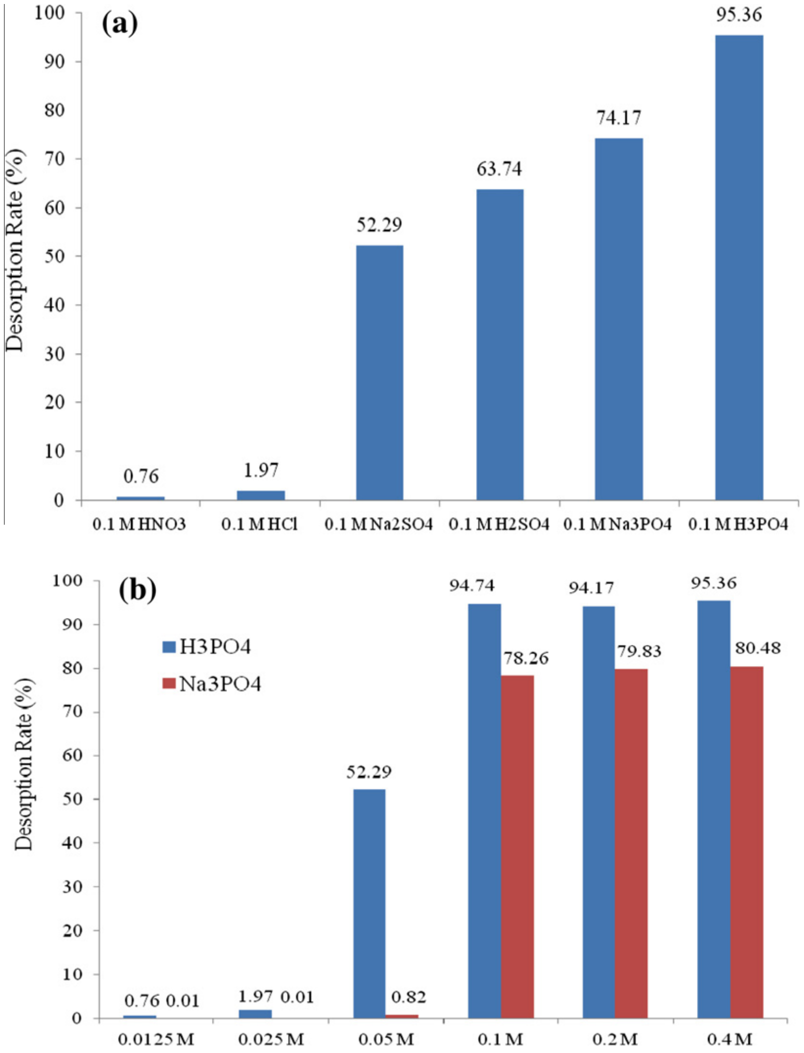

Fig. 7. (a) The rates of As(V) desorption from the copper ferrite after interacted with 0.1 M HNO_3, HCl, Na_2SO_4, H_2SO_4, Na_3PO_4 and H_3PO_4 solutions for 30 min at 27 °C. (b) Effects of H_3PO_4 and Na_3PO_4 concentrations on the As(V) desorption from the copper ferrite after 30-min interaction at 27 °C.

Table 3
Removal efficiency of As from five contaminated groundwaters using the recycled copper ferrite.

Well station no.	Adsorption pH	As (μg L^{-1})			Fe (mg L^{-1})		Cu (mg L^{-1})	
		Before[a]	After[b]	Removal (%)	Before[a]	After[b]	Before[a]	After[b]
1	7.25	89.3	3.6	95.9	0.15	0.15	b.d.	b.d.
	3.08	89.3	b.d.[c]	100	0.15	0.17	b.d	0.03
2	7.13	47.6	b.d.	100	0.06	0.06	b.d.	b.d.
	3.15	47.6	b.d.	100	0.06	0.06	b.d	0.02
3	6.99	81.8	4.2	94.9	2.34	2.36	b.d.	b.d.
	3.19	81.8	b.d.	100	2.34	3.38	b.d	b.d
4	7.24	64.3	b.d.	100	1.35	1.35	b.d.	b.d.
	3.34	64.3	b.d.	100	1.35	1.42	b.d	b.d
5	6.91	31.6	b.d.	100	0.65	0.65	b.d.	b.d.
	3.23	31.6	b.d.	100	0.65	0.68	b.d	b.d

Note: 1. Amount of adsorbent = 0.005 g $CuFe_2O_4$, volume = 10 mL, temperature = 27 °C, time = 1 h. 2. The adsorption pH were operated at neutral (pH 6.91–7.25) and acidic (pH 3.08–3.34) conditions to compare the As removal efficiency.

[a] Concentration before adsorption.

[b] Concentration after adsorption.

[c] b.d.: Below detection limit (for As: 2.3 μg L^{-1}, Fe: 5.6 μg L^{-1}, Cu: 4.1 μg L^{-1}).

tration was 4.2 μg L^{-1}, lower than the maximum contamination level of drinking water regulated by WHO. Additionally, both Fe and Cu were not detected in solution under neutral (pH 7) or acidic (pH 3) conditions, supporting the stability of recycled copper ferrite. These results confirmed that our recycled copper ferrite generally exhibited a high efficiency of As removal in groundwater.

3.6. Kinetic models

Fig. 8 demonstrates a kinetic time profile of As(V) adsorption from a solution containing 100 mg L^{-1} of As(V). It shows that As(V) was adsorbed rapidly in the first 60 min. After 300 min, the amount of As(V) adsorption did not increase further with contact-

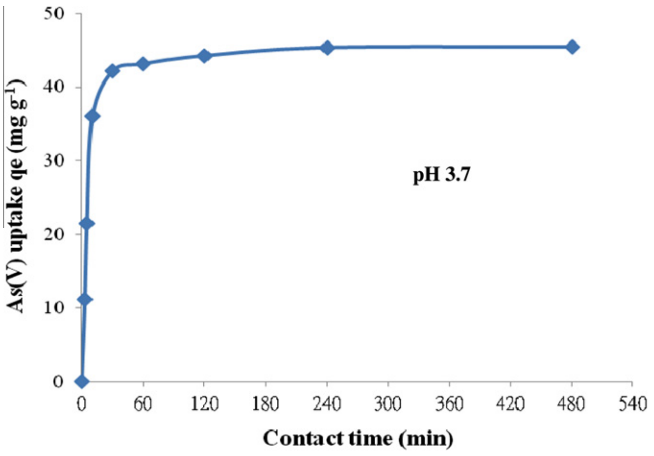

Fig. 8. Effect of the contact time on As(V) adsorption rate. Conditions: pH = 3.7, T = 27 °C, 10 mL solution volume, and 0.01 g $CuFe_2O_4$.

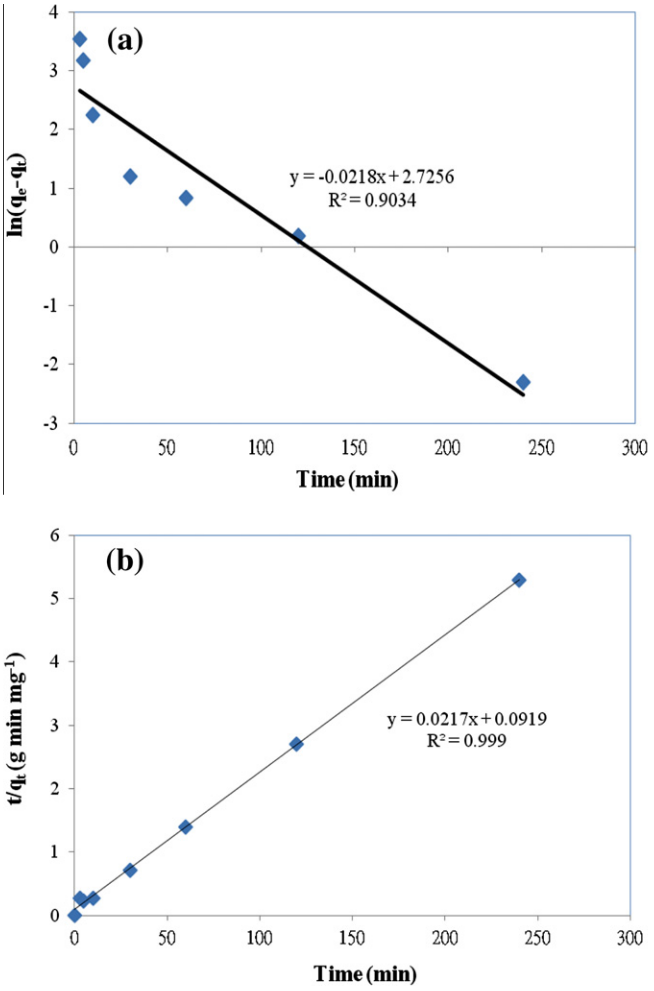

Fig. 9. Kinetics of As(V) adsorption on the recycled copper ferrite. (a) Pseudo-first-order plot and (b) pseudo-second-order plot. Conditions: pH = 3.7, T = 27 °C, 10 mL solution volume, and 0.001 g $CuFe_2O_4$.

ing time. Therefore, a contact time of 300 min is sufficient to achieve an equilibrium state. The equilibrium values of As(V) uptake (q_e) on recycled copper ferrite, and As(V) left in solution (C_e) at the end of 300 min were estimated to be 45.48 (mg g^{-1}) and 54.52 (mg L^{-1}), respectively.

Two well-known kinetic models, pseudo-first-order [49] and pseudo-second-order [50], were used to fit the data (Fig. 8). Eqs. (4) and (5) present the linear forms of pseudo-first-order and pseudo-second-order kinetics, respectively.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{4}$$

$$\frac{t}{q_t} = \frac{1}{k_2} q_e^2 + \frac{t}{q_e} \tag{5}$$

where t is the contact time (min); q_e (mg g^{-1}) and q_t (mg g^{-1}) is the amounts of As(V) adsorbed at equilibrium and at any time t, respectively; k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) is the rate constants of pseudo first-order and pseudo-second-order kinetics, respectively. Fig. 9a represents the plot of $\ln(q_e - q_t)$ vs. t. It shows a linearity of R^2 = 0.9034. The plot of t/q_t vs. t is given in Fig. 9b and shows that the pseudo-second-order model fits well with the data (R^2 = 0.9990). These results suggest that the kinetics in As(V) adsorption on recycled copper ferrite can be described as pseudo-second-order reaction.

4. Conclusion

Magnetic copper ferrite was successful fabricated from industrial sludge and can be used as an effective adsorbent for As(V). The experimental results show that this adsorbent has a great potential for treating As-containing groundwater and can be recovered effectively using a magnet. Because of the recycled copper ferrite PZC (7.3), it exhibits a better As(V) removal rate at low pH. It is recommended that the nano-copper ferrite to be used at low-to-neutral pH as an adsorbent for As(V). The pseudo-second-order kinetic model provides the best correlation with the experimental data compared to the pseudo-first-order model. Based on regression coefficient values, the Langmuir model yields a better fitting than the Freundlich model for As(V) at all investigated pHs. The removal of As(V) using this material in alkaline waters and wastewaters can be enhanced significantly by acidification of the waters.

Acknowledgments

The authors would like to thank the Environmental Protection Administration (EPA) for the financial support (Contract Number: EPA-99-GA103-03-A236-18). We thank Prof. Jiang Wei-Teh and Mr. Lee Po-Shu for their support on XRD analysis under the project of NSC 1002116M006002. We also thank NSRRC staff for useful discussions and experimental support.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2012.06.006.

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