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Nanostructured iron(III)-copper(II) binary oxide: A novel adsorbent for enhanced arsenic removal from aqueous solutions

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ABSTRACT

To obtain a highly efficient and low-cost adsorbent for arsenic removal from water, a novel nanostructured Fe–Cu binary oxide was synthesized via a facile co-precipitation method. Various techniques including BET surface area measurement, powder XRD, SEM, and XPS were used to characterize the synthetic Fe–Cu binary oxide. It showed that the oxide was poorly crystalline, 2-line ferrihydrite-like and was aggregated with many nanosized particles. Laboratory experiments were performed to investigate adsorption kinetics, adsorption isotherms, pH adsorption edge and regeneration of spent adsorbent. The results indicated that the Fe–Cu binary oxide with a Cu: Fe molar ratio of 1:2 had excellent performance in removing both As(V) and As(III) from water, and the maximal adsorption capacities for As(V) and As(III) were 82.7 and 122.3 mg/g at pH 7.0, respectively. The values are favorable, compared to those reported in the literature using other adsorbents. The coexisting sulfate and carbonate had no significant effect on arsenic removal. However, the presence of phosphate obviously inhibited the arsenic removal, especially at high concentrations. Moreover, the Fe–Cu binary oxide could be readily regenerated using NaOH solution and be repeatedly used. The Fe–Cu binary oxide could be a promising adsorbent for both As(V) and As(III) removal because of its excellent performance, facile and low-cost synthesis process, and easy regeneration.

1. Introduction

Arsenic, a ubiquitous element found in the environment, is well-known and extensively concerned with high toxicity and carcinogenicity. It is introduced into the water and groundwater through a combination of natural processes such as weathering reactions, dissolution of minerals and biological activity as well as through anthropogenic activities such as mining, agriculture and manufacturing (Cullen and Reimer, 1989; Smedley and Kinniburgh, 2002). Elevated arsenic levels in groundwater near human populations have been reported in many countries and regions throughout the world, which

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poses a significant threat to human health (Mandal and Suzuki, 2002; Smedley and Kinniburgh, 2002). To abate health problems associated with arsenic in drinking water, the World Health Organization (WHO) recommended a more stringent limit of 10 μg L^{-1} as the maximum permissible arsenic level. Therefore, developing economical, effective and reliable treatment technique for arsenic removal from groundwater is critical and has gained considerable attention in recent years.

Arsenic occurs mostly in two inorganic forms as oxyanions of arsenate [As(V)] and arsenite [As(III)] in groundwater, with the latter being more toxic, soluble, and mobile (Goddington, 1986). Under oxidizing conditions, negatively charged $H_2AsO_4^-$ is the major arsenic species at pH lower than 6.9, while $HAsO_4^{2-}$ is dominant at higher pH. For arsenite, the uncharged H_3AsO_3 dominates at pH lower than 9.0 under reducing conditions (Yan et al., 2000; Smedley and Kinniburgh, 2002). Various treatment techniques such as coagulation/precipitation (Scott et al., 1995), ion-exchange (Kartinen and Martin, 1995), sorption (Jang et al., 2006; Zhang et al., 2007a) and membrane processes (Kartinen and Martin, 1995; Waypa et al., 1997) have been developed and employed for arsenic removal. Due to its simplicity, high efficiency and cost-effectiveness, sorption processes are regarded as the most promising methods and largely used for arsenic removal from water and wastewater (Jang et al., 2006; .Sharma and Sohn, 2009).

Different sorbents, including natural and synthetic materials have been extensively investigated to remove arsenic from aqueous solutions (Mohan and Pittman, 2007). Recently, increasing attention has been focused on metal oxide sorbents such as iron (Raven et al., 1998; Dixit and Hering, 2003), aluminum (Lin and Wu, 2001; Patra et al., 2012), titanium (Pena et al., 2005; Jegadeesan et al., 2010; Xu et al., 2010), manganese (Lenoble et al., 2004; Lafferty et al., 2010), and zirconium (Hristovski et al., 2008; Hang et al., 2012). Among these iron (hydr)oxides were the mostly studied because of their high affinity to arsenic species, low cost and environmental friendliness.

Most recently, developing composite sorbents containing two or more metal oxides have gained considerable attention, since the composite not only inherits the advantages of parent oxides but shows obviously synergistic effect. For instances, Zhang et al. (2005) developed an Fe–Ce bimetal oxide sorbent, which has a much higher As(V) adsorption capacity than the individual Ce and Fe oxide. Zhang et al. (2007a) prepared an Fe–Mn binary oxide sorbent, exhibiting a greater enhancement in both As(V) and As(III) removal. Gupta and Ghosh (2009) reported the synthesis and use of an Fe–Ti binary mixed oxide for arsenic sorption. Li et al. (2010) synthesized a Ce–Ti oxide sorbent with high efficiency at both As(V) and As(III) removal. Ren et al. (2011) found that an Fe–Zr binary oxide prepared in their laboratory had high sorption capacity towards arsenic.

Recently, it was reported that cupric oxide was an effective sorbent for both As(V) and As(III) removal over a wide pH range and performed well in the presence of competing anions (Martinson and Reddy, 2009). They attributed the effective arsenic removal by CuO to its high point of zero charge of approximate 9.4 (Yoon et al., 1979). Although CuO sorbent is effective in removing arsenic from water, it is not economical to use pure CuO as sorbent, due to its relatively high cost (The current price of powder CuO (98%) is US $6000–8800/Ton, while the iron oxide (96%) is US $500–1000/Ton). Therefore, to develop low-cost, effective and reliable alternatives for arsenic removal is still necessary. To combine CuO with iron oxides to produce a novel composite sorbent may reduce the cost and maintain the high performance simultaneously. However, to our best knowledge, no information is available on the synthesis of Fe–Cu binary oxides and their performance for arsenic removal from water.

Thus, in this study, a facile chemical precipitation method was developed to synthesize Fe–Cu binary oxides at room temperature. The main objectives of this research were (1) to optimize the Cu/Fe molar ratio in the Fe–Cu binary oxides; (2) to characterize the prepared Fe–Cu binary oxides with a variety of techniques; (3) to evaluate their arsenic adsorption capacity and investigate sorption kinetics as well as the influences of solution pH and co-existing ions on arsenic sorption, and finally (4) to study regeneration and reusability of spent adsorbent.

2. Materials and methods

2.1. *Materials*

All chemicals are analytical grade and were used without further purification. Reaction vessels (glass) were cleaned with 1% HNO_3 and rinsed several times with deionized water before use. As(V) stock solution was prepared with deionized water using $NaHAsO_4 \cdot 7H_2O$ and As(III) stock solution was prepared with NaOH solution using As_2O_3. As(V) and As(III) working solutions were freshly prepared by diluting arsenic stock solutions with deionized water.

2.2. *Synthesis of Fe–Cu binary oxide sorbents*

A series of Fe–Cu binary oxides were synthesized at 0:1, 1:10, 1:5, 1:3, 1:2, 1:1.5, 1:1, and 1:0 Cu:Fe molar ratios at room temperature. The Fe–Cu binary oxides were prepared according to the following procedure: A certain amount of ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) and copper(II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) were dissolved in 400 ml deionized water. The Cu:Fe molar ratio was adjusted to the predetermined value via changing the amount of $CuSO_4 \cdot 5H_2O$ or $FeCl_3 \cdot 6H_2O$ added. Under vigorous magnetic-stirring, sodium hydroxide solution (3 mol/L) was added dropwise to raise the solution pH to around 7.5. The formed suspension was continuously stirred for 1 h, aged at room temperature for 4 h and then washed several times with deionized water. The suspension was then filtrated and dried at 55 °C for 24 h. The dry material was crushed and stored in a desiccator for use. The obtained material appeared in the form of fine powder.

2.3. *Characterization of Fe–Cu binary oxide*

The composition of the 1:2 Fe–Cu binary oxide was determined by classical chemical analysis. A definite amount of the oxide was treated with 10% oxalic acid solution. The oxide was reduced and dissolved by the oxalic acid and formed Fe^{3+} and

Cu^{2+} entered into solution. The content of Cu^{2+} and Fe^{3+} in the solution was determined using an ICP–OES (Optima 7000 DV, Perkin Elmer Co. USA).

X-ray diffraction (XRD) analysis was carried out on a Rigaku D/Max-3A diffractometer using Ni-filtered copper Kα 1 radiation. The morphology of the particles was observed using a field scanning electron microscope (FESEM) (Hitachi S-4800, Japan). The specific surface area was measured via nitrogen adsorption using the BET method with a surface area analyzer (Nova, 2000e; Quantachrome Instruments, USA). X-ray photoelectron spectra (XPS) were collected on an ESCA-Lab-220i-XL spectrometer with a monochromatic Al Kα X-ray source (1486.6 eV). C1s peaks were used as an inner standard calibration peak at 284.7 eV. For wide scan spectra, an energy range of 0–1100 eV was used with pass energy of 80 eV and step size of 1 eV. The high-resolution scans were conducted according to the peak being examined with pass energy of 40 eV and step size of 0.05 eV. The XPS results were collected in binding energy forms and fitted using a nonlinear least–square curve fitting program (XPSPEAK41 Software).

The point of zero charge (PZC) was measured via a slightly modified method described by Kinniburgh et al. (1975). The Fe–Cu binary oxide powder was suspended in 0.01 M $NaNO_3$ for 24 h, after which the rate of pH change with time was very slow. 50 ml of suspension was then adjusted to various pH values with NaOH or HNO_3 solution. After agitation for 60 min for equilibrium, the initial pH was measured; then 1.5 g of $NaNO_3$ was added to each suspension to bring final electrolyte concentration to about 0.45 M. After an additional 12 h, the final pH was measured. The results, plotted as ΔpH (final pH-initial pH) against final pH, yielded the pzc as the pH, at which ΔpH equals to 0.

2.4. Batch sorption and desorption experiments

Sorption kinetics, sorption isotherm and the effects of Cu:Fe molar ratio, solution pH and coexisting anions on arsenic sorption were determined in batch sorption experiments.

To determine the optimal Cu:Fe molar ratio, batch tests were carried out by adding 10 mg of prepared sorbents into 150-mL glass vessels, containing 50 ml of 14.6 mg/L arsenic solution. The pH of the solutions was adjusted every four hours with dilute HNO_3 or/and NaOH solution to around pH 7.0 during shaking process. The equilibrium pH was measured and the supernatant was filtered through a 0.45 μm membrane after the solutions were mixed for 24 h. Then, the residual arsenic concentration in the supernatants was determined.

For sorption kinetics, defined amount of As(V) or As(III) stock solution was added in a 1000-ml glass vessel containing 1000 ml 0.01 M $NaNO_3$ solution, to make 10 mg/L of initial arsenic concentration. The solution pH was adjusted to 7.0 ± 0.1 by adding 0.1 M HNO_3 and/or NaOH and then 1:2 Fe–Cu binary oxide was added to obtain a 0.2 g/L suspension. The suspension was mixed by magnetic-stirring, and the pH was maintained at 7.0 ± 0.1 throughout the experiment by addition of the acid and base solutions. In the whole process, only several drops of acid or base were added into the solution and the total volume was no more than 0.5 ml, which did not significantly influence the arsenic sorption. Approximately 5 ml aliquots were taken from the suspension at certain time intervals. The samples were filtered through a 0.45 μm membrane filter and analyzed for arsenic.

To investigate the influence of pH on arsenic sorption, experiments were carried out by adding 10 mg of 1:2 Fe–Cu binary oxide into 150-mL glass vessels, containing 50 ml of 10 mg/L arsenic solution. The pH of the solutions was adjusted every four hours with dilute HNO_3 or/and NaOH solution to designated values during sorption process. The equilibrium pH was measured and the supernatant was filtered through a 0.45 μm membrane after the solutions were mixed for 24 h. Then, the residual arsenic concentration in the supernatants was determined. Additionally, to evaluate the leaching of Fe and Cu from the sorbent at different pHs, the Fe and Cu concentrations in the supernatant solutions were also measured using ICP–OES.

For sorption isotherms, the experiments were performed at pH 7.0. The pH of suspensions was adjusted with 0.1 M of NaOH and HNO_3 during the experiment. Initial arsenic concentration varied from 5 mg/L to 60 mg/L. In each test, 10 mg of 1:2 Fe–Cu binary oxide was loaded in the 100-mL glass vessel and 50 ml of solution containing differing amounts of arsenic were then added to the vessel. The vessels were shaken on an orbit shaker at 200 rpm for 24 h at 24 ± 1 °C. Then, all samples were filtered by a 0.45 μm membrane filter and analyzed for arsenic.

The influence of commonly coexisting anions in water such as sulfate, bicarbonate, and phosphate on the removal of arsenic was investigated by adding sodium sulfate, sodium bicarbonate and sodium phosphate to 10 mg/L of arsenic solution, respectively. The anion concentrations ranged from 5 to 100 mg/L. The solution pH was adjusted to 7.0 ± 0.1. A defined amount (10 mg) of 1:2 Fe–Cu binary hydrous oxide was added and the solutions were agitated at 200 rpm for 24 h at 24 ± 1 °C. After filtration by a 0.45 μm membrane filter, the concentration of residual arsenic was analyzed using ICP–OES.

Four cycles of adsorption and desorption were carried out to evaluate the reusability of the prepared binary oxide. For the adsorption test, 0.5 g Fe–Cu binary oxide was added into a vessel containing 1 L solution with 25 mg/L arsenic, the solution was stirred for 24 h and maintained at about pH 7.0, and then the adsorbent was separated and collected from the solution. The residual arsenic concentration was measured using the ICP–OES. For the desorption test, the arsenic-containing Fe–Cu binary oxide was added into a 100 ml 0.5 M NaOH solution. The mixture was stirred for 6 h and then regenerated adsorbent was separated from the NaOH solution. After washing and drying, it was used in the next adsorption–desorption cycle.

2.5. Analytical methods

Arsenic was measured using an inductively coupled plasma atomic emission spectroscopy machine (ICP–OES, Optima 7100 DV, Perkin Elmer Co. USA). Prior to analysis, the aqueous samples were acidified with concentrated HCl in an amount of 1%, and stored in acid-washed glass vessels. All samples used in our analysis were analyzed within 24 h after collection.

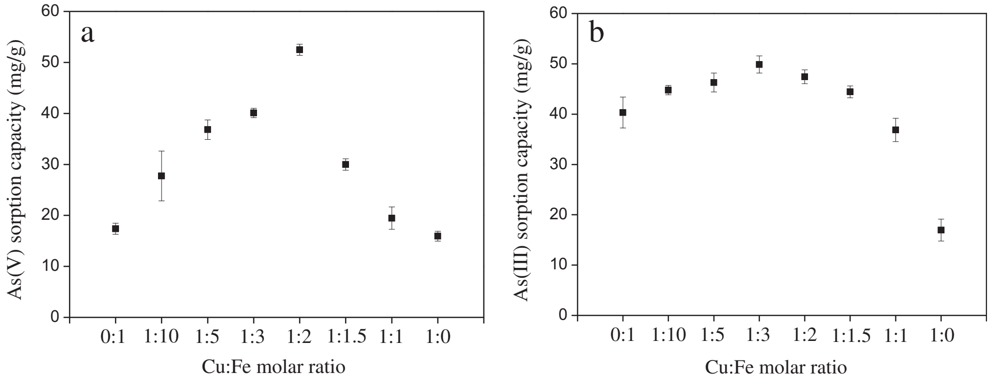

Fig. 1 – Effect of Cu:Fe molar ratio on (a) As(V) and (b) As(III) sorption by Fe–Cu binary oxide. Arsenic initial concentration = 14.6 mg/L, sorbent dose = 200 mg/L, pH = 7.0 ± 0.1, T = 25 ± 1 °C.

3. Results and discussion

3.1. *Effect of Cu:Fe molar ratio on arsenic sorption*

To determine the optimal Cu:Fe molar ratio, a series of Fe–Cu binary oxide adsorbents with different Cu:Fe molar ratios from 0:1 to 1:0, were synthesized and tested for arsenic sorption. The results are shown in Fig. 1. As(V) sorption by the Fe–Cu binary oxide increases obviously with an increase in Cu:Fe molar ratio and reaches a maximum of approximately 53 mg g^{-1} when the ratio is 1:2. Then, As(V) sorption decreases significantly with further increase in Cu:Fe molar ratio. The As(V) sorption capacity decreases to 20 mg g^{-1} at a Cu:Fe molar ratio of 1:1. This value is very close to that of pure iron oxide (17.4 mg g^{-1} at Cu:Fe molar ratio of 0:1). At Cu:Fe molar ratio of 1:0, namely for the pure copper oxide, As(V) sorption capacity further fell to about 16 mg g^{-1}. Theoretically, if no synergy effect occurred between iron oxide and copper oxide, the As(V) sorption capacity of 1:2 Fe–Cu binary oxide should be 16.9 mg g^{-1}, which is far less than the real value of 53 mg g^{-1}. For As(III), similar phenomena were observed, except that maximal As(III) sorption occurred at 1:3 Fe–Cu binary oxide and variation in sorption capacity was less remarkable than that of As(V). These results suggest that the combination of copper oxide with iron oxide results in a

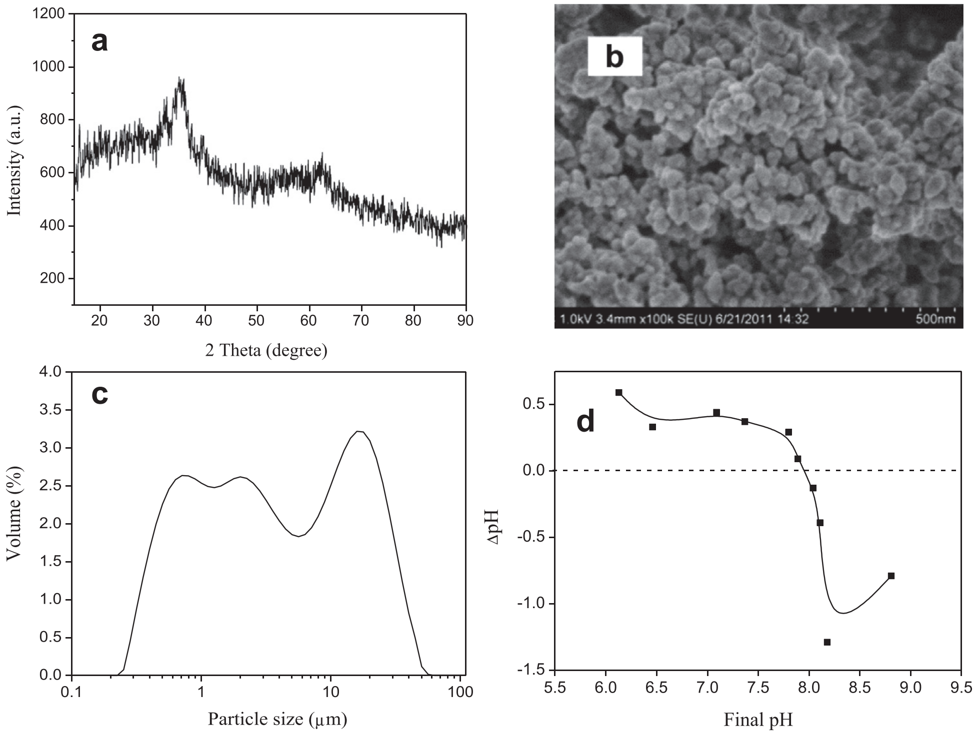

Fig. 2 – (a) XRD diffraction pattern, (b) FESEM image, (c) particle size distribution, and (d) point of zero charge (pzc) of Fe–Cu binary hydrous oxide.

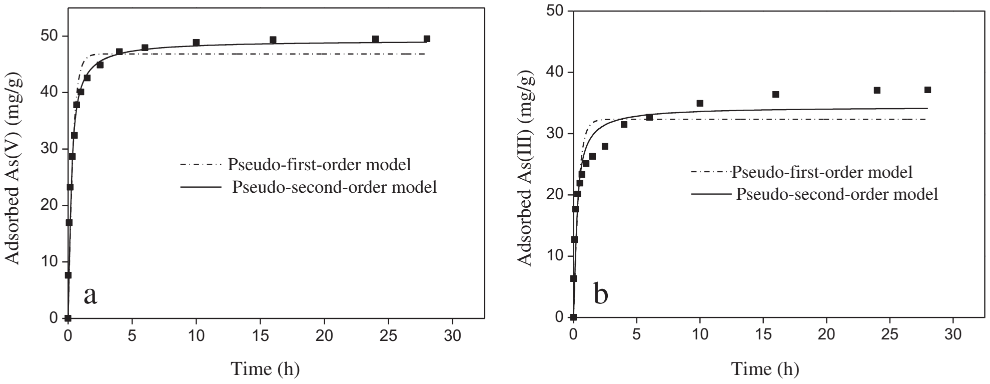

Fig. 3 – Kinetics of (a) As(V) and (b) As(III) sorption onto Fe–Cu binary oxide at pH = 7.0 ± 0.1. Arsenic initial concentrations = 10 mg/L, adsorbent dose = 200 mg/L and T = 25 ± 1 °C.

significant improvement in arsenic sorption. And the Cu:Fe molar ratio is a key factor influencing the sorption capacity of the Fe–Cu binary oxide.

Considering comprehensively effectiveness and cost, the Fe–Cu binary oxide with the Cu:Fe molar ratio of 1:2 was chosen as feasible sorbent and was detailed examined in the following sections.

3.2. *Characterization of 1:2 Fe–Cu binary oxide*

The chemical analysis of the prepared 1:2 Fe–Cu binary oxide showed that the Cu:Fe molar ratio of the bulk was 0.491 ± 0.012. X-ray diffraction pattern of the oxide is illustrated in Fig. 2a. It demonstrates two broad peaks at approximately 35.1 and 62.2°, respectively, which are similar to those of poorly ordered 2-line ferrihydrite (Schwertmann and Cornell, 2000; Ren et al., 2011). This indicates that the prepared Fe–Cu binary oxide is amorphous and 2-line ferrihydrite-like. Fig. 2b illustrates the SEM image of the oxide particles, showing that they are aggregates formed by small nanograins (around 50 nm). The distribution of particle size of the powdered oxide is depicted in Fig. 2c, indicating that main particle size of this binary oxide is in the range of 0.3–40 μm. The amorphous Fe–Cu binary hydrous oxide has a high BET surface area of 282 m^2/g and a pore volume of 0.31 cm^3/g. Pore size distribution (PSD) of this oxide estimated by employing BJH (Barrett-Joyner-Halenda) method is shown in Fig. S1. The PSD pattern suggests that the pore is relatively uniform in size with an average pore size of 4.3 nm.

The value of point of zero charge (PZC) of the Fe–Cu binary oxide is approximate 7.9 (Fig. 2d). The PZC of pure ferrihydrite is about pH 7.4 (Zhang et al., 2012) and that of CuO is pH 9.4 (Yoon et al., 1979). Obviously, the incorporation of CuO with iron oxide makes the composite a higher PZC than that of pure ferrihydrite.

3.3. *Sorption kinetics*

The rate of arsenic sorption onto the Fe–Cu binary oxide was investigated by batch experiments. Fig. 3 shows the change of adsorbed arsenic as a function of contact time. As shown in Fig. 3, initial sorption of both As(V) and As(III) was very rapid. After 1 h of contact with Fe–Cu binary oxide, about 80% and 70% of equilibrium sorption capacity were achieved for As(V) and As(IIII), respectively. In the following period, the arsenic sorption slowed down and over 98% of equilibrium sorption capacity was reached for both As(V) and As(III) after a reaction of 16 h. The time taken to reach the equilibrium is about 24 h. Therefore, a reaction time of 24 h was chosen for all other batch experiments. For whole sorption process, As(III) sorbed more slowly than As(V). Similar results were observed for sorption of As(V) and As(III) by pure cupric oxide (Martinson and Reddy, 2009).

The pseudo-first-order model and pseudo-second-order model were employed to describe the kinetic data. The mathematical representations of the models are given in Eqs. (1) and (2), respectively.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{1}$$

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{2}$$

where q_e and q_t are the adsorption capacities (mg/g) of the adsorbent at equilibrium and at time t (h), respectively; k_1 (h^{-1}) and k_2 (g mg/h) are the related adsorption rate constants.

Table 1 – Adsorption rate constant obtained from pseudo-first-order model and pseudo-second-order model.

Arsenic species	Pseudo-first-order model pseudo-second-order model					
	k_1 (h^{-1})	q_e (mg/g)	R^2	k_2 (g/mg·h)	q_e (mg/g)	R^2
As(V)	2.952	46.8	0.949	0.099	49.3	0.989
As(III)	2.492	41.5	0.933	0.094	43.7	0.982

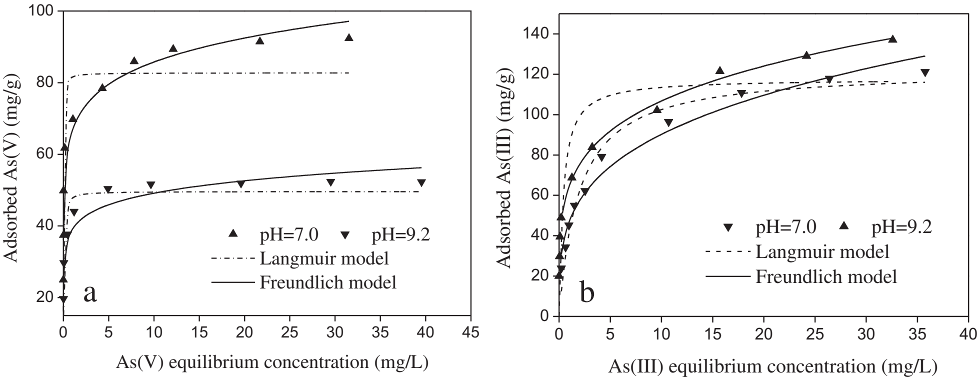

Fig. 4 – Adsorption isotherms for (a) As(V) and (b) As(III) by Fe–Cu binary oxide at two pHs and T = 25 ± 1 °C; (—) Langmuir model and (—) Freundlich model.

The rate constants obtained from pseudo-first-order and pseudo-second-order models are listed in Table 1. For both As(V) and As(III), the experimental data fitted better with pseudo-second-order model than pseudo-first-order model, which indicates that the adsorption process might be chemisorption.

3.4. *Sorption isotherms*

The arsenic sorption capacities of the Fe–Cu binary oxide at two pHs were evaluated using the isotherms and presented in Fig. 4. It can be seen that the Fe–Cu binary oxide has high sorption capacity for both As(V) and As(III). For As(V), its sorption capacity reduced greatly, when solution pH increased from 7.0 to 9.2. But for As(III), the increase in pH slightly enhanced its sorption. In addition, at low equilibrium concentration, the oxide is more effective in removing As(V) than As(III). For example, the As(V) adsorption capacity is as high as 62 mg/g and 37 mg/g at pH 7.0 and equilibrium concentration of 152 ppb and 9.7 ppb, respectively. While, the As(IIII) adsorption capacity is about 49 and 20 mg/g at pH 9.2 and equilibrium of 208 ppb and 6.8 ppb, respectively. However, it has higher sorption capacity for As(III) than that of As(V) at higher equilibrium concentration. These results indicate that the sorption of As(V) and As(III) might be dominated by different mechanisms.

Both Langmuir and Freundlich models were used to describe the adsorption isotherms. The Langmuir equation and Freundlich equation are represented as Eqs. (3) and (4), respectively.

$$q_e = \frac{q_{max} b C_e}{1 + b C_e} \tag{3}$$

$$q_e = K_F C_e^n \tag{4}$$

where q_e is the amount of arsenic adsorbed on the solid phase (mg/g), C_e is the equilibrium arsenic concentration in solution phase (mg/L), b is the equilibrium adsorption constant related to the affinity of binding sites (L/mg), q_{max} is the maximum amount of the arsenic per unit weight of adsorbent for complete monolayer coverage, K_F is roughly an indicator of the adsorption capacity and n is the heterogeneity factor which has a lower value for more heterogeneous surfaces.

The adsorption constants obtained from the isotherms are presented in Table 2. As shown in Table 2, higher regression coefficient suggests that the Freundlich model is more suitable for describing the sorption behavior of arsenic by Fe–Cu binary oxide than Langmuir model. The Langmuir model assumes that adsorption occurs on a homogeneous surface. A heterogeneous surface of the Fe–Cu binary oxide may be formed because of the simultaneous presence of cupric oxide and iron oxide in the binary oxide. The Freundlich model describes sorption where the sorbent has a heterogeneous surface with sorption sites that have different sorption energies. The maximal sorption capacities for As(V) and As(III) calculated from Langmuir model are 82.7 mg/g and 122.3 mg/g, respectively. Such high capacity indicates that prepared Fe–Cu binary oxide is very effective for both As(V) and As(III) removal. A comparison has been made between the prepared Fe–Cu binary oxide and previously reported sorbents for

Table 2 – Langmuir and Freundlich isotherm parameters for As(V) and As(III) sorption on Cu–Fe binary oxide at two pHs.

Langmuir model				Freundlich model		
As species and pH	q_m (mg/g)	K_L (L/mg)	R^2	K_F (mg/g)	n	R^2
As(V) pH 7.0	82.7	71.40	0.850	66.8	0.108	0.946
As(V) pH 9.2	49.6	27.02	0.861	39.2	0.098	0.890
As(III) pH 7.0	122.3	0.517	0.967	47.25	0.281	0.972
As(III) pH 9.2	117.7	2.675	0.819	64.86	0.216	0.996

Table 3 – Comparison of maximum arsenic sorption capacities for different adsorbents[a].

Adsorbent	As con. range (mg/L)	Max. As(III) adsorption capacity (mg/g)	Max. As(V) adsorption capacity (mg/g)	Ref
CuO nanoparticles	0–100	26.9 (pH 8.0)	22.6 (pH 8.0)	Martinson and Reddy, 2009
Doughnut-like CuO	0–90	4.7 (4.0)	–	Cao et al., 2007
Copper(II) oxide	0.5–1	1.08 (7.0)	–	Goswami et al., 2012
Nano-TiO_2	0–130	99.0 (pH 7.0)	–	Xu et al., 2010
Fe–Zr binary oxide	0–40	120.0 (pH 7.0)	46.1 (pH 7.0)	Ren et al., 2011
Fe–Mn binary oxide	0–40	100.4 (pH 6.9)	53.9 (pH 6.9)	Zhang et al., 2007b
NHITO	5.0–250	85.0 (pH 7.0)	14.3 (pH 7.0)	Gupta and Ghosh, 2009
$Al_2O_3/Fe(OH)_3$	7.5–135 mmol	9.0 (pH 6.6)	36.7 (pH 7.2)	Hlavay and Polyák, 2005
MBOP	1.0	16.9 (7.0)	–	Dhoble et al., 2011
Fe–Cu binary oxide	0–60	122.3 (pH 7.0)	82.7 (pH 7.0)	Present study

a pH is shown in parentheses.

arsenic sorption (Table 3). The analytical result of comparison shows that the prepared Fe–Cu binary oxide outperforms remarkably many other sorbents. This indicates that the Fe–Cu binary oxide is a rather promising alternative for arsenic removal.

3.5. *Influence of pH on arsenic sorption and metal leaching*

Fig. 5 shows the effect of solution pH on sorption of As(V) and As(III). As shown in Fig. 5, the As(V) sorption on the Fe–Cu binary oxide is very effective under acidic and weak basic conditions. Although higher pH is not favoring its sorption, the oxide has an As(V) sorption capacity as high as 39 mg/g at pH about 9.1. This may be attributed to the relatively high PZC value (7.9) of the Fe–Cu binary oxide. Generally, As(V) sorption is dependent on pH and decreases with an increase in solution pH. Similar phenomena were also observed for the sorption of As(V) onto other iron oxides or iron–containing oxides (Hingston et al., 1972; Ren et al., 2011). The reason is that adsorption of strong acid anions by metal oxides and hydroxides typically decreases with an increasing pH (Stumm, 1996). On the contrary, As(III) sorption gradually increases with the increasing of solution pH and reaches a maximum at a pH of approximately 9.1. Then, it decreases slowly with further increase in pH. Adsorption of weak acid anions by metal oxides usually reaches a maximum at pH values similar to pk_{a1} of the acid (Stumm, 1996). The pk_{a1} of arsenious acid is 9.2. The decrease in As(III) sorption at pH over 9.1 may be due to the coulumbic repulsion between As(III) species and the negative surfaces of Fe–Cu binary oxide ($pH_{pzc} = 7.9$).

Fig. S2 demonstrates the concentrations of dissolved Fe and Cu under different pHs. The Fe concentrations are all below 0. 1 mg/L under tested pH range, which are far below the limit of drinking water standard (USEPA). The leaching of Cu is serious under acid condition. But its release is very small and the concentrations of Cu are all below the limit of drinking water of 1 mg/L at pH over 6.0. Obviously, the prepared sorbent could be safely used in the majority of water supplies, in which pH is in a range of 6.5–8.5 (Gu et al., 2005).

3.6. *Influence of coexisting anions on arsenic sorption*

The effects of commonly present anions such as sulfate, bicarbonate, silicate and phosphate in water on arsenic sorption were examined at different concentrations (from 5 to 100 mg/L) and at pH of 7.0 ± 0.1. The results are illustrated in Fig. 6. The presence of sulfate and bicarbonate does not greatly influence the As(V) sorption. Only a slight reduction in As(V) sorption is observed when the coexisting sulfate or bicarbonate concentration is as high as 100 mg/L. However, the present phosphate hinders significantly As(V) sorption, especially at high concentration levels. The influences of these anions on As(III) sorption are similar to those of As(V), except for a lower sorption rate. The greatest decrease in As(V) sorption resulting from the presence of phosphate may be due to the strong competition for the binding sites of the sorbent between phosphate and arsenic. Both phosphate and arsenic are located in the same main group, and the structure of phosphate ion is very similar to that of arsenic ion. Thus, the present phosphate ions might strongly compete with arsenic ions for adsorptive sites on the surface of Fe–Cu binary hydrous oxide.

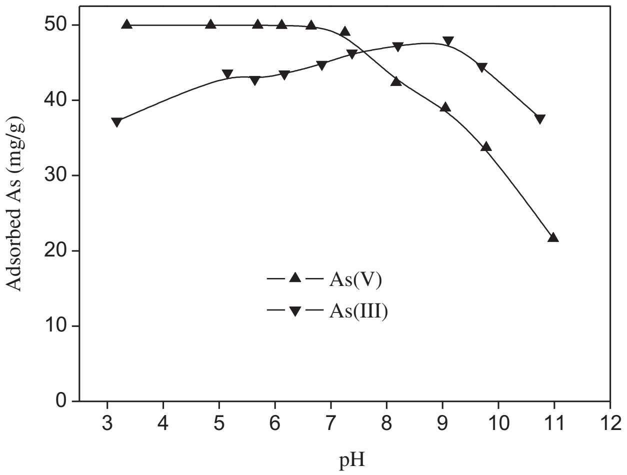

Fig. 5 – Effect of solution pH on As(V) and As(III) sorption by Fe–Cu binary oxide. Initial arsenic concentration = 10 mg/L, adsorbent dose = 200 mg/L and T = 25 ± 1 °C.

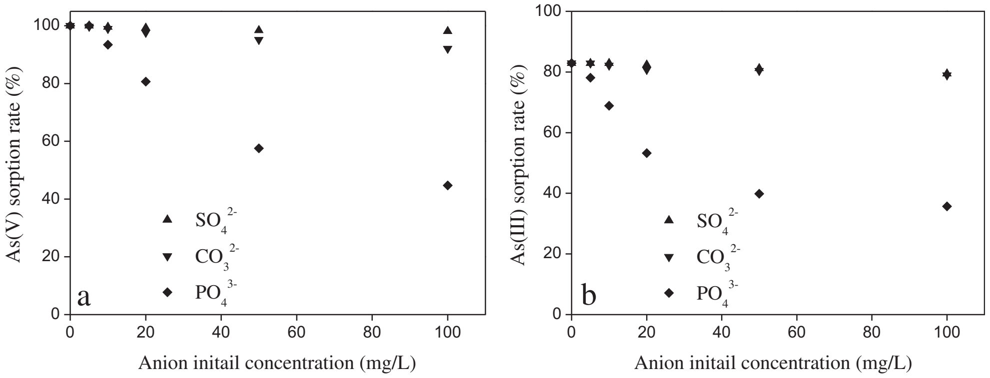

Fig. 6 – Effects of co-existing anions on (a) As(V) and (b) As(III) sorption at different concentrations. Initial arsenic concentration = 10 mg/L, adsorbent dose = 200 mg/L, pH = 7.0 ± 0.1 and *T* = 25 ± 1 °C.

Although phosphate influences greatly arsenic sorption on the Fe–Cu binary oxide at high concentration, it does not significantly hinder arsenic sorption when the phosphate and arsenic concentrations were in the same level. This suggests that the binary oxide has a high sorptive selectivity to arsenic and is able to remove arsenic even at high concentrations of the competing anions used in present work.

3.7. *Analysis of XPS spectra*

To verify the presence of arsenic and determine the oxidation state on the surface, XPS spectra of the Fe–Cu binary oxide before and after reaction with As(V) or As(III) were collected and analyzed. The results are shown in Fig. 7. New As3d core level peak as well as AsLMM and As3p peaks appeared in the spectra of Fe–Cu binary oxide after its reaction with As(V) or As(III), indicating clearly the presence of arsenic on the surface of the samples.

The As3d core level peaks of the Fe–Cu binary oxide after reaction with arsenic demonstrated in Fig. 8. For the samples reacted with As(V) and As(III), the As3d binding energies are 45.4 and 44.3 eV, respectively. The binding energy of As3d core level for As(V) and As(III) in arsenic oxides are reportedly 45.2–45.6 and 44.3–44.5 eV, respectively (Nesbitt et al., 1998; Ouvrard et al., 2005). Clearly, the arsenic species adsorbed on the surface of the Fe–Cu oxide after the reaction with As(V) and As(III) still remained as As(V) and As(III), respectively. Namely, no change in oxidation state of As(III) was observed during the sorption process. These results are very similar to those found by Ren et al. (2011) in the case of Fe–Zr binary oxide. However, they are different from the results reported by Martinson and Reddy (2009) in the case of pure CuO nanoparticle. They found that As(III) was completely converted to As(V) after its sorption onto the surface of CuO.

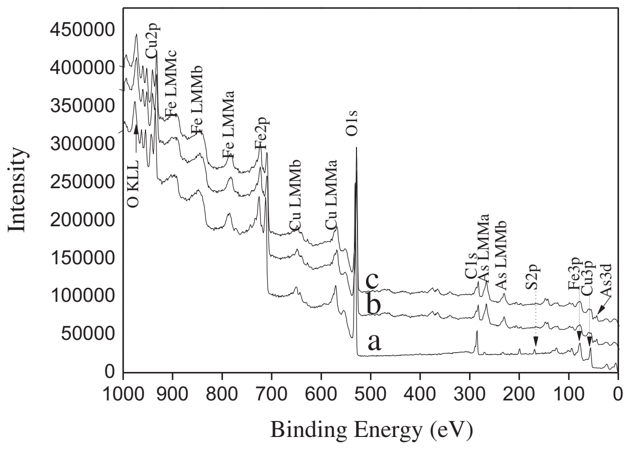

Fig. 7 – XPS spectra of Fe–Cu binary oxide (a) as prepared; (b) after reaction with As(V); and (c) after reaction with As(III).

3.8. *Regeneration and reusability of Fe–Cu binary oxide*

To evaluate the reusability of the synthetic Fe–Cu binary oxide, the adsorption capacity of the composite for arsenic

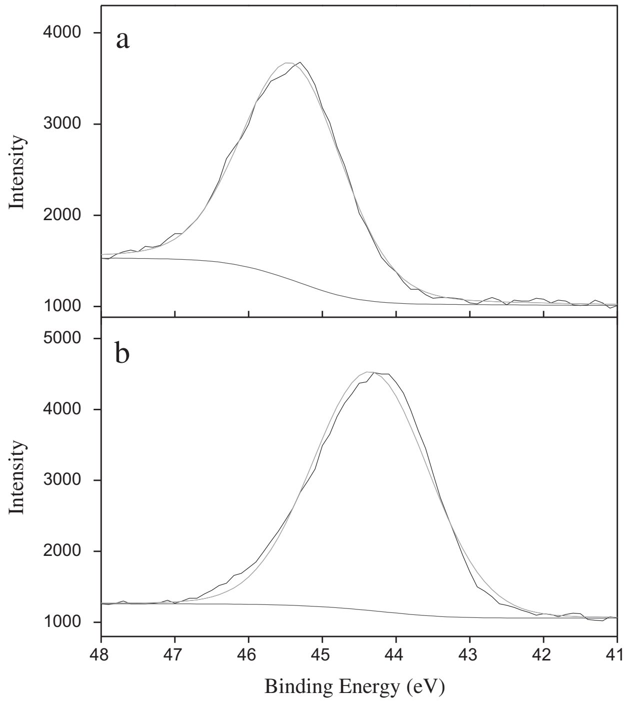

Fig. 8 – As3d core level of the Fe–Cu binary oxide (a) after reaction with As(V) and (b) after reaction with As(III).

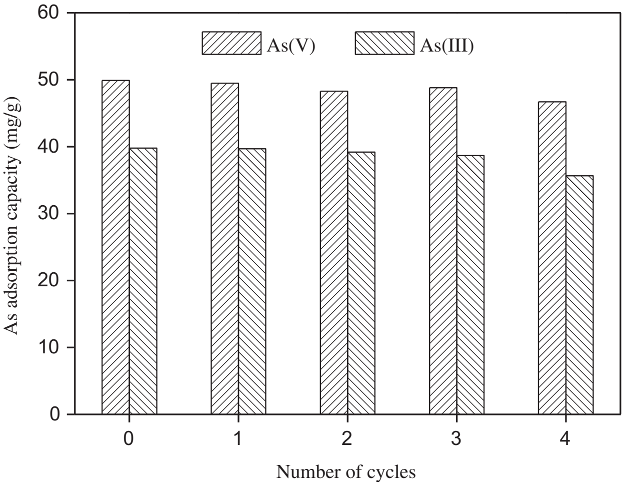

Fig. 9 – Variation of the adsorption capacity of the Fe–Cu binary oxide as a function of regeneration cycle number.

after its regeneration has also been studied. These adsorption–regeneration cycles were carried out up to four times. The results obtained are depicted in Fig. 9. The value of cycle 0 corresponds to the adsorption capacity of the fresh Fe–Cu binary oxide.

Generally, the adsorption capacity of the Fe–Cu binary oxide for arsenic decreases as the number of regeneration cycle increases. However, the decrease was not significant and after the forth regeneration, the reduction in As(V) and As(III) adsorption capacity was only 6.2% and 10.6%, respectively. These results show that the prepared Fe–Cu binary oxide could be easily regenerated via NaOH treatment and has a high durability.

4. Conclusions

A novel nanostructured Fe–Cu binary oxide was synthesized by a facile coprecipitation method. The synthetic Fe–Cu binary oxide is amorphous and 2-line ferrihydrite like. The prepared Fe–Cu binary oxide particles are aggregates formed by smaller nanosized particles and are very effective at removing both As(V) and As(III) from aqueous solution. The maximal adsorption capacities for As(V) and As(III) are 82.7 and 122.3 mg/g at pH 7.0, respectively, which outperform most of reported sorbents. The coexisting sulfate and carbonate have no great effect on arsenic removal. However, the presence of phosphate obviously reduces the arsenic removal, especially at high concentrations. Furthermore, the Fe–Cu binary oxide could be readily regenerated and repeatedly used. Due to its excellent arsenic removal performance, simple and low-cost synthesis process, and easy regeneration, the Fe–Cu binary oxide could be a promising adsorbent for both As(V) and As(III) removal from aqueous solution. Further research is currently being performed to granulate the nanostructured Fe–Cu binary oxide particles, which could be readily used in fixed beds of water treatment facilities.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2012.11.059.

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