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Arsenic sorption and redox transformation on iron-impregnated ordered mesoporous carbon

Zhimang Gu and Baolin Deng*

Department of Civil and Environmental Engineering, University of Missouri-Columbia, Columbia, MO 65211, USA

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Ordered mesoporous carbon has been actively investigated for its potential applications as catalyst supports, electrochemical materials and gas separation media. In this study, we tested an iron-modified ordered mesoporous carbon (FeOMC) for its ability to adsorb arsenic from the aqueous phase. The FeOMC synthesis involved the preparation of an ordered silica template SBA-15, *in situ* polymerization of acrylic acid in the template, carbonization and template removal to obtain the ordered mesoporous carbon, and iron impregnation. Batch experiments showed that the pH level of the solution had a major impact on arsenic sorption. Further, we found that the presence of anions (i.e. PO_4^{3-} and SiO_3^{2-}) could significantly decrease the sorption of both arsenate and arsenite. Arsenite oxidation to arsenate was observed in alkaline solutions, with or without anions being present. The oxidation of arsenite was attributed to both direct and catalytic reactions with the surface functional groups on the ordered mesoporous carbon. Adsorption of arsenic on FeOMC could be well explained by the surface complexation model.

KEYWORDS: arsenic; adsorption; surface complexation; redox transformation; ordered mesoporous carbon (OMC); iron-containing adsorbent

INTRODUCTION

With their uniform nano-pore structure, ordered mesoporous materials have attracted a good deal of attention for their potential in industrial applications.[1,2] One area of particular interest is their use in removal of contaminants.[3–5] For example, Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+} have the potential to be fixed by functionalized ordered mesoporous materials as sorbents.[6,7] Their high capacity and selectivity for target contaminants can be attributed to the specific interactions between the contaminant metals and specific surface functional groups.

Activated carbon is a common adsorbent used for pollution control in the water and air. Surface modification of carbon materials can be achieved through complexation of various surface functional groups with metal ions, promoting unique chemical, physical and biological properties and functions useful for contaminant removal.[8] For example, activated carbon modifications by ferric iron have produced advanced materials with characteristics optimized for removing arsenic from drinking water.[9–11]

Recent success with the synthesis of ordered mesoporous carbon (OMC)[12,13] has drawn attention for its industrial applications, including its potential for removing toxic contaminants—such as arsenic[14]—from water. In contrast to the mesoporous carbons prepared previously by colloidal imprinting methods with natural organic materials (sucrose, pitch, etc.),[15] our work on iron-modified OMC (FeOMC)[14] used a water-soluble industrial monomer (acrylic acid) as the source of carbon, incorporated into the porous structure of silica templates through *in situ* polymerization (Scheme 1). Subsequent iron impregnation was accomplished following an established procedure.[11] The advantages of using FeOMC include the high specific surface area with dispersed iron and the ordered nanostructure, resulting in a high arsenic adsorption capacity as well as rapid adsorption kinetics. Additionally, use of a carbon-based material overcomes the problems associated with granular ferric oxides (GFH), another common sorbent for arsenic: the weak mechanical strength and

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*Correspondence to: Baolin Deng, Department of Civil and Environmental Engineering, University of Missouri-Columbia, Columbia, MO 65211, USA.
E-mail: dengb@missouri.edu
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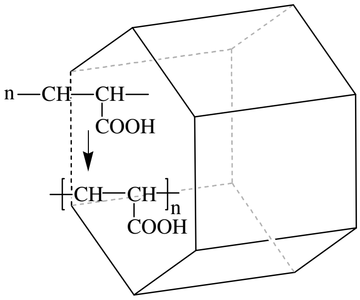

Scheme 1. *In situ* polymerization of acrylic acid monomer inside a hexagonal silica template.

breakup of GFH, which leads to the build-up of head-loss.

Continuing our previous studies, we explored arsenic sorption and redox transformation of FeOMC in this paper. Prepared FeOMC was characterized by transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR) and acid–base titration. Adsorption of arsenic was examined under various pH levels, with/without different anions (i.e. phosphate, silicate, sulfate, chloride and fluoride). Redox transformation was observed during arsenic adsorption experiments. Arsenic adsorption data were found to be represented well by the double layer surface complexation model (DLM).

EXPERIMENTAL SECTION

Synthesis of silica template, OMC and FeOMC

Silica template, SBA-15, was synthesized according to the established synthesis procedure.[16,17] Concentrated HCl (37%), H_2O and triblock copolymer Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, BASF) were mixed at a ratio of 100 ml:525 ml:20 g. Tetraethylorthosilicate (TEOS, 98%, Aldrich) was used as a silica precursor. The template SBA-15 was synthesized via a structure-directing process under hydrothermal conditions.

The synthesis of OMC was accomplished by *in situ* polymerization of acrylic acid monomer in the porous structure of SBA-15, in a basic aqueous solution. Potassium persulfate ($K_2S_2O_8$) was used as a free radical initiator for the polymerization. Polyacrylic acid (PAA) with the silica template was dried in an oven at 200 °C and then heated under N_2 flow at 700 °C for 8 h for carbonization. OMC was recovered by the dissolution of silica template using aqueous hydrofluoric acid (HF, 48%, Aldrich). The prepared OMC was used primarily as a supporting medium to prepare FeOMC by an iron impregnation procedure.[11] Jeol 2010 high-resolution TEM was used for the sample imaging. Characteristics of surface functional groups on OMC were analyzed by FTIR.

Acid–base titration

A measured amount (0.500 ± 0.0001 g) of OMC or FeOMC was suspended in 100 ml of 0.1 M $NaNO_3$ acidified with 2 ml of 0.1 M HNO_3. The adsorption system was equilibrated to a constant pH level under a protective nitrogen flow to eliminate the influence of atmospheric CO_2. The solution was stirred magnetically throughout the measurements. The titration was carried out with 0.1 M NaOH, using a Titrino 798 microburette (Metrohm, Switzerland) interfaced to a computer using Datalog software. The pH level was measured after an equilibration time of 10 min with MET mode by a Ross pH electrode.

Arsenic adsorption and redox transformation

We assessed the potential of FeOMC for arsenic removal in batch systems, using arsenate and arsenite prepared from $NaAsO_2$ and $Na_2HAsO_4 \bullet 7H_2O$, respectively. In each test, a 0.090 g adsorbent was added to a 30.00 ml arsenic solution resulting in a solid loading of 3.00 g/l. After mixing on a shaker for 24 h at 25 ± 1 °C, the sample was filtered and the filtrate analyzed for arsenic. The speciation analysis was accomplished by HPLC (Shimadzu) separation, followed by detection with hydride generation–atomic fluorescence spectroscopy (HG-AFS), using a PSA millennium analytical system (P.S. Analytical Ltd). Adsorption experiments were conducted as a function of pH with a solution of 9.98 mg/l As(III) and 9.98 mg/l As(V). We assessed the effect of co-anions on arsenate removal using three oxyanions (PO_4^{3-}, SiO_3^{2-}, SO_4^{2-}) and two halide anions (Cl^-, F^-). We also evaluated arsenite oxidation as a function of pH.

Surface complexation modeling of arsenic adsorption

The adsorption of ionic species onto hydrous iron oxides is influenced by both chemical and electrostatic interactions at the solid surface. Arsenic adsorption onto oxide surfaces occurs via a ligand exchange mechanism, forming an inner-sphere surface complex.[18] We based the modeling effort in this study on this concept, using known acid constants for surface hydroxyl groups and aqueous species.[19,20] The computer software FITEQL (version 4.0)[21] was used to obtain the intrinsic arsenic surface complexation constants. The model calculations used molar concentrations, with solution and adsorption equilibrium constants adjusted for the ionic strength of 0.1 mol/l, using the activity coefficients as given in Dzombak and Morel.[22] While both monodentate and bidentate bridging surface species might be present for arsenic adsorbed onto amorphous iron,[23,24] the modeling here assumed only monodentate complexation.

RESULTS AND DISCUSSION

TEM and FTIR characterization

As seen in the TEM micrographs in Fig. 1(a), the prepared silica templates clearly showed the existence of long-range orders and uniform mesoporous structures of SBA-15. Carbon particles derived from PAA impregnation into the SBA-15 template maintained the highly ordered two-dimensional

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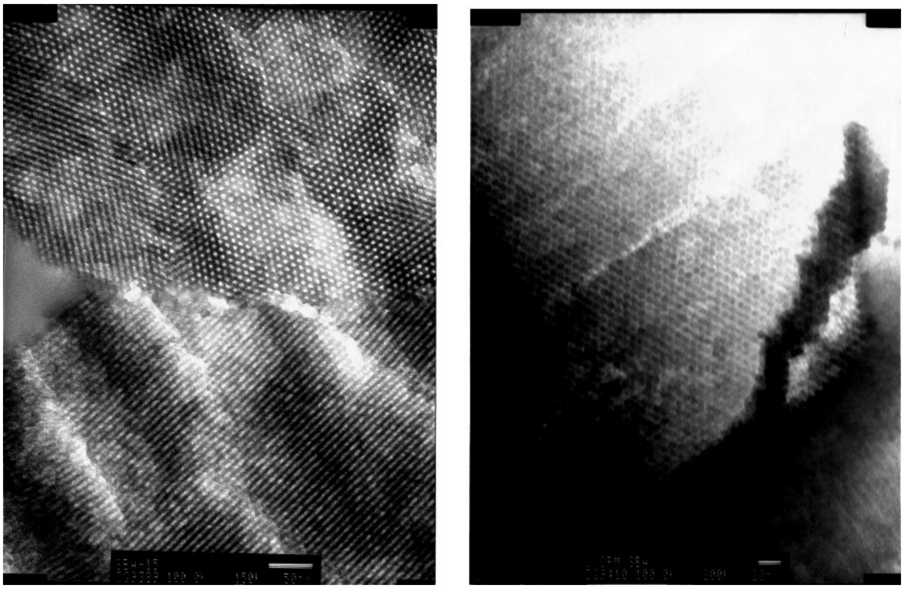


(a) (b)

Figure 1. TEM micrographs of (a) SBA-15 and (b) OMC.

hexagonal symmetry of the parent SBA-15 [Fig. 1(b)]. The carbon was an inverse replica of the original template and had an average pore size of 4.10 nm, as determined by BJH analysis. The synthesized OMC from the SBA-15 template had a structure similar to CMK-3.[25] Compared with OMC, FeOMC has a smaller but comparable pore volume and specific surface area. The pore volume decreased from 0.62 to 0.46 cm^3/g and the BET surface area decreased from 607 to 466 m^2/g, following iron impregnation. The original carbon structure was maintained, as indicated by their similar nitrogen adsorption/desorption patterns.[17]

FTIR analysis was conducted to obtain a better insight into the surface characteristics of synthesized ordered mesoporous carbon. As summarized in Table 1, the FTIR spectra are dominated by functional groups with carbon–oxygen–hydrogen atoms. The absorption band detected at 3400–3700 cm^{-1} is assigned to –OH. Another major band at 1618 cm^{-1} is attributed to a carboxylate group or quinone functional groups. Both of these two bands became weaker after iron impregnation, indicating iron complexation with these functional groups.

Table 1. FTIR characteristics of synthesized ordered mesoporous carbon

Wave number of OMC (cm^{-1})	Peak style	Functional groups assignment
3735	Small sharp peak	ν(OH)
3433	Broad band	ν(OH) or ν(NH)
3118	Shoulder peak	δCOOH
2911, 2843	Two small sharp peaks	νC–H ($-CH_2$, $-CH_3$)
1618	Major peak	νC=O or C=C
1399	Major sharp peak	δ(–CH)
1108	Major peak	ν (–C–OH)
781	Small sharp peak	δ(=C–H)

Acid–base titration of adsorbents

Raw titration data were transformed into proton binding isotherms using a proton balance equation and a blank as reported.[26] In the system with OMC or FeOMC, the mean surface charge can be calculated as a function of pH, from the difference between total added base or acid, and the equilibrium OH^- and H^+ ion concentration for a given quantity of solid a (g/l).

$$Q_{(\mathrm{OMC})} = \frac{[-\mathrm{COH_2}^+] - [-\mathrm{CO}^-]}{a_{\mathrm{OMC}}} = \frac{(C_\mathrm{A} - C_\mathrm{B} + [\mathrm{OH}^-]_\mathrm{e} - [\mathrm{H}^+]_\mathrm{e})(V_0 + V_t)}{m_{\mathrm{OMC}}} \quad (1)$$

$$Q_{(\mathrm{FeOMC})} = \frac{[\equiv\mathrm{CFeOH_2}^+] + [-\mathrm{COH_2}^+] - [\equiv\mathrm{CFeO}^-] - [-\mathrm{CO}^-]}{a_{\mathrm{FeOMC}}} = \frac{(C_\mathrm{A} - C_\mathrm{B} + [\mathrm{OH}^-]_\mathrm{e} - [\mathrm{H}^+]_\mathrm{e})(V_0 + V_t)}{m_{\mathrm{FeOMC}}} \quad (2)$$

where [] indicates concentrations of solute and surface species per unit volume solution (M), C_A is the added acid (M), C_B is the added base (M), V_0 and V_t are the volumes of background electrolyte and titrant added, respectively, m is the mass of the adsorbent and $[\mathrm{H}^+]_\mathrm{e}$ and $[\mathrm{OH}^-]_\mathrm{e}$ are the proton and hydroxyl group equilibrium concentrations, respectively, which were calculated from the measured pH level. The ionic strength

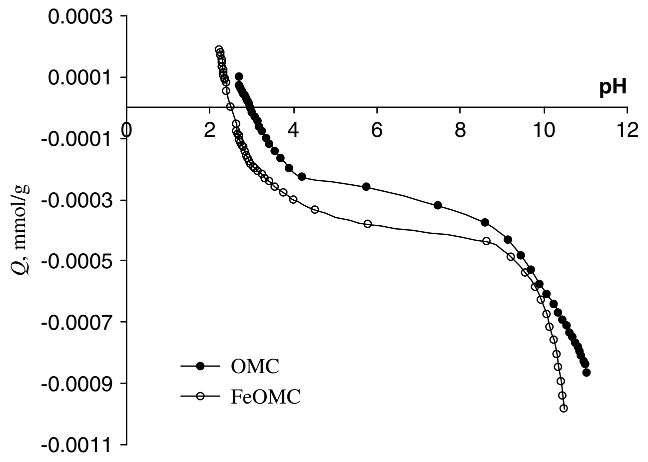


Figure 2. Net surface charges of OMC and FeOMC in solutions with ionic strength of 0.01 M controlled by $NaNO_3$.

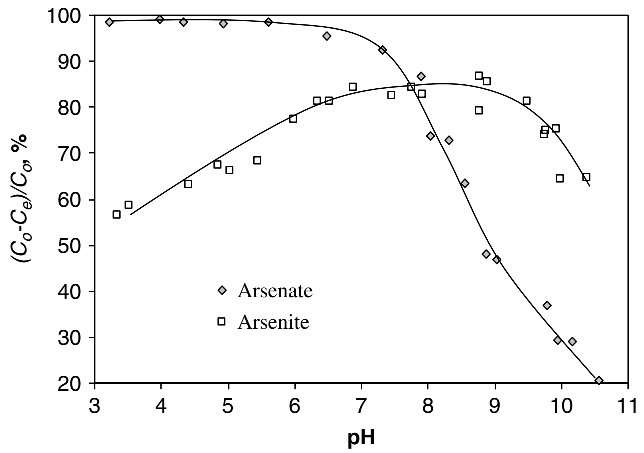


Figure 3. Effects of pH on the arsenic removal of total arsenic in pure As(III) and As(V) solutions {0.01 M $NaNO_3$, original [As(III)] and [As(V)] are both 9.98 mg/l}.

was corrected using Davis' equation:

$$\log f = 0.5 \times \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.2I\right)$$

The resulting surface charges of original OMC and FeOMC from proton binding are shown in Fig. 2, covering a pH range from 2.0 to 11.0. The pH at the point of zero charge (pH_{pzc}) is 2.97 for OMC, indicating that the carbon surface is negatively charged at near neutral pH. The pH_{pzc} is decreased to 2.50 for FeOMC following iron impregnation. The low pH_{pzc} of FeOMC must be caused by the particular preparation process of the sample, in which acetic acid was used to strengthen the complex of iron oxides and carbon material. Since arsenate ($H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-}) and arsenite (H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{2-}$, AsO_3^{3-}) are either negatively charged or neutral,[27] arsenic adsorption on FeOMC at a pH higher than 2.5 must be caused by strong specific chemical interactions, overcoming the unfavorable electrostatic repulsion of negatively charged surfaces.

Redox transformation during adsorption by FeOMC

The effects of pH levels on arsenate [As(V)] or arsenite [As(III)] removal by FeOMC were examined at an initial arsenic concentration of 9.98 mg/l. The pH level of the solution was adjusted by HNO_3 and NaOH and the ionic strength was controlled by 0.01 M $NaNO_3$. As shown in Fig. 3, in the arsenate tests, over 95% arsenate removal was measured after 24 h in all acidic solutions, from pH 3.0 to 7.0; removal rates gradually decreased to approximately 30% with increases in the pH level from 7.0 to 10.0. There was no As(III) detected in the final solution, suggesting that As(V) was not reduced under the experimental condition.

Arsenite adsorption increased from 55 to 80% with increasing pH, from 3.5 to 6.5. Adsorption levels stabilized at a maximum level in the pH range of 6.5–9.5, and decreased as pH was further increased. The pH edge of As(III) was significantly different from that of As(V), which suggests the interactions of different arsenic species with the adsorbent are different. Since the pH_{pzc} for FeOMC is 2.50 and the surface is always negative in the pH range examined, the different patterns reflect different forces of interaction for As(V) and As(III) with the surfaces.

Interestingly, in our As(III) adsorption tests, As(V) could be detected in the final solution when the pH level was higher than 8.9 (Fig. 4). Clearly, some of As(III) has been oxidized to As(V) in the presence of FeOMC. The oxidized fraction is relatively small within the 24 h of the experiment, but may partially explain the observed decrease of As(III) sorption in Fig. 3, because sorption of As(V) is minimal in the alkaline solutions where As(III) oxidation has taken place.

As(III) oxidation was observed in our system, but not As(V) reduction. In many other environmental systems, however, redox conditions and biological activities could affect arsenic redox speciation differently. The presence of As(III) may be maintained in oxygenic waters by biological reduction of As(V), particularly in the summer.[28] Under some other conditions, oxidation of As(III) could occur rapidly, through microbial activity.[29] Organic forms of arsenic are minor in surface waters, generally produced by microorganisms.[30]

The sorption of As(V) and As(III) onto FeOMC may be similar to their sorption onto iron oxides, which is also strongly affected by pH levels.[19] This finding is not surprising, since the adsorption by FeOMC is caused primarily by impregnated iron oxides through formation of different surface complexes, such as bidentate complex or non-protonated bidentate complex.[31] The contribution of carbon itself is minimal.[17] As(III) could also be oxidized to As(V) on the surface of iron oxides under the strong alkaline condition.[32]

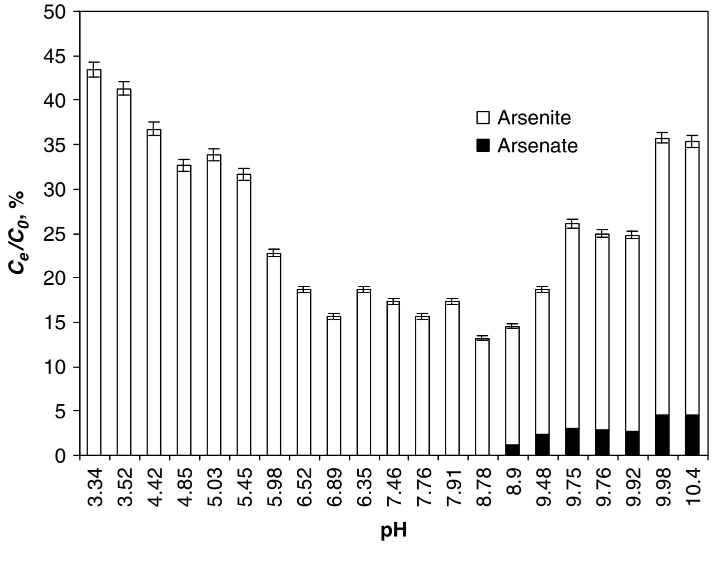


Figure 4. Effects of pH level on arsenic redox transformation during As(III) adsorption.

Table 2. Effects of anions on the arsenic removal by FeOMC

		Arsenic Removal (%)				
	Anion (mmol/l)	PO_4^{3-}	SiO_4^{3-}	SO_4^{2-}	Cl^-	F^-
Arsenite	0	81.5	81.5	81.5	81.5	81.5
	0.1	71.9	77.5	74.9	73.9	74.58
	1.0	66.3	72.2	72.8	74.3	74.27
	10	45.5	56.9	70.4	72.7	73.99
Arsenate	0	99.0 ± 1.0	99.0 ± 1.0	99.0 ± 1.0	99.0 ± 1.0	99.0 ± 1.0
	0.1	99.5 ± 0.5	99.5 ± 0.5	99.5 ± 0.5	99.5 ± 0.5	99.5 ± 0.5
	1.0	83.4	95.8	99.5 ± 0.5	99.5 ± 0.5	99.5 ± 0.5
	10	59.2	70.6	99.2	99.5 ± 0.5	99.5 ± 0.5

Effects of anions on the arsenic removal

Three oxyanions (SO_4^{2-}, PO_4^{3-}, SiO_3^{2-}) and two halide anions (Cl^-, F^-) were selected to assess the effects of co-anions on arsenate and arsenite adsorption. At a fixed pH level of 6.5, the effects of different anions at three concentration levels (0.1, 1.0 and 10 mM; Fig. 5) showed that 1.0 and 10 mM of phosphate and silicate decreased As(V) adsorption. The effects of sulfate, chloride and fluoride, even at 10 mM concentration, were minimal under the experimental conditions. When compared with As(V), As(III) adsorption was influenced to a lesser degree by all anions (Table 2). The results in Table 2 indicated that the amounts of As(V) and As(III) adsorbed were reduced by phosphate and silicate to a similar extent. When phosphate concentration increased from 0.1 to 10 mM, As(III) and As(V) adsorption were reduced by 37 and 40%, respectively. When silicate concentration increased from 0.1 to 10 mM, As(III) and As(V) adsorption were reduced by 27 and 29%, respectively.

The effect of phosphate was further examined as a function of pH. With 1.0 mM total phosphate, the percentage

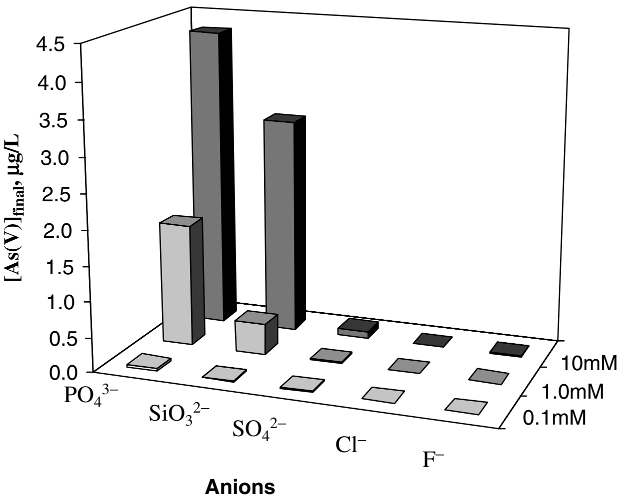
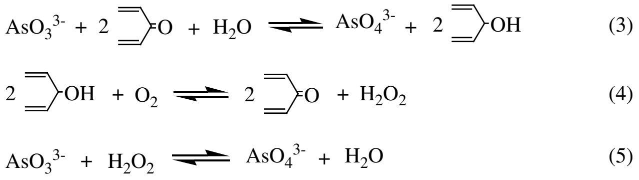


Figure 5. Effects of different anions on the final arsenic concentration from initial arsenate (5040 μg/l; pH 6.5; 3.0 g/l of FeOMC with 3.85% iron).

removal of As(V) decreased dramatically in the pH range of 3–11 (Fig. 6), when compared with the system without phosphate (Fig. 3). For arsenite, phosphate not only decreased the adsorption amount (comparing Figs 6 and 3), but also accelerated the rate of As(III) oxidation (Fig. 7). When the pH was higher than about 7, arsenate was detected in the final solution. With increasing pH levels, an increasing amount of As(V) was detected in the final solution.

Additional experiments showed that arsenite could be oxidized to arsenate by FeOMC directly, under anoxic conditions in alkaline solutions (data not shown), indicating that the surface oxidative functional groups are the main oxidants for As(III) oxidation. The rate of As(III) oxidation in the presence of O_2 was higher than that in the anaerobic system. Since direct As(III) oxidation by the dissolved oxygen in the aqueous phase was insignificant during the experimental time period, this result suggests that the reactive moieties on FeOMC had a catalytic effect on As(III) oxidation. The catalytic mechanism for the oxidation of arsenite by FeOMC is hypothesized to follow reactions (3)–(5), where the quinone group is first reduced to hydroquinone with concurrent arsenite oxidation, and then hydroquinone is oxidized by oxygen,[33] regenerating endoperoxide intermediate[34] and quinone capable of more arsenite oxidation.



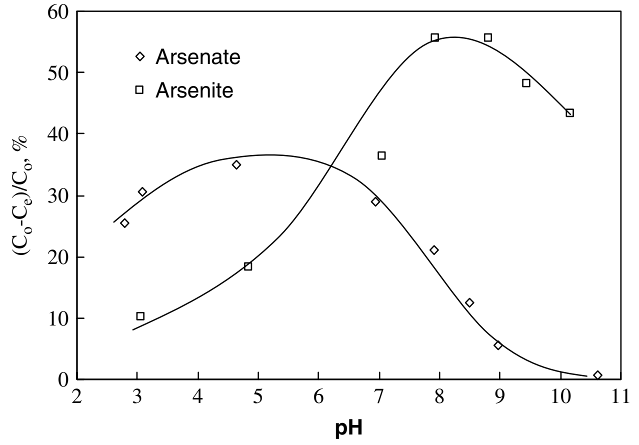


Figure 6. Effects of pH level on the arsenic removal with 10 mM phosphate {0.01 M $NaNO_3$, original [As(V)] is 10.5 mg/l and [As(III)] is 10.2 mg/l}.

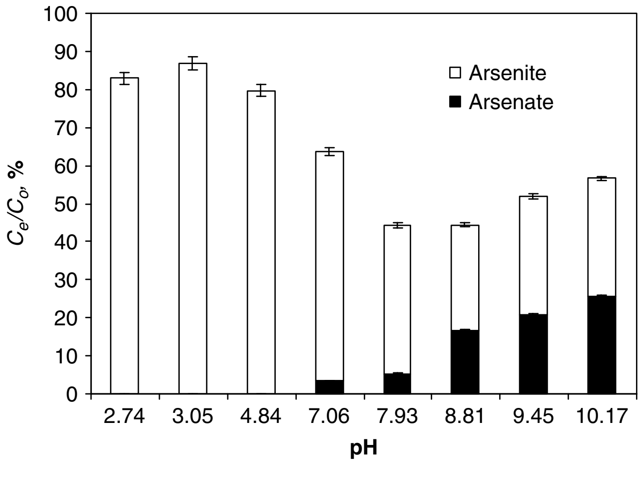


Figure 7. Effects of pH level on arsenic speciation transformation with 0.1 mM phosphate {0.01 M $NaNO_3$, original [As(III)] is 10.2 mg/l}.

In the acidic solution, the excess protons impeded the oxidation and catalytic activities of the carbon surface functional groups.[35] With increasing pH, the functional groups were released from the impediment of protons, and the oxidation and catalytic activities increased in alkali solutions. The production of hydroquinone from quinone [reaction (3)] was prohibited in the acidic solution, so the whole catalysis and oxidation happened more slowly.

Modeling of arsenic adsorption

The adsorption of arsenic by FeOMC can be explained by the surface complexation model. The stoichiometries of the surface complex reactions used to fit sorption data are listed in Table 3. The intrinsic arsenic surface complexation constants were obtained and optimized by the computer program FITEQL version 4.0. The model fits the data well, as illustrated in Fig. 8. For the total arsenic concentration of 1.33×10^{-4} M, the reactive surface sites are always in excess of the total arsenic left in bulk solution. The results show that, for As(V), the sorbed species is mainly $=X-(HAsO_4^{-})$ at pH levels lower than 7.2 and $=X-(AsO_4^{2-})$ at higher levels of pH. For As(III), the sorbed species is mainly $=X-(HAsO_3^{-})$ at pH levels lower than 5.8 and $=X-(AsO_3^{2-})$ at higher levels of pH. Since partial oxidation of arsenite to arsenate occurred when the pH was higher than 8.9 (Fig. 4), the effects of redox reaction on the adsorption should be analyzed. The results in Fig. 4 showed that about 2% of arsenic could be detected as arsenate in the final solution at a pH level of 8.9. Based on the arsenate adsorption ratio at this pH [Fig. 8(a)], adsorbed arsenate coming from arsenite oxidation is about 2%. Because the total adsorbed arsenite is more than 75% [Fig. 8(b)], the effects of arsenite oxidation and subsequent adsorption can be ignored for arsenite modeling. When the pH level is higher than 9.0, the adsorption of arsenate markedly decreased with increasing pH [Fig. 8(a)]. The detected concentration of arsenate in the arsenite system was low, so the adsorbed arsenate derived from arsenite oxidation was not high and adsorbed arsenic could be modeled as arsenite [Fig. 8(b)].

Table 3. Experimental conditions and complexation reactions

Specific surface area (m^2/g)	466	As(V)	
Solid concentration (g/l)	3.0	mol As per mol Fe	0.042
Equilibrium time (h)	24	sites per nm^2	0.037
Total arsenic concentration (μM)	10–100	As(III)	
Fe content (mg/g)	38.5	mol As per mol Fe	0.053
		sites per nm^2	0.047

Intrinsic surface complexation reactions	log *K*
$\equiv CFeOH + AsO_4^{3-} + 3H^+ = \equiv CFeH_2AsO_4 + H_2O$	28.9 ± 0.12
$\equiv CFeOH + AsO_4^{3-} + 2H^+ = \equiv CFeHAsO_4^- + H_2O$	25.7 ± 0.06
$\equiv CFeOH + AsO_4^{3-} + H^+ = \equiv CFeAsO_4^{2-} + H_2O$	18.7 ± 0.05
$\equiv CFeOH + AsO_3^{3-} + 3H^+ = \equiv CFeH_2AsO_3 + H_2O$	32.2 ± 0.16
$\equiv CFeOH + AsO_3^{3-} + 2H^+ = \equiv CFeHAsO_3^- + H_2O$	26.6 ± 0.10

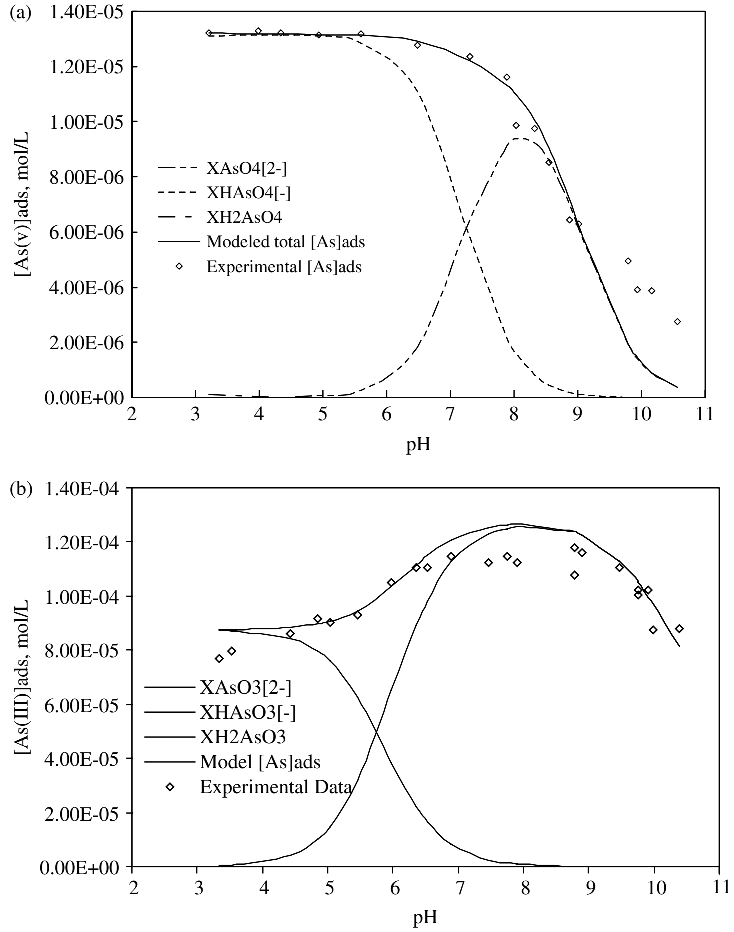


Figure 8. Fit of model of (a) arsenate and (b) arsenite adsorption on FeOMC (X is the adsorption sites, curves are modeled using the surface complexation model).

CONCLUSIONS

In this study, we examined arsenic sorption onto FeOMC, a new nanostructured adsorbent made of OMC, prepared from *in situ* polymerization of mono acrylic acid in the porous structure of silica template SBA-15. The prepared OMC and FeOMC have an ordered mesoporous structure and various functional groups, including phenol, quinone and carboxylic acid. We found the pH level of the solution to have a strong effect on the removal of both As(V) and As(III) species from water. The presence of phosphate and silicate at concentrations higher than 1.0 mM notably decreased arsenic adsorption. Adsorption of arsenate and arsenite as a function of pH level could be explained by the surface complexation model. A small fraction of arsenite is oxidized in the system with FeOMC, while no arsenate reduction occurred.

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