Porous Nanobimetallic Fe–Mn Cubes with High Valent Mn and Highly Efficient Removal of Arsenic(III)

Gong Zhang,^{†,‡,||} Xiufang Xu,^{†,⊥} Qinghua Ji,^{#,||} Ruiping Liu,^{*,#,||} Huijuan Liu,^{‡,||} Jiuhui Qu,^{#,||} and Jinghong Li^{*,§,||}

[‡]State Key Laboratory of Environmental Aquatic Chemistry and [#]Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

[§]Department of Chemistry, Beijing Key Laboratory for Microanalytical Methods and Instrumentation, Tsinghua University, Beijing 100084, China

[⊥]Department of Chemistry, Nankai University, Tianjin 300071, China

^{||}University of Chinese Academy of Sciences, Beijing 100039, China

S Supporting Information

ABSTRACT: Iron (Fe) oxides are the most commonly used adsorbent materials for the aqueous removal of Arsenic (As), but they have deficiencies, including low uptake and poor removal of the relatively higher toxicity As(III). Introduction of transition metals into Fe-containing adsorbents, an inexpensive method of altering Fe chemical states, is likewise of interest for removing As(III) from water by means of adsorption. Porous cubic Fe–Mn structures with BET surface area of 450 m² g^{−1} were herein prepared via chemical etching of Mn-substituted Prussian Blue analogues (PBAs). Cyclic voltammetry showed a “protective” role of polyvinylpyrrolidone (PVP) during the preparation process, so that Mn with high valence state was readily preserved in this binuclear corner-sharing structure. The calculated reaction Gibbs free energy, which was the most negative of the studied adsorbents, indicated that the adsorption was promoted in the presence of high valence Mn. The structures were capable of directly capturing As(III) oxyanions to below the acceptable limits in drinking water standards, and the saturation uptake capacity of 460 mg g^{−1} was substantially higher than comparable materials under consideration. The work therefore presents a new benchmark for As-adsorbent materials and demonstrates the promise of the porous Fe–Mn structure for rapid removal of other metal ions from contaminated water for environmental remediation.

KEYWORDS: Prussian blue, porous structure, adsorption, arsenic(III), remediation

INTRODUCTION

Because of its potentially toxic and carcinogenic effects, contamination of the aquatic environment by inorganic arsenic derived from natural processes and anthropogenic sources has dire consequences to public health worldwide.¹ Inorganic oxyanions of trivalent arsenite (H₃AsO₃, As(III)) and pentavalent arsenate (AsO₄^{3−}, As(V)) are commonly found in natural waters.² As(III), with much higher toxicity, is dominant in reduced groundwater, whereas the As(V) contaminant is the major arsenic species in oxygenated water.³ Adsorption is considered the most promising approach for aqueous removal of As(III), and the adsorption process between sorbents and arsenic mainly involves complexation or ion exchange with the active groups (hydroxyl groups) on the surface.^{4,5} A wide range of metallic oxides have therefore been developed for efficient As immobilization, such as MgO,⁶ Al₂O₃,⁷ ZrO₂,⁸ and Fe₂O₃,⁹ as well as nanostructured bimetallic oxides.^{10,11}

Until now, the Fe–Mn binary oxide (FMBO) sorbent, with the adsorption capacity of ~150 mg g^{−1}, has been the benchmark for highly effective removal of As(III). The combination of

Mn(IV)O₂ with Fe oxide has the potential for converting the As(III) to As(V) at the solid–liquid interface, which is the prerequisite for effectively transporting As to the Fe oxide surface.¹² Hence, the precise regulation of Mn chemical state is significant in the removal of As(III) using Fe–Mn complex oxides. In a typical FMBO preparation process, the bulk FMBO materials can be obtained via the redox reaction between Fe²⁺ and KMnO₄. In view of its strong oxidation ability, is the KMnO₄ reduction process generally involves production of Mn(IV). The FMBO adsorbent inevitably faces various sorts of handicaps difficulties such as low surface area and uneven distribution of Mn species with low valence, thereby limiting its effectiveness and efficiency for removal of As(III). To preserve high valence Mn species, an alternative reaction between Fe²⁺ and Mn(VII) should be applied for the preparation of novel Fe–Mn complexes.

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Figure 1. Formation of PB (Prussian blue) and its analogues (Mn-doped PB) after hydrothermal reaction: FESEM images of (a) the $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ and (b) Mn-doped PB cubes; (c) XRD patterns of PB and Mn-doped PB analogue with (d) the detailed crystalline information.

Prussian blue analogues (PBAs), a family of cyanide-bridged coordination polymers, have great potential to combine Mn and Fe with different chemical states.^{13,14} Mixed-valence FeMn Prussian blue should be rich in microporosity and open metal coordination sites, which provide abundant channels for entrance of OH^- ions, so that Fe–Mn complexes can be formed after $\text{Fe}(\text{CN})_6^{4-}$ diffuses out. In addition, structures with large enclosed cavities and thin shells on the surface are of significance due to the potential for exposing a large number of sites for reaction or adsorption.^{15–17} Templating methods have been considered as a representative approach toward controlling the structures of materials with multiple components.^{18–20} Various cavities can be created in solid templates via manipulation of physiochemical and chemical properties between the templates and shell materials. In particular, PBAs are inorganic–organic hybrid materials with high surface area, and might be therefore applicable as templates for the preparation of ideal structures.^{21–23} Research has shown that structure control and tuning of composites made from sacrificial PBA templates have been effective methods, resulting in materials with improved performance that can be utilized in various domains.^{24–26}

By chemically etching FeMn Prussian Blue (PB), we herein prepared a porous-structured Fe–Mn porous complex (FMPC) for aqueous removal of As(III). A superior As(III) removal efficacy with adsorption capacity of 460 mg g^{-1} can be achieved using FMPC as adsorbent. The preservation of high valence Mn in the Fe–Mn complex produced a more negative value for the Gibbs free energy of the adsorption reaction with the trivalent arsenic. The high surface area and permanent porosity of the sorbent enabled the rapid removal of As(III) from aqueous solutions. In contrast to the two-step removal path in FMBO, the framework constructed by Fe and Mn in the FMPC possessed trap sites for directly capturing As(III) oxyanions.

RESULTS AND DISCUSSION

A brilliantly colored solid pigment, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$, is prepared by the addition of ferric ions to an aqueous ferrocyanide solution.

The structure of the pigment comprises a cubic lattice of alternating Fe^{2+} and Fe^{3+} ions that are connected by cyanide bridges.²⁷ In the framework, nearly one-quarter of the $[\text{Fe}(\text{CN})_6]^{4-}$ units are missing in the unit cell.²⁸ Water molecules bonded with unsaturated Fe^{3+} ions are often located at the true center in each cubic octant of the unit cell, which are readily removed by exchange, and thereby the Fe^{3+} can be easily replaced. In the presence of KMnO_4 , Mn-doped PB cubes were obtained through partial substitution of Mn for Fe. Scanning electron microscopy (SEM) images of PB and Mn-doped PB structures are shown in Figure 1a, b. The morphologies of two structures were composed of cubic and oval-shaped particles with sizes of 200 and 250 nm, respectively. The larger size of Mn-doped PB was mainly due to the substitution of Mn ions, with a larger ionic radius than Fe ions. The crystallography and phase information on the PB products were further investigated by X-ray powder diffraction (XRD) (Figure 1c). The same characteristic diffraction pattern of a face-centered cubic phase with space group $Fm3m$ was observed, with the only change being an increase in the lattice constant, indicating that the introduction of Mn into the PB crystal lattice did not change the crystal phase (Figure 1d).²⁹

To investigate the Mn doping process, UV–visible spectrophotometry was first applied to gain insight into the reaction. At room temperature, addition of a certain amount of PVP to the acidic KMnO_4 solution resulted in a color change from purple to brown. The characteristic peak belonging to MnO_4^- at 525.3 nm

Figure 2. (a) UV-vis spectral change of KMnO_4 in the presence of PVP. (b) ^{13}C NMR spectra for PVP, PVP, and KMnO_4 mixture, and product after reaction with $\text{K}_4\text{Fe}(\text{CN})_6$. Inset: high resolution at C-4 position in PVP molecular. (c) Cyclic voltammetry (CV) of KMnO_4 , KMnO_4 -PVP mixture, and KMnO_4 -PVP- $\text{K}_4\text{Fe}(\text{CN})_6$ solutions at pH 1.0. (d) Photographs of red light irradiated the three mixtures in quartz vessels. Transparent mixture can be obtained in the presence of PVP, in stark contrast to the plenty of black sedimentation in the absence of PVP.

gradually vanished in the presence of PVP, indicating the chemical or physical transformation of KMnO_4 induced by the ligands of PVP molecules (Figure 2a).^{30,31} The possible intermediates produced by KMnO_4 oxidation were then evaluated by ^{13}C nuclear magnetic resonance spectroscopy. However, in comparison with the PVP solution, no obvious peak shifts or emerging peaks were observed in the PVP- KMnO_4 mixture (Figure 2b), and the possibility of a redox reaction was thereby ruled out. The disappearance of the characteristic peak in the UV spectrum could most likely be attributed to chelation between $-\text{CN}$ and MnO_4^- , which can be observed by the slightly changed fine structure at the $-\text{C}=\text{O}$ position (C-4).³²

Cyclic voltammetry (CV) was then performed in detail for solutions of KMnO_4 , KMnO_4 -PVP, and KMnO_4 -PVP- $\text{K}_4\text{Fe}(\text{CN})_6$. The CV curve for the KMnO_4 solution showed a distinct peak around 0.82 V vs Ag/AgCl, corresponding to $\text{Mn}(\text{VII})/\text{MnO}_2$ reduction (Figure 2c). The characteristic peak corresponding to $\text{Mn}(\text{VII})/\text{MnO}_2$ vanished after the introduction of PVP, indicating inhibition of the strong oxidation ability of KMnO_4 . After introduction of $\text{Fe}(\text{CN})_6^{4-}$, new redox peaks appeared around 0.42 and 0.72 V. The oxidation peak at 0.42 V can be assigned to $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}^{3+}$, whereas the reduction peak with much higher current density at 0.38 V was attributed to $\text{Fe}^{3+}/\text{Fe}^{2+}$. The peak at 0.72 V was much lower than the oxidation peak of $\text{Mn}(\text{VII})/\text{MnO}_2$, and was possibly derived from $\text{Mn}(\text{VI})/\text{Mn}(\text{VII})$ oxidation. However, no reduction peak was observed in its CV curve, which was mainly the result of the strong chelation effect. The weakened oxidation ability prevented the violent reaction between KMnO_4 and $\text{Fe}(\text{CN})_6^{4-}$, in stark contrast to the rapid emergence of black MnO_2

sedimentation in the absence of PVP (Figure 2d). The formation process of FeMn PB can be therefore deduced as the following

Generally, PB cubes are insoluble in neutral or acidic water, with an extremely small solubility constant ($K_{\text{sp}} = 3.3 \times 10^{-41}$). In high pH conditions, PB undergoes an ion exchange reaction

Because of the inward diffusion of OH^- and outward migration and precipitation of $\text{Fe}(\text{OH})_3$ to form a shell, the solid cubes gradually converted to hollow structures with large interior cavities by means of chemical etching.³³ A $\text{Fe}(\text{OH})_3$ hollow structure comprising numerous sheetlike subunits was eventually formed (Figure S1). FeMn PB cubes followed a similar reaction route. Both Fe and Mn in the Mn-doped PB cubes were readily associated with hydroxide ions, so that the Fe-Mn complex precipitate was obtained. However, compared with the reaction between OH^- and PB, in the presence of Mn, the route of outward migration of Fe aggregates to the shell was partially blocked, leading to a porous structure instead.

SEM and transmission electron microscopy (TEM) confirmed the presence of a porous cubic structure with particle size around 200 nm (Figure 3a, b). Moreover, the porous structure exhibited exceptionally high N_2 uptake ($150 \text{ cm}^3 \text{ g}^{-1}$), and the surface area was calculated to be $450 \text{ m}^2 \text{ g}^{-1}$ by applying the BET model

Figure 3. Formation of porous Fe–Mn structures by sacrificing FeMn PBAs. (a) SEM and (b) TEM images of porous Fe–Mn structures; (c) N_2 gas sorption isotherm taken at 77 K temperature and corresponding pore distribution (inset); (d) the first-order derivatives of Mn K-edge XANES in Mn-containing samples; (e) Fourier transform of Fe and Mn K-edge extended EXAFS oscillations.

(Figure 3c),³⁴ which was much higher than the value of $150 \text{ m}^2 \text{ g}^{-1}$ in the $\text{Fe}(\text{OH})_3$ hollow structure and other Fe- or Mn-containing sorbents (Table S1). Energy-dispersive X-ray spectroscopy (EDS) analysis further revealed an even distribution of Fe, Mn, and O elements (Figure 3b, inset), with an atomic ratio of Fe to Mn around 3.0.

The X-ray absorption near-edge structure (XANES) technique is sensitive to the local electronic configuration of the photoabsorbing atom, thereby the valence state, chemical bonding character, and local Mn or Fe coordination can be revealed in the Fe–Mn complex.^{35,36} As shown by the first-order derivative plots of Mn–K XANES in Figure 3d, the absorption edge energy of Mn in the Fe–Mn complex was 6558.8 eV, so that a Mn valence state between Mn(IV) and Mn(VII) was confirmed based on the linear fitting calculation.^{37,38} Figure S3 exhibits the XPS spectra obtained from the Fe–Mn complex and MnO_2 reference. Red shifted peaks of Mn 2p_{3/2} and Mn 2p_{1/2} corresponded to higher Mn chemical valence state in Fe–Mn complex, which was in well agreement with XANES result. In contrast, the edge energy in the first-order derivative of Mn–K

XANES in the Fe–Mn binary oxide at 6550.6 eV corresponded to a valence state between +3 and +4.¹¹ Meanwhile, the pre- and post-edge regions of Fe K-edge XANES in the samples were almost the same as that in the hollow $\text{Fe}(\text{OH})_3$. The edge jump at 7127.0 eV is more pronounced, as shown explicitly in the first derivatives of the XANES spectra, indicating the existence of Fe(III) in all samples (Figure S4).

Extended X-ray absorption fine structure spectroscopy (EXAFS) measurements were performed to investigate atomic arrangements around photoabsorbers (Fe, Mn). Figure 3e bottom shows the k^3 -weighted EXAFS oscillations Fourier-transformed (FT) into R space for the Mn K-edge. Observed peaks at 1.5 and 2.5 Å in FT spectra corresponded to Mn–O and Mn–Mn distances, respectively.³⁹ In contrast to MnO_2 , the peaks slightly shifted to lower values in FMBO and FMPC, indicating the changed chemical states around the Mn atoms. To perform curve-fitting analysis, the spectra were then Fourier-transformed into k space. A two-shell model composed of Mn–O and Mn–Mn with six coordination was adopted for fitting. The Mn–O distance was fitted at around 1.89 Å in MnO_2 , while

Table 1. Gibbs Energy Changes for the Model Reactions of Forming Different Fe–O–Mn Structures

Entry	Reaction type	$\Delta_r G$ (kcal/mol)	Structure of complex
1	$\text{Fe}(\text{OH})_3 + \text{MnO}_4^{2-} \rightarrow$ cpx0a	−99.60
2	$\text{Fe}(\text{OH})_3 + \text{MnO}_2 \rightarrow$ cpx0b	50.79

^aNote: We designed two model geometries (denoted as **cpx0a** and **cpx0b**) for the Fe–Mn complex with different Mn valence states (IV, VII), and calculated Gibbs free energy changes for the model reactions of forming cpx0a and cpx0b structures by performing DFT computations.

it increased to 1.91 and 1.90 Å in FMBO and FMPC, respectively. The missing Mn–O coordination in the Fe–Mn complex was due to an unsaturated or disordered surface in the presence of Fe.⁴⁰ Additionally, the new peak at 3.31 Å was attributed to Fe–O–Mn coordination.

According to the Fourier transform (FT) function, peaks between 2.0 to 3.0 Å corresponding to the second Fe–Fe shell are well preserved in all of the samples. However, the Fe–Fe shell in FMPC was obviously smaller than that in FeOOH, indicating the reduced Fe–Fe bond length. With the presence of Mn, the intensity of the third Fe–Fe shell peak in 3.3 Å was decreased in FMBO, and disappeared in FMPC. This indicates that the third Fe–Fe shell appeared to distort greatly and its structural homogeneity was thereby reduced. Due to the novel coordination with Mn, an up-shifted Fe–O/Fe shell peak at 4.2 Å with enhanced intensity was observed in FMPC. The coordination number 4.1 for the Fe–O first shell in FMPC is slightly larger than that in FeOOH and FMBO, confirming mixed $\text{Fe}_{4\text{-co}}/\text{Fe}_{5\text{-co}}$ that can be deduced from XANES. The Fe–O bond length increased from 1.96 to 1.98 Å in FMBO and FMPC. Based on physical characterization, we were able to design some model geometries for the Fe–Mn complexes, and calculated the Gibbs free energy changes for model reactions forming the Fe–Mn complex via DFT computations. Among of these models, the Gibbs energy change for the reaction $\text{Fe}(\text{OH})_3 + \text{Mn}(\text{VI})\text{O}_4^{2-} \rightarrow \text{cpx0a}$ was only −99.60 kcal/mol (Table 1), indicating the formation of binuclear corner-sharing Fe–Mn complexes bridged by oxygen atoms. Additionally, the Gibbs free energy change for the reaction related to **cpx0a** is much more negative than that for reaction involving **cpx0b**, suggesting that Mn with high valence state was readily bonded by bridging O.

To evaluate arsenic adsorption capacities, we thereafter carried out sorption isotherm experiments using different adsorbents. The sorption capacities of As(III) by porous Fe–Mn at different pH are depicted in Figure 4. The Freundlich model exhibited a better fit for As(III) adsorption. In the pH range from 5.0 to 9.0, the predominant species of As(III) was H_3AsO_3 , and the adsorption was facilitated by electrostatic attraction between the neutral species and the negatively charged surface (Figure S5). However, in addition to the deprotonation of the surface at high pH (>7.0), competition from hydroxyls for adsorption sites, in

Figure 4. Adsorption isotherms of As(III) by FMPC at various pH (Solid line related to the Freundlich model, while dash line corresponded to the Langmuir model). Inset: the As(III) removal kinetic was measured by UPLC-ICP-MS at pH 7.0, with initial concentration of 1.0 mg L^{-1} and the adsorbent loading of 250 mg L^{-1} .

the meantime, decreased the adsorption efficacy. The maximum adsorption capacity of 460 mg g^{-1} for FMPC was achieved in neutral conditions, 9 times higher than the capacity of $\text{Fe}(\text{OH})_3$ hollow structures. Meanwhile, as shown in Figure 4 inset, the structures were capable of reducing As(III) oxyanions to below the acceptable limits in drinking water standards (10 μg/L) in several minutes. As-loaded FMPC can be regenerated by washing with NaOH (0.1 M) solution, resulting in nearly 100% removal of loaded arsenic. The regenerated FMPC almost maintained the same As(III) removal efficacy from water solution after three regeneration and reuse cycles (Figure S6). It is clear that introduction of Mn indeed improved sorption efficacy greatly. Moreover, adsorption performance was also the best among comparable sorbents, exhibiting its potential for water purification.^{41–43}

Adsorption kinetic experiments for the porous Fe–Mn complex with aqueous As(III) with an initial concentration of 2000 μg L^{-1} were further performed under the same

experimental conditions. As depicted in Figure 5, in contrast to the hours required for adsorption using FMBO, the As(III)

Figure 5. (a) As(III) adsorption kinetic for FMPC and (b) FMBO measured by UPLC-MS. The initial concentration of As was 2 mg L^{-1} ; the sorbents dosage was 250 mg L^{-1} . Retention time at 300 s attributed to the As(III), whereas the As(V) appeared at the retention time around 800 s.

concentration rapidly dropped in 30 s and was thoroughly removed from water in 2 min. Compared with As(V), As(III) is more toxic and mobile and exists at a high level in groundwater.⁴⁴

Fe–Mn binary oxide has traditionally been considered to be a mixture of iron oxide and manganese oxide, and expressed as FeOOH-MnO_x . In the current understanding of As(III) removal, MnO_x first oxidizes the As(III) to As(V), whereas FeOOH is responsible for the final removal. A synergistic effect between adsorption and oxidation contributes to effective As(III) removal for FeOOH-MnO_x . However, apparently this oxidation process, conversion of As(III) to As(V), was only involved in removal via FMBO (Figure 5b inset). Moreover, only a peak at 11875.2 eV related to As(V) was observed on the Fe–Mn binary oxide surface, while a peak located at 11872.1 (As(III)) was observed in the first-order derivative As K-edge XANES spectrum after adsorption of As by the porous Fe–Mn complex (Figure 6a). This indicated that the As(III) was directly captured by the trap sites on the porous Fe–Mn surface.

This high As(III) removal efficacy aroused our curiosity as to the role of Mn in the porous Fe–O–Mn complex. Adsorption of As oxyanions generally involves a two-step ligand-exchange reaction on the surface: the hydroxyl group ($-\text{OH}$) of the metal hydroxide is first protonated; the H_2O ligand is then replaced by an oxyanion.⁴⁵ To gain insight into the sorption process, k^3 -weighted As K-edge EXAFS spectra for As-containing materials were measured to determine the arrangements and chemical states of atoms surrounding As atoms. Radial distribution function (RDFs) profiles of samples exhibited a dominant signal attributed to an As–O first-neighbor contribution and a weaker signal from an As–O–Fe second-neighbor contribution (Figure 6b). The As–O coordination shell at $1.72 \text{ \AA}$ was found to be composed of 4.1 oxygen atoms in the As–Fe–Mn complex, compared to fitting of 3.9 and 2.9 oxygen atoms at 1.68 and $1.75 \text{ \AA}$ in As–Fe–Mn binary oxide and As- FeOOH , respectively. In the presence of As, coordination number of the Fe–O first shell in Fe–Mn complex was increased to 5.1, indicating that 90% of Fe ions occupied five-coordinated sites, while the others were in six-coordinated sites.⁴⁶ The introduction of As onto the surface wedged the bridge O atoms into internal sites to bind with adjacent $\text{Fe}_{5\text{-co}}$, resulting in six-coordinated Fe ions. The possible formation of a bidentate corner-sharing (^2C) complex was therefore conjectured, with a dominant ^2C surface complex between AsO_3 and FeO_6 .

At pH ranging from 5.0 to 9.0, the predominant species of As(III) was H_3AsO_3 . Based on the as-confirmed configuration,

Figure 6. (a) First-order derivatives of As K-edge XANES in various As-containing samples and (b) the Fourier transform of As K-edge extended EXAFS oscillation.

Table 2. Gibbs Energy Changes for the Model Reactions of Removing As(III)

Entry	Reaction type	$\Delta_r G$ (kcal/mol)	Structure of complex
1	$\text{Fe}(\text{OH})_3 + \text{H}_3\text{AsO}_3 \rightarrow \text{cpx3} + 3\text{H}_2\text{O}$	78.41
2	$\text{Fe}(\text{OH})_3 + \text{H}_3\text{AsO}_3 \rightarrow \text{cpx4} + 2\text{H}_2\text{O}$	40.61
3	$\text{Fe}(\text{OH})_3 + \text{H}_2\text{AsO}_3^- \rightarrow \text{cpx5} + 2\text{H}_2\text{O}$	15.49
4	$\text{Fe}(\text{OH})_3 + \text{HAsO}_3^{2-} \rightarrow \text{cpx4} + 2\text{OH}^-$	-3.40
5	$\text{Fe}(\text{OH})_3 + \text{AsO}_3^{3-} \rightarrow \text{cpx3} + 3\text{OH}^-$	-175.72
6	$\text{cpx0a} + \text{H}_3\text{AsO}_3 \rightarrow \text{cpx1a} + 2\text{H}_2\text{O} + \text{OH}^-$	-30.34
7	$\text{cpx0a} + \text{H}_3\text{AsO}_3 \rightarrow \text{cpx2a} + \text{H}_2\text{O}$	-21.91

^aNote: Gibbs energy changes for the model reactions of removing H_3AsO_3 by $\text{Fe}(\text{OH})_3$ were positive values, indicating the unspontaneous adsorption reaction on $\text{Fe}(\text{OH})_3$ surface in pH ranging from 5.0 to 9.0. The introduction of high valence Mn into the $\text{Fe}(\text{OH})_3$ can decrease Gibbs energy values for adsorption of H_3AsO_3 by FMPC (**cpx0a**) (entries 6 and 7), so that the corresponding removal efficacy was promoted.

thermodynamic parameters including ΔG (Gibbs free energy) and ΔH (enthalpy) for the model reactions of H_3AsO_3 removal by FMPC were calculated, accordingly. The negative value of ΔH indicated the exothermic nature of adsorption.⁴⁷ In contrast to pure FeOOH and FMBO , a lower value of ΔH in Fe-O-Mn demonstrated the fact that a smaller repulsion between the as-anchored As and aqueous As in solution. Meanwhile, ΔS (entropy) increased due to release of structured hydration water in the presence of high valence Mn. According to the following formula

$$\Delta G = \Delta H - T\Delta S \quad (4)$$

It is reasonable to speculate that the enhanced enthalpy change and entropy increase collectively promoted the spontaneous reactions. Meanwhile, the transport of inorganic arsenic in the environment depends on the degree to which the species partition into different phases, which could be characterized by the partitioning coefficient (K_D) of a chemical distribution between these phases. The definition of K_D is

$$K_D = \exp\left(-\frac{\Delta G}{RT}\right) = \frac{C_{\text{phase1}}}{C_{\text{phase2}}} \quad (5)$$

where C_{phase1} and C_{phase2} are the equilibrium concentrations of the arsenic after distribution between different phases, R is the universal gas constant, and T is temperature. On the basis of eq 5, a highly efficient As-adsorption capacity can be described by the

more negative value of Gibbs free energy change. The Gibbs free energy change for the reaction removing H_3AsO_3 by $\text{Fe}(\text{OH})_3$ had positive values (Table 2), indicating that H_3AsO_3 molecule is not easily bonded by $\text{Fe}(\text{OH})_3$. Thus, conversion of As(III) into As(V) by Mn(IV) oxide in FeOOH-MnO_x is crucial to the adsorption. On the contrary, the Gibbs free energy changes for the reaction removing H_3AsO_3 by FMPC had much more negative values, suggesting that the introduction of high valence Mn had a significant effect on Fe chemical state, decreasing the reaction Gibbs energy values to promote the adsorption reaction, so that the As(III) oxyanion was readily to be bonded with Fe-O directly (Figure 7).

CONCLUSION

In summary, we here demonstrate an approach toward facile synthesis of a Fe-Mn complex by manipulating a template-engaged reaction. Reaction between the Fe-Mn PB analogue with NaOH led to a porous structure with a surface area of $450 \text{ m}^2 \text{ g}^{-1}$. The porous Fe-Mn complex exhibited the highest adsorption efficacy (460 mg g^{-1}) toward aqueous removal of As(III). According to XAFS analysis and theoretical calculations, the high valence state Mn in Fe-O-Mn framework can make the Gibbs free energy change for adsorption reaction with As(III) oxyanions more negative, thereby superior removal performance can be ultimately achieved. In consideration of the high effectiveness and low cost, the porous structures promise to

Figure 7. Illustration of aqueous As(III) adsorption on FMPC surface.

play a beneficial role in removing heavy metal oxyanion contaminants in water purification. Further, the discovery that PVP has the potential to “weaken” the oxidation ability of KMnO_4 provides a meaningful pathway to novel and useful materials in other domains, such as material science or bioscience.

EXPERIMENTAL SECTION

Chemical Materials. Chemical reagents were purchased and used without purification, including polyvinylpyrrolidone (PVP) (K30), $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, KMnO_4 , and As(III) (Na_3AsO_3) from sigma Aldrich.

Mn-Doped PB. First, 40 mg of KMnO_4 was dissolved in 50 mL of hydrochloric acid (0.1 M) under vigorous stirring for 2 min; 3800 mg of PVP was thereafter added carefully to the KMnO_4 solution to obtain a homogeneous solution, and 110 mg of $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ was then added to the above homogeneous solution followed by stirring for 30 min. The vessel was placed into an electric oven and heated at 80 °C for 24 h. The obtained product was centrifuged and washed several times with water and ethanol and finally dispersed into 20 mL of ethanol for further use.

Porous Fe–Mn structure. Porous Fe–Mn cubes were obtained by a reaction of FeMn PB with 0.2 M NaOH. Typically, 10 mL of the cubes-containing suspension was mixed with 17 mL of NaOH aqueous solution. After shaking by end-overend rotation for 24 h, the as-prepared product was collected by rinse-centrifugation cycles.

Characterization. The crystal structure of samples was characterized by powder X-ray diffraction (XRD) (PANalytical Inc.) using $\text{Cu K}\alpha$ radiation operating at 40 kV and 40 mA with a fixed slit. The morphology of samples was observed by a Zeiss field-emission scanning electron microscope (FESEM). Pore distribution and elemental composition were directly obtained from a JEOL high-resolution electron microscope (HRTEM) combined with an energy-dispersive spectrometer (EDS). The pore structure and specific surface area were determined by N_2 adsorption at 77 K using the volumetric method on an automatic adsorption instrument. ^{13}C cross-polarization/magic angle spinning (CP/MAS) NMR spectra were collected on a Bruker 400 MHz spectrometer equipped with a triple-resonance, z-axis gradient cryoprobe. Mn and Fe k-edge X-ray absorption fine structure spectroscopy (XAFS) was carried out at BL14W1 beamline of Shanghai Synchrotron Radiation Facility (SSRF) China.

Electrochemical measurements were performed at room temperature using a working electrode made of glassy carbon (GC) connected to a CHI 660e electrochemical workstation. The GC electrode was first polished to a mirror finish and thoroughly cleaned before use. A Pt wire and Ag/AgCl (3.5 M) were applied as the counter and reference electrodes.

Sorption Experiments. Sorption experiments were conducted in 50 mL amber glass vials. Ten mg sorbent was added into each vial, and vials were filled with 40 mL of As(III)-containing solution. Initial As(III) concentrations varied from 1 to 200 mg L^{-1} , and 0.1 M NaOH or HNO_3

solutions were used to maintain the desired pH values. After the reaction period, samples were filtered by a 0.45 μm membrane filter for further analysis. The concentrations of total arsenic were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES). The species of arsenic were separated via ultraperformance liquid chromatography with a PRP-X100 anion-exchange column, and then detected by a Mass Spectrometry (MS) detector. The mobile phase, produced by dissolving 1.36 g of $(\text{NH}_4)_2\text{HPO}_4$ and 0.80 g of NH_4NO_3 into 1 L of water, was delivered at 1.0 mL min^{-1} .

Computational Methods. Geometry optimizations and frequency analysis were performed using the B3LYP functional and a mixed basis set of SDD for As and Fe and 6-31G(d) for other atoms. Single-point energy calculations were performed with the M06 functional, a mixed basis set of SDD for As and Fe and 6-311+G(d,p) for other atoms. All the reported Gibbs free energy values are the sum of the electronic energy from the single point calculations and the thermal corrections obtained by the frequency calculations. All of the calculations were performed with Gaussian 09.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b02127.

Experimental details, partial results of calculations, and some characterizations (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: liuruiping@rcees.ac.cn.

*E-mail: jhli@mail.tsinghua.edu.cn.

ORCID

Huijuan Liu: 0000-0003-0855-0202

Jinghong Li: 0000-0002-0750-7352

Author Contributions

[†]G.Z. and X.X. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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