

Interference of Phosphate in Adsorption of Arsenate and Arsenite over Confined Metastable Two-Line Ferrihydrite and Magnetite

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ABSTRACT: Contamination of groundwater by arsenic (As(III/V)) is a serious global issue, and phosphate (P(V)) is known to be the biggest interference in adsorption-based remediation methods. The present study is focused on understanding the interaction between phosphate and iron oxides/oxy-hydroxides with two well-known classes of potential adsorbents in the important pH range of 5-9 and the effect of such interactions on the uptake of arsenite and arsenate. Spectroscopic studies such as X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) spectroscopy were used to understand the binding of various oxyanions of phosphorous and arsenic with the iron oxides/oxy-hydroxides, exploring the core levels of P 2p and Fe 2p. Materials used for adsorption experiments were magnetite (MAG) and a nanocomposite, confined metastable



two-line ferrihydrite (CM2LF); CM2LF is used for arsenic remediation in the affected states in India. Further, we studied the interference of P(V) in As(III/V) adsorption. The kinetics of adsorption was quantified using ion chromatography (IC), where P(V) alone followed a pseudo-second-order model. In the case of mixed solutions, namely, AP_{mix1} (P(V) + As(III)) and AP_{mix2} (P(V) + As(V)), kinetics data suggested that P(V) or As(III/V) oxyanions partially follow the pseudo-second-order model. Results also confirmed that CM2LF performed better than magnetite (MAG) for As(III/V) uptake in the presence of P(V). As(III) and As(V) species are more competitive than P(V) at neutral pH. A model for the adsorption of P(V) species in water on ferrihydrite particles was developed using density functional theory (DFT). This accounted for phosphate complexation at various pH values. The study is highly useful in developing an affordable solution for sustainable arsenic remediation. Various aspects of sustainability are discussed.

INTRODUCTION

Phosphorus (P) is the 11th most common element and is essential for all known life forms on earth.^{1,2} It exists in different inorganic and organic forms having various oxidation states (+V, +III, +I, 0, and -III). The dominant biological forms of P are H₂PO₄¹⁻, HPO₄²⁻, and PO₄³⁻ at biologically relevant pH (7-9).³ There are similarities between P and arsenic (As). Arsenic is a metalloid that sits just below P in the periodic table with larger atomic radii, the same number of valence electrons, and nearly identical electronegativity. Arsenic exists preferentially in +V, +III, and 0 oxidation states. The similarity between phosphorus and arsenic translates to the various species that they form, importantly phosphate (PO_4^{3-}) and arsenate (AsO_4^{3-}) . The dissociation constants for P(V) in H₃PO₄ are close to those of As(V) in H₃AsO₄ over a range of physiological conditions. Also, As(V) can retain a negative charge even when it bonds with two other species, similar to P(V). Due to these similarities, As(V) and P(V) are not easily distinguishable by most life forms.³ As(V) is taken up by cells via phosphate transporters and can substitute for

P(V) in the early steps of many phosphate-based metabolic pathways. $\!\!\!^3$

Interaction of arsenic with metal oxides or metal oxyhydroxides is mainly influenced by pH (H⁺/OH⁻ ions) and competing ions (phosphates, silicate, iron, manganese, calcium, magnesium, nitrate, chloride, and sulfate) generally present in groundwater.⁴ The mobility of these oxyanions (P(V), As(III/ V)) in the environment is influenced by redox potential, pH conditions, organic matter, and other competing oxyanions.⁵ Phosphate can interact with iron oxide surfaces through Fe– O–P bonds. These are relevant processes in bacterial adhesion as in the case of organisms such as *Bacillus subtilis* and *Pseudomonas aeruginosa*.⁶ Phosphate and arsenate are consid-

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Figure 1. (A) (a) TEM image and (b) 3D reconstructed tomographic image of the two-line ferrihydrite composite (CM2LF); ED, electron density. (B) XPS P 2p spectra of aqueous phosphate solutions at various pH values of (a) 5, (b) 7, and (c) 9 after drying. The XPS samples were prepared by dropcasting the phosphate solutions onto an ITO plate and drying at room temperature for 2 days. (C) ATR-FTIR spectra of 100 mM phosphate at various pH values of (a) 5, (b) 7, and (c) 9 in the region of interest. All IR spectra shown here were subtracted from those of water.

ered to have similar adsorption characteristics because they have very similar protonation tendencies in aqueous medium.^{7–10} Due to their structural similarities, PO_4^{3-} competes with AsO_4^{3-} during sorption and coprecipitation on iron oxy-hydroxides.^{11–14} The presence and mobility of contaminants (in the context of arsenic and other heavy metal ions) in groundwater systems are strongly dependent on the interaction with iron and aluminum-based materials present in soils and waterways.¹⁵ Studies on the desorption of arsenic compounds were reported in the presence of PO_4^{3-} and Cl^- and other constituents.¹⁶

While numerous PO_4^{3-} adsorption studies have been performed in view of its importance to soil,¹⁷ in water, it is treated as a pollutant depending on its concentration levels.¹⁸ For its removal, the adsorbents used are mainly iron oxides (hematite¹⁹ and magnetite^{20,21}) and iron oxy-hydroxides (ferrihydrite,²² goethite,²³ and maghaemite²⁴). Adsorption of phosphate onto iron oxides/oxy-hydroxides (commonly present in soils) plays a significant role in soil fertility as it influences the surface charge responsible for the attachment of organic matter to the soils.²³ The effect of pH on various complexation mechanisms, such as inner-sphere and outersphere adsorption on the hematite surface, was reported.²⁵ The molecular-scale structure of surface complexes depends on the mineral surfaces, and there is a brief discussion on models of surface complexation in a study by Wang et al.²⁶ Sodium phosphate interaction with iron oxide (Fe_2O_3) was understood using density functional theory (DFT) calculations.²⁷ Adsorption of phosphate on ferrihydrite¹⁵/magnetite²⁸ has been studied using X-ray photoelectron spectroscopy (XPS). Earlier, attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy was also used to study the influence of phosphate on the adsorption of As(V) on goethite and ferrihydrite.²⁹ Binary oxy-hydroxide such as Fe and Mn-based mixed oxy-hydroxide were used to study the competitive adsorption of arsenate and phosphate.³⁰ This suggests that the adsorption of arsenate (6-80 μ M) on binary oxy-hydroxide

decreased by approximately 7–20% in the presence of P(V) (120–300 μ M). Even after considerable research, phosphate interference during arsenic adsorption is not well understood and needs a more comprehensive effort.

The present work focuses on elucidation of phosphate adsorption and its interference in the arsenic uptake on MAG and CM2LF substrates in a qualitative and quantitative manner. Experiments were conducted with different ionic forms of P and As. CM2LF is a nanoscale material that has been developed in our laboratory and is being used to supply arsenic-free water to over 1.2 million people every day. All adsorption experiments were conducted in the environmentally relevant pH range of 5-9. While XPS and IR spectroscopy were performed to obtain a detailed understanding of the surface complexation phenomenon during adsorption, all uptake experiments were quantified using ion chromatography (IC) and inductively coupled plasma-mass spectrometry (ICP-MS). Finally, DFT calculations were performed on various phosphate complexes at model surfaces, such as bidentate binuclear (^{2}C) [>(FeO)₂(OH)PO or >(FeO)₂(OH)₂P], bidentate mononuclear (²E) [>FeO₂(OH)PO or >FeO₂(OH)₂P], monodentate mononuclear (^{1}V) [>FeO- $PO_2(OH)$ or >FeO-PO(OH)₂], and physically adsorbed species (T) [>FeOH...O-PO₂(OH) or >FeO...HO- $PO_2(OH)$], to support the XPS results. ²C, ²E, and ¹V are referred to as inner-sphere complexes, and T is referred to as an outer-sphere complex. Also, a brief discussion is given on the sustainability aspects of both materials.

EXPERIMENTAL SECTION

Stock solutions of 100 mM P(V), As(III), and As(V) were prepared using KH₂PO₄, NaAsO₂, and Na₂HAsO₄·7H₂O salts, respectively. P(III) was not examined as it is not a dominant form in the environment. A combination of P(V) and As(III) is referred to as AP_{mix1} and a mixture of P(V) and As(V) is referred to as AP_{mix2} . A 100 mM AP_{mix1} stock solution was prepared by mixing equimolar amounts of NaAsO₂ and



Figure 2. XPS spectra of the (A) P 2p region of (a) KH_2PO_4 solid, adsorbed phosphate on CM2LF at various pH values of (b) 5, (c) 7, and (d) 9. (B) Fe 2p region showing $2p_{3/2}$ and $2p_{1/2}$ features of (a) CM2LF before adsorption and (b–d) Fe 2p after phosphate adsorption at various pH values of 5, 7, and 9. (C) FTIR spectra of CM2LF before adsorption; it was treated with distilled water and adjusted to various pH values of (a1) 5, (a2) 7, and (a3) 9. FTIR spectra of CM2LF measured after phosphate adsorption at pH values of (b) 5, (c) 7, and (d) 9. The difference between the FTIR features before and after phosphate adsorption at various pH values of 5, 7, and 9 is represented by curves (e), (f), and (g), respectively. Various component features observed in the difference spectra are also shown.

KH₂PO₄. The mixture AP_{mix2} was made with equimolar quantities of Na₂HAsO₄·7H₂O and KH₂PO₄. The pH of the stock solutions was adjusted to 7 by adding dil. HCl or dil. NaOH whenever necessary. Further, 150 mg of CM2LF was added to 100 mL of 40 mM solutions of P(V), AP_{mix1} , and AP_{mix2}, each in 250 mL polypropylene conical flasks. The same process was followed for the MAG material. The flask was held on an orbital shaker for 24 h until an adsorption equilibrium was reached. The solution was centrifuged, and the residue (adsorbent) was washed several times with deionized water to remove the unreacted species (P or As) from the surface of the material. Thereafter, about 2-3 mg of the cleaned residue was suspended in 300 μ L of distilled water for sample preparation for XPS, and similar sample preparation was carried out for IR spectroscopy. The suspension was dropcast on a $1 \text{ cm} \times 1 \text{ cm}$ indium tin oxide (ITO) plate (nonconducting surface) that was kept in a vacuum desiccator for 48 h for complete drying and to prevent contamination. For a clear understanding of the kinetics of phosphate uptake and its interference in arsenic adsorption kinetics, IC and ICP-MS measurements were performed. For this, 100-150 mg of CM2LF was added to 5-20 ppm of 100 mL of P(V), AP_{mix1} , and AP_{mix2} solutions, each in a 250 mL polypropylene conical flask. The same process was followed for MAG. The solution was held on an orbital shaker, and 1 mL of the solution was collected at various time intervals of 3, 5, 10, 15, 20, 40, 60, and 90 min. The solutions were subjected to centrifugation immediately after collecting them. The material, if any, separated as residue, was discarded, the supernatant was filtered using a 0.2 μ m membrane filter, and the filtrate was diluted to 5 mL using Millipore water of 18 M Ω resistance. Details of materials, instrumentation, and computational aspects are provided in the Supporting Information (SI).

RESULTS AND DISCUSSION

Figure 1A-a shows a transmission electron microscopy (TEM) image of CM2LF. The image suggests that the material is composed of amorphous particles, in agreement with the

literature.³¹ To further investigate the morphology of the CM2LF aggregates, transmission electron tomographic reconstruction was performed for CM2LF and its composites with As(III) and As(V). Accordingly, a series of two-dimensional (2D) projections were collected between $\pm 69^{\circ}$ with a 3° increase (see Supporting Information 2 for details). Threedimensional (3D) reconstruction of CM2LF suggests that the material has a porous structure with random aggregation but with no well-defined packing patterns (Figures 1A-b and S1Ai,ii). Such random aggregation and porous structure are beneficial for the uptake of various species such as As(III/V) and P(V). Further, the tomographic reconstruction of As(III/ V)-bound CM2LF nanoparticles shows no change in the morphological features (Figure S1B-i,ii for As(III)-adsorbed CM2LF and Figure S1C-i,ii for As(V)-adsorbed CM2LF). This suggests that the structures are intact even after As(III/V) binding. XPS and FTIR spectra of phosphate species were measured at pH 5, 7, and 9 to understand the degree of protonation and phosphate speciation at room temperature. P 2p energy levels of phosphate species are shifted to lower binding energies (134.3 > 133.8 > 133.5 eV) with increase in pH (Figure 1B). Note that the XPS spectra were measured in the dry state of materials. The materials, magnetite,^{28,32,33} and two-line ferrhydrite^{12,34} nanoparticles embedded into organic matter (chitosan and cellulose) are stable in the pH range of 5-9. Previous spectroscopic (XPS and Mossbauer) studies suggest that phosphate-adsorbed wet magnetite nanoparticles remain as magnetite after drying.^{28,32,33} Kumar et al. studied arsenic-adsorbed CM2LF (in the dry state) using X-ray powder diffraction and electron energy-loss spectroscopy.³ These studies demonstrated that there is no phase change in two-line ferrihydrite. These materials are converted from one phase to another, taking months or years under natural circumstances. However, the current study does not target studying dehydration,³⁵ surface reactivity,³⁶ and aggregation^{36,37} of the bare two-line ferrihydrite nanoparticles. We dried the wet (after adsorption) samples at room temperature

(24-30 °C) for measurements. These experimental conditions cannot affect the chemical state of the elements (P, Fe, and As). Magnetite and CM2LF materials are stable even above 80 °C. Considering the previous reports, XPS data are valuable for identifying chemical states and for quantifying the elements, although the samples were dried prior to measurements. XPS data of each peak before and after the interaction of P(V)/AP_{mix1}/AP_{mix2} with CM2LF and MAG used in this work are shown in Supporting Information, Table S1. Deprotonation of hydroxyl groups attached to P causes an increase in the electron density (ED) on O atoms (P–OH to $P-O^{-}$), which results in an increase in the electron density on the P atom. This change leads to a fall in the binding energy (BE) of P 2p. These results are supported by theoretical calculations (Table S2). P(V) in solution at pH 5 has two vibrational features at 1076 and 1157 cm⁻¹ (Figure 1C-a). These correspond to the symmetric stretching frequencies of -P-OH and -P = O of $H_2PO_4^{1-}$, with $C_{2\nu}$ structure.^{22,38} At pH 9, it shows two features at 990 and 1079 cm^{-1} (Figure 1C-c) corresponding to the bending of $-PO_2$ and the symmetric stretching of -P-OHgroups of HPO₄²⁻, with C_{3v} structure.^{22,38} However, at pH 7, P(V) shows three characteristic peaks at 1155 and 1078 and 991 cm⁻¹ (Figure 1C-b) due to $H_2PO_4^{1-}$ and HPO_4^{2-} , respectively.

Adsorption on CM2LF. The XPS analysis of phosphate standard in the solid form (KH_2PO_4) is shown in Figure 2A-a. The P 2p peak appears at 133.4 eV. The P 2p peak was deconvoluted into $2p_{3/2}$ and $2p_{1/2}$. The P 2p peak was shifted from 133.4 (KH₂PO₄) to 134.2, 134.1, and 133.9 eV upon its adsorption on CM2LF at pH values 5, 7, and 9, respectively. Throughout this paper, a blue shift indicates that the selected peak shifted to higher binding energy from a reference peak, and a red shift indicates the opposite. A large blue shift was observed at pH values 5 (0.8 eV) and 7 (0.7 eV) (Figure 2Ab,c). This suggests that P(V) forms more stable inner-sphere complexes (²C) at pH values 5 and 7. On the other hand, a small blue shift was observed for pH 9 (Figure 2A-d), indicating that there is some amount of outer-sphere complexes (T) along with inner-sphere complexes. In contrast, P(V) may form more number of less stable inner-sphere complexes (²E and ¹V). However, there is more chance of forming outer-sphere complexes at pH 9 due to the increase of the Fe-O⁻ groups. A minor change observed in the position of the P 2p peak while comparing with pH values 5 and 7 arises due to the variation in the extent of protonation of surface complexes. Figure 2B-a shows Fe 2p fitted with three pairs of peaks of CM2LF.³⁹ The lowest binding energy corresponds to -Fe-O-Fe- groups, the next refers to the surface >Fe-OH groups (Fe(III)surf), followed by a satellite peak (Fe(III)sat). A significant blue shift was observed in Fe 2p due to adsorption of P(V) at various pH values, as shown in Supporting Information, Table S1. The shifted peaks did not match with Fe 2p of Fe(II) and Fe(IV) ions. Thus, the Fe 2p data suggest that there was no reduction or oxidation of iron (Fe(III)) upon P(V) uptake (Figure 2B). The observed blue shift in Fe 2p is due to the formation of inner-sphere complexes (-Fe-O-P-), which are discussed in Figure 7. FTIR spectroscopic studies were used to identify the innersphere complexes of P(V) with CM2LF. At first, we studied the pH influence on CM2LF in the range of 4-9 using FTIR spectroscopy. The results suggest that CM2LF functional groups are not affected by varying pH (Supporting Information, Figure S2). The IR spectrum at pH 5 (Figure

2C-e) was fitted with five peaks: 900, 963, 1015, 1087, and 1148 cm⁻¹. The 1015 cm⁻¹ was assigned to -Fe-O-P-, 1148 cm^{-1} to P=O stretching, 1087 cm⁻¹ to the PO₂ group, while 900 and 963 cm⁻¹ corresponded to P-OH symmetric bending vibrations. These features refer to bidentate binuclear (^{2}C) species $[>(FeO)_2(OH)PO \text{ or }>(FeO)_2(OH)_2P]^{22,38,40}$ These features also correspond to C1 symmetry complexes. In previous reports, at pH 4.5, the formation of less stable inner-sphere complexes (²E and ¹V) were observed⁴¹ when P(V) loadings were increased from 1.25 to 10 μ mol/m² $(\mu mol/m^2 \approx ppb)$, i.e., a higher P(V) loading increases the chance of formation of less stable complexes (²E and ¹V). Here, the P(V) loadings used were higher than 10 μ mol/m². Thus, there may be some amount of ²E and ¹V complexes. The spectrum observed at pH 7 (Figure 2C-f) shows four features at 910, 961, 1015, and 1076 cm⁻¹ that refer to bidentate binuclear species [>(FeO)₂(OH)PO].^{22,34} The pH 9 spectrum (Figure 2C-g) shows only two features at 945 and 997 cm^{-1} . These features are similar to 961 and 1015 cm⁻¹ features (at pH 5) with a shift (16 cm⁻¹) that may correspond to deprotonated bidentate binuclear species $[>(FeO)_2PO_2]$. However, from these data, it is difficult to understand the exact surface complexes. XPS data confirm that the CM2LF surface is covered with more outer-sphere complexes than inner-sphere complexes at pH 9 (Figure 2A-d).

Adsorption on MAG. In the case of MAG, Fe $2p_{3/2}$ was deconvoluted into four peaks that corresponded to Fe(II), Fe(III), and two separate shake-up peaks for Fe(II) (Fe(II)sat) and Fe(III) (Fe(III)sat).^{39,42} Similarly, deconvolution was performed for Fe $2p_{1/2}$. The Fe $2p_{3/2}$ (for Fe(II) and Fe(III)) feature of MAG appears at 707.9 eV before phosphate adsorption (Figure 3B-a), and after adsorption, it is blue-



Figure 3. XPS spectra of the (A) P 2p region of (a) KH_2PO_4 solid, adsorbed phosphate on MAG at various pH values of (b) 5, (c) 7, and (d) 9. (B) Fe 2p region showing $2p_{3/2}$ and $2p_{1/2}$ features of MAG (a) before and (b–d) after adsorption at pH values of 5, 7, and 9, respectively.

shifted by 0.6 and 0.4 eV at pH values 5 and 7, respectively, and no shift was observed in the case of pH 9 (Figure 3B-d). The shifts are shown in Supporting Information, Table S1. Upon P(V) interaction with MAG at various pH values, a considerable change was observed in P 2p. The P 2p was shifted from 133.4 (KH_2PO_4) to 134.5, 134.0, and 132.8 eV at pH values 5, 7, and 9, respectively, when P(V) interacted with



Figure 4. XPS spectra of CM2LF treated with (a) P(V), (b) AP_{mix1} , and (c) AP_{mix2} and MAG treated with (d) P(V), (e) AP_{mix1} , and (f) AP_{mix2} . The spectra show the regions corresponding to O 2s (20–28 eV), As 3d (40–50 eV), Fe 3p (52–60 eV), and P 2p (130–136 eV). The atomic compositions of O, As, Fe, and P in the materials were calculated after adsorption from the corresponding XPS spectrum; the values are presented in the table on the right-hand side.



Figure 5. XPS spectra of (A) P 2p, (B) As 3d, and (C) Fe 2p. In the (A) P 2p region, CM2LF treated with (a) P(V), (b) AP_{mix1} , and (c) AP_{mix2} , and MAG treated with (d) P(V), (e) AP_{mix1} , and (f) AP_{mix2} , respectively, are presented. In the As 3d region (B), the red and blue traces correspond to NaAsO₂ and Na₂HASO₄·7H₂O. Only As(III)-adsorbed materials are (a-i) CM2LF and (d-i) MAG and, on the other hand, As(V)-adsorbed materials are (a-ii) CM2LF and (d-ii) MAG and, on the other hand, As(V)-adsorbed materials are (a-ii) CM2LF and (d-ii) MAG. Traces (b) and (c), (e), and (f) are after adsorption of ions while using mixed solutions (AP_{mix1} and AP_{mix2}) as indicated above. In the (C) Fe 2p region, (a) CM2LF and (d) MAG are before adsorption and the remaining (b and c, e, and f) are after adsorption of ions while using mixed solutions, as above.

MAG (Figure 3A). The P 2p is more blue-shifted at pH 5 and less at pH 7 (Figure 3A-b,c). These results are similar to those of CM2LF, which suggest that phosphate forms monoprotonated bidentate binuclear (^{2}C) species at pH values 5 and 7.²⁸ According to the literature, the P 2p binding energy for adsorbed phosphate on magnetite is 133.6 eV when the P(V) uptake is in the range of 2–5 mg/g.²⁸ Previous FTIR and

Mossbauer spectroscopic studies reflected that phosphate is attached to Fe(III) at the octahedral sites as monoprotonated bidentate binuclear complexes.²⁸ At pH 9, P 2p of the adsorbed phosphate shows a shift toward lower binding energy as compared to the KH_2PO_4 (Figure 3A-a,d). No shift was observed in the Fe $2p_{3/2}$ peak upon P(V) uptake as discussed before. The results at pH 9 suggest that most of the species are



Figure 6. Pseudo-second-order kinetics plot for adsorption of (a), (b), and (c) indicating phosphate, AP_{mix1} , and AP_{mix2} , respectively, on (A) CM2LF and (B) MAG. The q_t of each data point was evaluated using the linear form of the pseudo-second-order equation where the unit of q_t is mg/g. In the case of CM2LF treated with AP_{mix1} and AP_{mix2} , the adsorption kinetics data showed two slopes from 0 to 10 and 15 to 90 min indicating varying rates of adsorption.

adsorbed through hydrogen bonding (outer-sphere complexes or physically bonded species). The physically bonded (T) species have lower P 2p binding energy compared to innersphere complexes. The binding energy of P 2p of various phosphate complexes (${}^{2}C$, ${}^{2}E$, ${}^{1}V$, and T) was calculated from theoretical studies (see Figure 7).

The atomic percentage (Figure 4) shows the interference of P(V) in the adsorption of arsenic (As(III/V)) while each had a concentration of 20 mM. The P(V) uptake is higher for CM2LF (3.6%) than for magnetite (2.9%) (Figure 4a,d, respectively). In the case of mixtures (AP_{mix1} and AP_{mix2}), CM2LF (Figure 4b,c) shows better As(III/V) uptake capacity than magnetite (Figure 4e,f). This can be attributed to a lower number of adsorption sites (Fe $-OH_2^+$, Fe-OH) available in magnetite than CM2LF. The porous structure of CM2LF provides additional adsorption sites, as shown in Figure 1A-b. At pH 7, in the case of AP_{mix1}, the component As(III) and in the case of AP_{mix2} , the component $As(V\bar{)}$ were more adsorbed on CM2LF/MAG than P(V) (Figure 4b,c,e,f). The complexation of phosphate in the presence of As(III/V) was further evaluated by studying the energy levels of P 2p, As 3d, and Fe 2p (Figure 5).

In the case of CM2LF, there is no considerable shift observed in the P 2p peak between P(V) and AP_{mix1} (P(V) = 134.0, AP_{mix1} = 134.1 eV (Figure 5A-a,b)), and while looking at the corresponding As 3d region for AP_{mix1}, which showed a peak at 45.4 eV (Figure 5B-b), this is slightly blue-shifted from the As(III)-treated sample (45.1 eV (Figure 5B-a(i))). This blue shift indicates that the ratio of inner-sphere and outersphere complexes of As(III) is more in the case of AP_{mix1} than As(III) alone. The corresponding IR spectrum (Supporting Information, Figure S3d) shows features at 790, 830, 886, 970, 1010, and 1075 cm⁻¹, where the features at 790 cm⁻¹ belong to the As–OH stretching, 830 cm⁻¹ due to Fe–O–As bonds, 1075 cm⁻¹ due to the PO₂ group, 970 cm⁻¹ due to P–OH, and 1010 cm⁻¹ to -Fe-O-P. IR data suggest that P(V) and As(III/V) are chemisorbed when they are co-adsorbed. Hence, XPS data suggest P(V) interference in As(III) complexation.

A slight red shift was observed in the P 2p peak in the case of AP_{mix1} adsorption ($AP_{mix1} = 133.7$ eV, Figure 5A-e) as compared to P(V) adsorption (P(V) = 134.1 eV, Figure 5A-d) on the MAG surface. This shift refers to physically adsorbed species. Thus, there are some amount of physically adsorbed phosphate species on the surface of MAG along with the chemically adsorbed species at pH 7. The AP_{mix1} -treated MAG shows the As 3d peak at 45.7 eV, and it is more blue-shifted as compared to As(III) alone (44.3 eV) (Figure 5B-d(i),e). The observed shift is high (1.4 eV), which suggests that there is a greater fraction of chemically adsorbed species in the case of AP_{mix1} compared to As(III) alone (in overall surface complexes). Thus, there is a positive effect on As(III) complexation in the presence of P(V), but vice versa is not true.

While comparing AP_{mix2}-treated CM2LF and P(V)-treated CM2LF, there is a noticeable shift (0.3 eV) observed in P 2p; the P 2p peaks are at 134.4 and 134.1 eV, respectively (Figure 5A-a,c). This may be due to the increased ratio of the innerand outer-sphere complexes or a plausible conversion of less stable inner-sphere complexes (¹V) to more stable innersphere complexes (²C) of P(V) in the presence of As(V). For the As 3d region of AP_{mix2}- (Figure 5B-c) and As(V) (Figure 5B-a(ii))-treated CM2LF, the peaks are at 46.5 and 45.3 eV, respectively. The shift between them is 1.2 eV, which suggests increased chemisorption of As(V) in the presence of P(V) than

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adsorbate 100 mL	adsorbent (mg)	species pH 7	$q_{\rm e} ({\rm mg/g}) \pm 1\%$	$k (\min(mg/g))^{-1} \pm 2\%$	initial rate $h = kq_e^2 \pm 5\%$	R^2
20 ppm P(V)	CM2LF: 100	H _x PO ₄ ^{y-}	18.26	0.02	6.67	0.99
	MAG: 100	$H_x PO_4^{y-}$	15.83	0.02	5.01	0.99
5 ppm P(V)+	CM2LF: 100	H _x PO ₄ ^{y-}	3.39 (avg)	0.13 (avg)	1.49 (avg)	0.99
		H ₃ AsO ₃	2.67 (avg)	0.29 (avg)	2.07 (avg)	0.99
5 ppm As(III)	MAG: 100	$H_x PO_4^{y-}$	3.30	0.51	5.55	0.96
		H ₃ AsO ₃	2.28	0.28	1.45	0.99
5 ppm P(V)+	CM2LF: 100	$H_x PO_4^{y-}$	3.06 (avg)	0.04 (avg)	0.37 (avg)	0.74
		$H_x AsO_4^{y-}$	4.16 (avg)	0.05 (avg)	0.87 (avg)	0.99
5 ppm As(V)	MAG: 100	H _x PO ₄ ^{y-}	2.30	1.64	8.67	0.99
		H _x AsO ₄ ^{y-}	2.40	1.89	10.89	0.99

Table 1. Adsorption Data in Terms of Initial Rates, Rate Constants, and Uptake of As at Equilibrium



Figure 7. Various phosphate complexes with a small ferrihydrite cluster: (1) bidentate binuclear complex (²C), (2) bidentate mononuclear complex (²E), (3) monodentate mononuclear complex (¹V), (3a) deprotonated monodentate mononuclear complex (¹V-H), (4) outer-sphere complex (T), and (4a) deprotonated outer-sphere complex (T-H). Here, theoretical binding energies ($\Delta = T_{BE2}$) of P 2p in phosphate complexes are reported in eV.

As(V) alone. The corresponding IR spectrum (Supporting Information, Figure S3e) shows two features at 820 and 871 cm⁻¹; 820 cm⁻¹ is assigned to the Fe–As–O–bond stretching and 871 cm⁻¹ is due to As=O; these features correspond to stable inner-sphere complexes (^{2}C).

However, in the case of AP_{mix2}-treated MAG, no shift was observed in P 2p as compared to AP_{mix2}-treated MAG and P(V)-treated MAG at pH 7 (AP_{mix2} = 134.1 eV, P(V) = 134.1 eV (Figure 5A-d,f)). As(V) shows a 3d peak at 46.6 eV (Figure 5B-f). The results are the same as in the case of CM2LF. Hence, similar complexes (²C or ³C (tridentate trinuclear complex)) can be expected here. These results suggest that the ratio of inner- and outer-sphere complexation of As(III/V) increases in the presence of P(V). On the other hand, these results may be obtained due to strong hydrogen bonding with the surrounding ferric hydroxyl groups (-Fe-OH) or arsenic hydroxyl groups (-As-OH). The consolidated results are presented in Table S3 in the Supporting Information.

The adsorption kinetics of oxyanions like P(V) with iron oxides/oxy-hydroxides was reported to follow pseudo-secondorder kinetics that correlates with our experimental data as well (Figure 6A-a,B-a).⁴³⁻⁴⁵ Initially, phosphate adsorption with CM2LF and MAG occurs rapidly, but 5 min onward, it becomes slower (Supporting Information, Figures S4A-a and S5A-a). In our earlier studies,⁴⁶ Raman spectroscopy measurements suggested pseudo-second-order kinetics for the adsorption of As(III/V) on CM2LF and MAG (Supporting Information, Figure S8). However, in the case of AP_{mix1} , P(V)and As(III) ions were competitive up to the initial 15 min for CM2LF (Supporting Information, Figure S4B-b), but at a later stage, As(III) reached an equilibrium state earlier than P(V), both following the pseudo-second-order kinetics with two slopes and variable adsorption rates (Figure 6A-b). In the case of AP_{mix2} , As(V) clearly showed a faster rate than P(V) on the CM2LF surface (Supporting Information, Figure S4B-c), showing similar kinetics behavior as the former (Figure 6Ac). These results confirm the interference (or competition) between P(V) and As(III/V) species during adsorption on CM2LF.

In the case of magnetite, while P(V) adsorption was faster than As(III) initially (Supporting Information, Figure S5B-b), and after 10 min, desorption of P(V) was observed for AP_{mix1} . However, in the case of AP_{mix2} , both P(V) and As(V) showed comparable rates of adsorption throughout with higher As(V)uptake (Supporting Information, Figure S5B-c). Thus, As(III/ V) shows different adsorption kinetics for CM2LF and

Article



Figure 8. Schematic of a (010) plane of ferrihydrite (k) before adsorption, (l), (m), and (n) after phosphate adsorption at pH values of 5, 7, and 9, respectively.

magnetite. Kinetics data are given in Table 1. These results are presented as a schematic diagram (Supporting Information, Figure S7).

To understand the mechanism of adsorption of various phosphate species on CM2LF, theoretical studies were performed as discussed in the Supporting Information. In Figure 7, to find the theoretical binding energy (T_{BE}) of P 2p in various complexes, equation $T_{\text{BE2}} = -E + R = \Delta$ was used, where E is the orbital energy, R is the relaxation energy, and Δ is computed using the Δ SCF method. Based on Δ , the binding energy of P 2p for the complexes given above follows the order $^{1}V > ^{2}E > ^{2}C > ^{1}V-H > T > T-H$ (Figure 7; Supporting Information, Table S2). Theoretical calculations of binding energy have been extended to As(III/V) complexes. Based on K, the binding energy of As 3d for the As(III) complexes follows the order ${}^{2}C > {}^{1}V > {}^{2}E > T$ (Supporting Information, Figure S6). In the case of As(V) complexes, it follows the order ${}^{2}E > {}^{2}C > {}^{1}V > T$ (Supporting Information, Figure S6). The binding energies of As 3d for As(V) complexes are higher than those of As(III) complexes.

To show phosphate adsorption on two-line ferrihydrite schematically at various pH values 5, 7, and 9, we used the unit cell parameters of two-line ferrihydrite as reported in Michel et al.^{48,49} A rectangular slab was made with four unit cells and surfaces parallel to the (010) plane of FeOOH (Figure 8). In general, the ferrihydrite structure has three symmetry-distinct Fe atoms. Here, we represented them as octahedral Fe1 center (orange), octahedral Fe2 center (sky blue), and tetrahedral Fe3 center (blue) as reported by Pinney et al.⁴⁹ The CM2LF $-O^{-}/-OH$ groups are shown in red, while phosphorousattached $-O^-$, -OH, and =O groups are marked in sky blue, blue, and indigo, respectively. XPS and FTIR spectroscopy results suggest that phosphate species bind the surface Fe atoms through a ligand-exchange mechanism, at pH values 5 and 7. The results are supported by the literature 28,50,51 In the ligand-exchange mechanism, $-P-(O^{-}/OH^{-})$ groups replace

the Fe- $(\underline{O}^{-}/-\underline{OH}^{-})$ groups. Moreover, the formation of possible stable complexes of phosphate with two-line ferrihydrite is shown in Figure 8. Herein, P(V) forms ²C (major) and ¹V (minor) complexes at pH 5 and 7 due to the presence of more labile groups Fe- $(\underline{OH}/\underline{OH}_{2}^{+})$; on the other hand, at pH 9, P(V) forms T (major), ²C(minor), and (¹V) (minor) complexes as a result of an increase of less labile groups Fe- \underline{O}^{-} .

Sustainability Aspects of CM2LF and Magnetite Materials. To study the sustainability of CM2LF and magnetite systems, the following factors can be considered: (1) green synthesis, (2) material efficiency, (3) material stability, and (4) cost of production. Upon carefully observing these factors for both the materials, CM2LF was found to be a greener option than magnetite, owing to its ease and waterborne synthesis, higher arsenic uptake capacity, mechanical robustness, and cost-effective production process. Each aspect is discussed in quantitative detail in the SI.

Of the phosphate ions, $H_2PO_4^{1-}$ is dominant at pH 5 and HPO_4^{2-} is dominant at pH 9. Both species exist in water at pH 7 as confirmed by ATR-FTIR studies. The P 2p binding energy of adsorbed phosphate decreased gradually on CM2LF and MAG surfaces upon increasing pH from 5 to 9. The changes in P 2p energy levels suggest that surface complexes vary with changes in pH. The XPS and IR studies suggested that phosphate complexation with iron oxides/oxy-hydroxides was driven by the ligand-exchange mechanism, leading to the formation of Fe-O-P bonds at pH 5-7. The adsorbed materials showed P 2p binding energy in the order $AP_{mix2} >$ AP_{mix1} > phosphate-only samples. Time-dependent ion chromatography measurements allowed us to understand the adsorption kinetics of As(III)/As(V) on CM2LF and MAG in the presence of P(V) at neutral pH. The As(III)/As(V) adsorption kinetics was affected by phosphate. Phosphate

The Journal of Physical Chemistry C

desorbs from magnetite in the presence of As(III). At higher concentrations (i.e., 20 mM P(V) and 20 mM As(III/V)), XPS data suggest that phosphate uptake by iron oxides/oxy-hydroxides is affected by As(III) and As(V). These studies confirm that As(III/V) is more competitive than P(V) toward iron oxides/oxy-hydroxides. However, P(V) levels in natural water are 100–1000 times higher than that of As(III/V), and, therefore, P(V) is an obvious interfering ion during arsenic adsorption. DFT calculations suggest that P 2p and As 3d binding energies vary with the type of complexation (²C, ²E, ¹V, and T). The degree of protonation of P(V) in phosphate surface complexes affects the P 2p binding energy. The binding energies of As 3d for As(V) complexes are higher than those of As(III) complexes.

ASSOCIATED CONTENT

1 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.1c04317.

Materials and instrumentation; 3D reconstructed tomographic images of the two-line ferrihydrite composite (CM2LF) before and after arsenic adsorption; IR spectra of CM2LF treated in distilled water at various pH values; IR spectra of CM2LF after arsenic adsorption in the presence of P(V); time-dependent chromatograms of the interaction of CM2LF/magnetite with $P(V)/AP_{mix1}/AP_{mix2}$; equations for the pseudo-secondorder model; theoretical binding energy of As 3d in various As(III/V) complexes with a small ferrihydrite cluster; schematic illustration of P(V) interference in As(III/V) adsorption based on time-dependent ion chromatography and XPS studies; pseudo-second-order adsorption kinetic plots for the adsorption of As(III) and As(V) on ferrihydrite; XPS data of materials before and after treatment with P(V), AP_{mix1}, and AP_{mix2}; and sustainability aspects of CM2LF and magnetite materials (PDF)

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Notes

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The Journal of Physical Chemistry C

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