

FIGURE. A.1. XRD pattern of Cr-containing magnetite. Power X-ray diffraction (PXRD) were recorded between 10° and 80° (2θ) at a step of 1° min⁻¹ using a Bruker D8 advance diffractometer with Cu Kα radiation (40 kV and 40 mA). The XRD pattern of Cr containing magnetite well corresponds to the standard card of magnetite (JCPDS: 19-0629), confirming that the prepared sample has spinel structure.

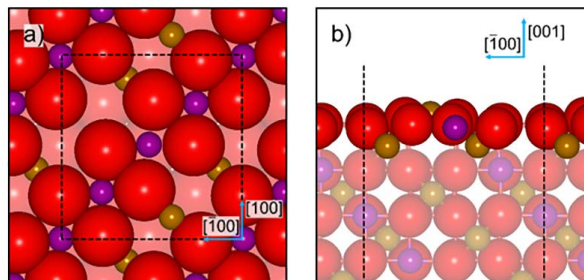


FIGURE A.2. (a) Top and (b) side view of the simulation slab for the $\text{Fe}_3\text{O}_4(001)$ surface. Layers containing atoms with dangling bonds are highlighted. Tetrahedral Fe_A atoms are in orange, octahedral Fe_B atoms are in violet and O atoms are in red. Dashed lines mark the limits of the computational cell. Crystallographic directions are indicated.

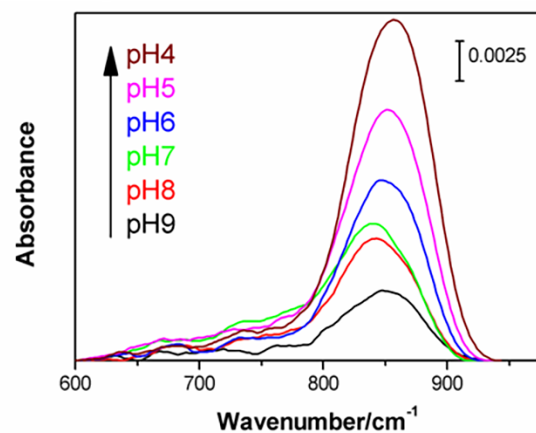


FIGURE. A.3. Spectrum of arsenate adsorbed on magnetite at different pH (arsenate concentration: $100 \mu\text{mol L}^{-1}$, range of pH: 4-9). The adsorption of arsenate on magnetite in pH range of 4-9 is studied by in situ ATR-FTIR, as the intensity of the band is proportional to the content of arsenate species adsorbed on magnetite surface. With the decrease of pH, the arsenate adsorption is obviously increased (Figure. A.3).

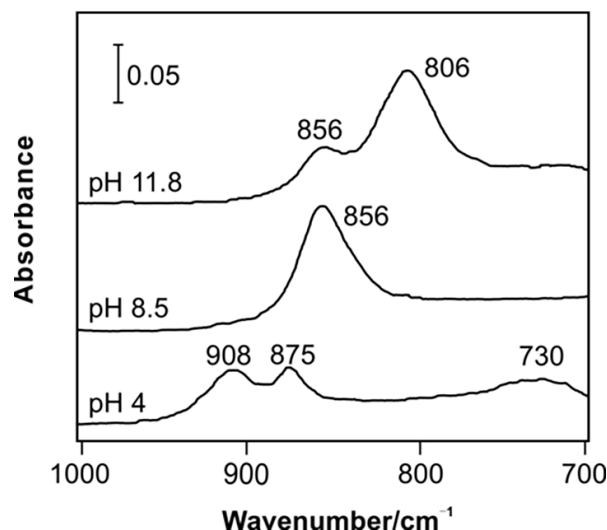


FIGURE. A.4. Spectrum of free arsenate oxyanions recorded at different pH. Based on the pK_{a1} (2.2), pK_{a2} (6.7) and pK_{a3} (11.2) values of arsenate (Mohan and Pittman, 2007), the predominant aqueous species at pH = 3.0 was $H_2AsO_4^-$, while $HAsO_4^{2-}$ was dominant at pH = 9 and AsO_4^{3-} together with $HAsO_4^{2-}$ dominated at pH = 12. The differences in protonation and thus symmetry of the above aqueous arsenate species were well-illustrated by IR spectra (Figure. A.4) (Carabante et al., 2009). At pH = 4, three bands appeared at 908, 878 and 738 cm^{-1} , assigned to the As-O asymmetrical stretching (ν_3) of the $H_2AsO_4^-$ aqueous species with C_{2v} symmetry. The spectrum recorded at pH = 8.5 for $HAsO_4^{2-}$ with C_{3v} symmetry showed a broad signal at 858 cm^{-1} composed of two ν_3 bands overlapped at 865 and 846 cm^{-1} , due to the stretching of As-O (Myneni et al., 1998). At pH = 11.8, the main signal at 802 cm^{-1} was related to the ν_3 band of AsO_4^{3-} with tetrahedral symmetry (T_d), which was accompanied by a weak band at 858 cm^{-1} originating from $HAsO_4^{2-}$. Thus, with the reduction of symmetry from T_d to C_{3v} and subsequently to C_{2v} or C_1 , the ν_3 vibrational mode was split from a single band into two and then three bands.

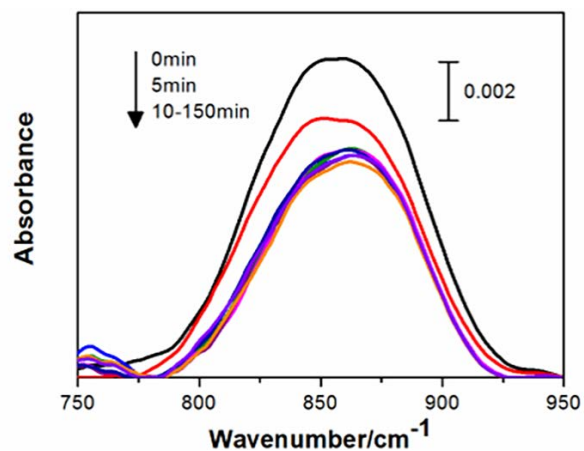


FIGURE. A.5. Spectral variation of arsenate adsorbed on Cr containing magnetite during its desorption by NaCl solution (NaCl concentration: 100 mmol L⁻¹, pH: 4.0). Once the arsenate solution in ZnSe cell is replaced by NaCl solution at pH 4.0, the band quickly decreases in intensity to some extent, but then keeps stable even after long period of desorption.

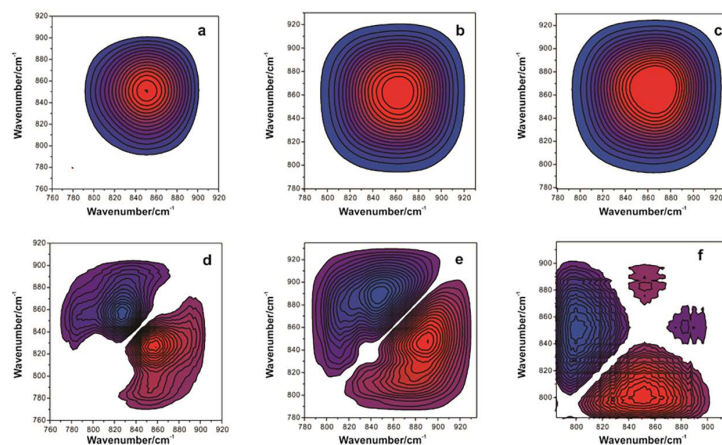


FIGURE A.6. The two-dimensional synchronous (a-c) and asynchronous spectra (d-f) of arsenate adsorption on magnetite at pH 4.0 (a, d), 7.0 (b, e) and 9.0 (c, f).

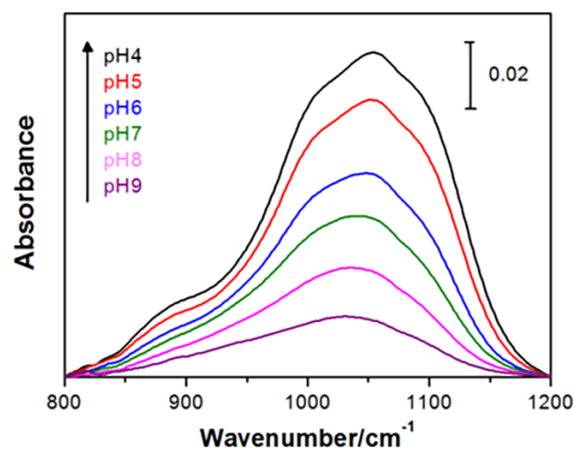


FIGURE. A.7. Spectrum of phosphate adsorbed on Cr containing magnetite at different pH (phosphate concentration: $100 \mu\text{mol L}^{-1}$, range of pH: 4-9). The adsorption of phosphate on magnetite in pH range of 4-9 is studied by in situ ATR-FTIR, as the intensity of the band is proportional to the content of phosphate species adsorbed on magnetite surface. With the decrease of pH, the phosphate adsorption is obviously increased (Figure. A.7).

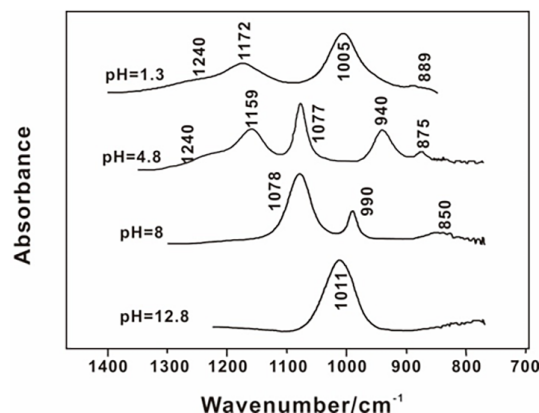


FIGURE. A.8. Spectrum of free phosphate oxyanions recorded at different pH. The pK_{a1} , pK_{a2} and pK_{a3} of phosphate were 2.2, 7.2 and 12.3, respectively. At pH = 12.8, the predominant aqueous species of phosphate was fully deprotonated (PO_4^{3-}) with T_d symmetry, which showed a single ν_3 vibration at 1006 cm^{-1} (Figure. A.8). At pH = 8, the main aqueous species became monoprotonated (HPO_4^{2-}) with C_{3v} symmetry, which was characterized by an active ν_1 band at 855 cm^{-1} and one ν_3 vibration, split into two bands at 1078 and 990 cm^{-1} . At pH = 4.8, the di-protonated species (H_2PO_4^-) with C_{2v} symmetry dominated, showing three ν_3 bands at 1159 , 1077 and 940 cm^{-1} and one ν_1 mode at 875 cm^{-1} . Further reduction of the pH value to 1.3, led to H_3PO_4 with C_{3v} symmetry to become the predominant species, producing two separate ν_3 bands at 1172 and 1005 cm^{-1} , and one ν_1 band at 889 cm^{-1} . For the two highest protonated H_2PO_4^- and H_3PO_4 aqueous species, the spectra displayed a broad band at 1240 cm^{-1} , which was attributed to the bending of $\delta(\text{POH})$ (Elzinga and Sparks, 2007).

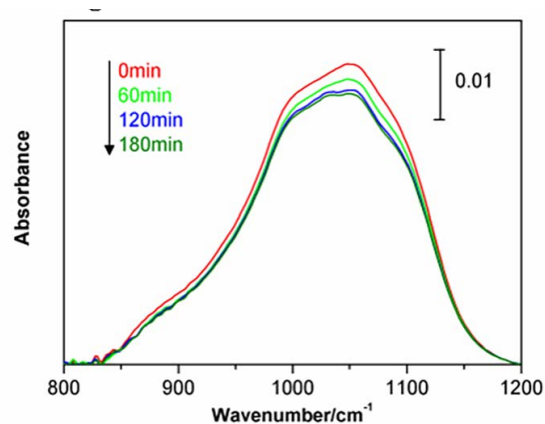


FIGURE. A.9. Spectral variation of phosphate adsorbed on Cr containing magnetite during its desorption by NaCl solution (NaCl concentration: 100 mmol L⁻¹, pH: 4.0). Although the phosphate solution in ZnSe cell was replaced by NaCl solution at pH 4.0 for a long period of desorption, the band just slightly decreased in intensity.

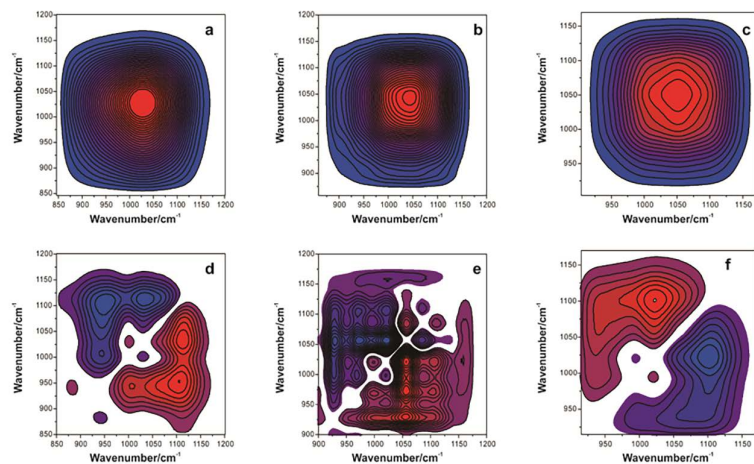


FIGURE. A.10. The two-dimensional synchronous (a-c) and asynchronous spectra (d-f) of phosphate adsorption on Cr-containing magnetite at pH 4.0 (a, d), 6.0 (b, e) and 9.0 (c, f).

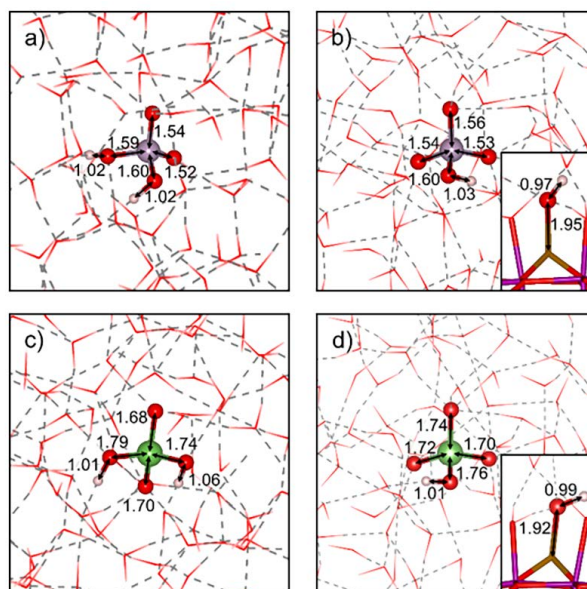


FIGURE. A.11. Schematic representation of the aqueous outer-sphere species (a) H_2PO_4^- , (b) HPO_4^{2-} , (c) H_2AsO_4^- , and (d) HAsO_4^{2-} . Di- and mono-protonated solute anions are under acid and alkaline conditions, respectively. Tetrahedral Fe_A atoms are in orange, octahedral Fe_B atoms are in violet, O atoms are in red, P atoms are in blue, As atoms are in green and H atoms are in pink. Surface atoms are represented as sticks, water solvent molecules are represented as wireframe and the solute molecules are represented as balls-and-sticks. Light and dark dashed lines mark hydrogen bonds and the limits of the computational cell, respectively. The double arrows indicate interatomic distances in Å.

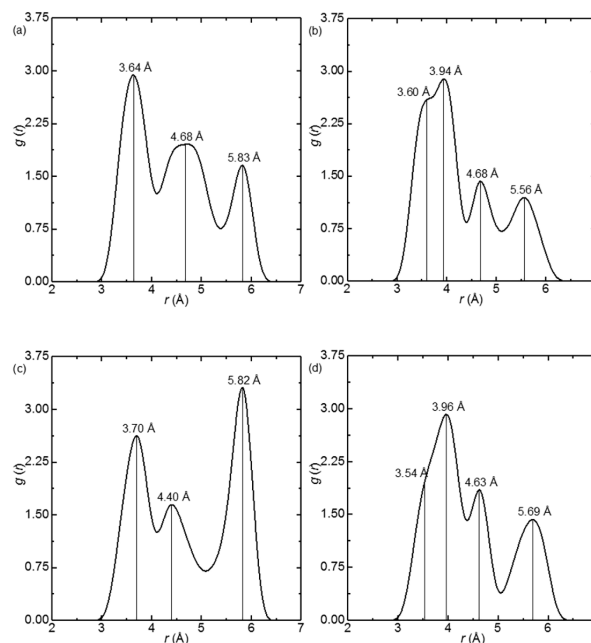


FIGURE A.12. Radial distribution function $[g(r)]$ plots for (a) H_2PO_4^- , (b) HPO_4^{2-} , (c) H_2AsO_4^- , and (d) HAsO_4^{2-} . Di- and mono-protonated solute anions are under acid and alkaline conditions, respectively. The radii are measured from the P or As solute central atom to the O of the water molecules. The radial distribution function was integrated using a width for the spherical shells of 0.3 Å.