Mechanistic modeling of arsenic retention on natural red earth in simulated environmental systems

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Abstract

Arsenic retention on natural red earth (hereafter NRE) was examined as a function of pH, ionic strength, and initial arsenic loading using both macroscopic and spectroscopic methods. Proton binding sites on NRE were characterized by potentiometric titrations yielding an average pH_{zpc} around 8.5. Both As(III)– and As(V)–NRE surface configurations were postulated by vibration spectroscopy. Spectroscopically, it is shown that arsenite forms monodentate complexes whereas arsenate forms bidendate complexes with NRE. When $4 < pH < 8$ and [total arsenic as As(III) or As(V)] = 0.385 μmol/L both arsenite and arsenate exhibit near 100% adsorption for a 10-fold variation of ionic strength that is ascribed to inner-sphere complexation of surface bonding. Arsenite exhibits an apparent bond-switching mechanism from inner-sphere to outer-sphere at excess As(III) loading (total arsenic as As(III) or As(V)] = 38.5 μmol/L. Competitive effect of arsenate for arsenite adsorption sites was observed when [initial As] = 0.385 μmol/L. In dual adsorbate systems the $\Gamma_{As(III)}$ was reduced over 20%, showing a competition of arsenite for arsenate binding sites (or vice versa). All experimental data were quantified with a 2pK generalized diffused layer model considering two site types for both protons and anions binding using reaction stoichiometries, as follows:

$$\equiv FeOH + H^+ \Leftrightarrow \equiv FeOH_2^+, \quad 4.744,$$
$$\equiv FeOH \Leftrightarrow \equiv FeO^- + H^+, \quad -9.03,$$
$$\equiv AlOH + H^+ \Leftrightarrow \equiv AlOH_2^+, \quad 7.229,$$
$$\equiv AlOH \Leftrightarrow \equiv AlO^- + H^+, \quad -9.316,$$
$$\equiv FeOH_{(s)} + H_3AsO_{3(aq)} \Leftrightarrow \equiv FeHAsO_{3(s)}^{2-} + H_2O, \quad 6.798,$$
$$\equiv AlOH_{(s)} + H_3AsO_{3(aq)} \Leftrightarrow \equiv AlHAsO_{3(s)}^{2-} + H_2O, \quad 5.319,$$
$$\equiv FeOH_{(s)} + H_2AsO_{4(aq)}^- \Leftrightarrow \equiv FeHAsO_{4(s)}^{2-} + H_2O, \quad 11.88,$$
$$\equiv AlOH_{(s)} + H_2AsO_{4(aq)}^- \Leftrightarrow \equiv AlHAsO_{4(s)}^{2-} + H_2O, \quad 9.061.$$

Keywords: Surface complexation; Generalized diffuse layer; Arsenite; Arsenate; Competitive adsorption; Natural red earth