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RESEARCH ARTICLE

ARSENITE REMOVAL FROM AQUEOUS SOLUTION BY MIXED MINERAL SYSTEMS II. THE ROLE OF SOLUTION COMPOSITION AND AGEING

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ABSTRACT

This study investigates arsenite removal onto binary mixed mineral sorbents from simulated wastewater, relevant to streams and groundwater impacted area. Mixed mineral suspensions of kaolinite/montmorillonite, goethite.kaolinite and goethite/montmorillonite exhibited different sorption behavior from the single mineral components, with goethite/montmorillonite demonstrating a stepwise decrease in arsenic sorption as pH increases. Changes in arsenic(III) sorption as particle concentration (Cp) increased was linear for goethite and mixed mineral systems containing goethite Kaolinite/goethite demonstrated a step down arsenite sorption for the first 288 hours, increasing arsenite sorption for the remaining residence time of the reaction. The complex behavior of mineral systems over the range of residence time investigated may be attributed to increased hydroxylation of the mineral surface resulting in the formation of new reactive sites.

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INTRODUCTION

Arsenic pollutants discharged by anthropogenic and natural could result in degraded surface and ground water chemistry) Altun and Pehlivan, 2012; Dupont *et al*, 2007; Ng, 2005; Ridge and Sedlak 2004). The need to reduce arsenic concentrations in water bodies remains a priority in both developed and most developing countries. The removal of dissolved arsenic species can be hampered by the absence of reliable sorbents and solution chemistry adequate to understanding arsenic sorption) Giménez *et al*, 2007; Nagar *et al*, 2010; Terminghoff *et al*, 1994). The removal of arsenic from contaminated water is controlled by the solution composition) Chowdhury and Yanful 2010; O. Altin, 1999), namely, pH and solid concentration, besides the residence time (ageing) of the solid phase in the water) Han *et al* 2013., Kitano *et al*, 1980; Banks *et al*, 1997; Schlegel *et al*, 2001). Since pH is considered a master variable in the removal of contaminants in aqueous environments, its effects on arsenic removal by mixed suspensions of clays and (hydr)oxides is an area of research interest) Lenoble *et al*, 2002; McBride, 19787). Solution pH controls (a) the solubilities of arsenic species; (b) hydrolysis behavior of arsenic ions; and (c) surface charge of the sorbent) Appel and Mao, 2002). Adsorption may decrease as particle concentration increases (outer sphere complexation) or not be significantly affected as particle concentration increases (inner sphere complexation))Sherman and Randall 2003., Goldberg and Johnston 2001; Petruzzelli and Pezzarossa, 2003; Di Toro, *et al*, 1986). Increase in adsorption as particle concentration increases (promotive particle concentration effects) for organic and inorganic substances sorbed on colloidal clay and oxide particles still remains an area of research interest in conventional surface complexation theory) Dzombak and

Morel, 1990; Lutzenkirchen, 2001). The solid concentration effect is an anomalous adsorption phenomenon (i.e., the adsorption isotherm declines as particle concentration increases). Although the cause of this phenomenon remains unclear, the nature of ionic species formed in solution is affected by changes in the mineral/ solution ratio) Lorenzen *et al* 1995; Fotova *et al* 1997). Prolonging the residence time of solid mineral phase in the absence of a sorbate could result in much mineral surface reorganization. This is due to the fact that high and new reactive sites are formed. However, this phenomenon on its own is not known to linearly affect arsenic sorption) Matis *et al*, 1999; Zhang *et al*, 2004; Philip 1999).

Theoretical models and isotherms

To address the suitability of mixed mineral suspensions of clay and (hydr)oxides for arsenite i.e. Arsenic(III) removal, a theory derived from Freundlich isotherm model is designed to explain the predicted behavior of mineral-arsenite interactions as influenced by extraneous factors of pH, solid concentration and contact time or ageing) O' zcan *et al* 2006., Awwal *et al* 2013). Detailed system characterization and an empirical model involving the distribution coefficient (Kd) as used in previous paper) Egirani *et al* 2005b). Distribution coefficient used in calculating arsenic sorbed was derived from the Freundlich model equation,

$$S = KdC^N \quad 1$$

where S is the sorbed concentration ($\mu\text{g}/\text{kg}$), Kd is the distribution coefficient, C is the equilibrium concentration ($\mu\text{g}/\text{g}$), and N = 1 is a chemical-specific coefficient derived from the slope of the plot. The empirical model as provided)Egirani *et al* 2005a) to address the mineral-arsenic interactions is given:

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Arsenic sorbed difference = arsenic sorbed-arsenic sorbed_{total}

$$\text{Arsenic sorbed}_{\text{total}} = \frac{S_1 + S_2 + S_n}{n} \quad 2$$

where arsenic sorbed_{total} is the theoretical sorption for a 1:1 mixed mineral suspension, S₁ is the arsenic sorbed on first single mineral suspension, and S₂ is the arsenic sorbed on second single mineral suspension, S_n is the arsenic sorbed on n number of mineral suspensions and n is the number of mineral suspensions.

The simple empirical model used for the partitioning of a sorbed arsenic contaminant between mineral phases in mixed suspension is based on the following assumptions:

1. No secondary mineral phase is developed by the mixed mineral suspension.
2. Components of minerals in the mixed mineral suspension act as individual networks and not as chemisorbed species.
3. Mass of mixed sorbent must be equal to the mass of the single mineral phases (i.e., there is no precipitation of arsenic complexes). The difference between the actual sorption and the theoretical sorption was used to clarify the effects of mineral mixing on arsenic sorption. Mineral mixing is said to (a) enhances arsenic removal where the difference is positive; (b) depresses arsenic removal where the difference is negative; and (c) have no effect on arsenic removal where no difference exist between arsenic sorbed and theoretical arsenic sorption.

In this paper the sorption relationship between simulated contaminated water containing arsenic and mixed mineral suspensions of kaolinite/montmorillonite, kaolinite/goethite and montmorillonite/goethite based on different solution composition such as pH, solid concentration and residence time (ageing) conditions was investigated.

EXPERIMENTAL METHODS

Sorption experiments

Batch mode experiments in this study were conducted using 1:1 single mineral suspensions of kaolinite, montmorillonite and goethite. Also, 1:1 mixed mineral suspensions of kaolinite/montmorillonite, kaolinite/goethite and montmorillonite/goethite were used to elucidate the difference in sorption between the single and mixed mineral phases. Characterization of sorbents used in this study included (a) particle size; (b) pH and (c) specific surface area (SSA) and details provided elsewhere in a companion paper I. For batch mode pH investigation, single and 1:1 mixed mineral suspensions made up to 50 ml containing 1% (by mass) mineral suspension were reacted with solution containing 15 ppm of arsenite at zero electrolyte background. Treated suspension was adjusted to the required pH (ranging from pH 4 to 8) using 0.1 M HNO₃ and 0.1 M NaOH. The treated suspensions were equilibrated for 24 h and pH measured using a Model 3340 Jenway ion meter.

For batch mode solid or particle concentration investigation, single and 1:1 mixed mineral suspensions were made up to 50 ml containing solid concentrations (g/l) of 2, 4, 6, 8 and 10 were reacted with solution containing 15 ppm of arsenite at zero electrolyte background. The treated suspensions were adjusted to pH 4 and equilibrated for 24 h.

Batch mode ageing investigations was carried out from 24 to 720 h using single and 1:1 aged mixed mineral suspensions containing 1% (by mass) were reacted with solution containing 15 ppm of arsenite at zero electrolyte background. The treated suspensions, adjusted to pH 4 with no added electrolyte, were equilibrated for 24 h.

In all experimental studies samples were stored in the dark at room temperature (23±3 °C) for a maximum of 24 h before analysis (Morton 2001). Supernatant was filtered through a cellulose acetate filter (pore size 0.2 µm) and analyzed for arsenic (III), using a Hitachi Atomic Absorption Spectrophotometer (HG-AAS).

RESULTS AND DISCUSSION

Mixed mineral suspensions and pH effects on arsenic (III) removal

Arsenic (III) demonstrated a near linear sorption increase with increasing pH for single mineral suspensions of kaolinite, montmorillonite, and mixed mineral suspensions of kaolinite/montmorillonite (Fig. 1). The behavior of goethite and mixed mineral systems containing goethite demonstrated a non-linear behaviour in arsenic (III) removal. Goethite and goethite/montmorillonite demonstrated a stepwise decrease in arsenic sorption as pH increases. Arsenic sorption by goethite/kaolinite increased linearly between pH 4 and pH 6, dipping upto pH 7 before increasing over the remaining range of pH. This variability in sorption may be attributed to increased deprotonation of reactive sites as pH was increased. However, sorption pattern appeared to be controlled by outer sphere complexation, inner sphere complexation and intra-particle diffusion for arsenic sorption on goethite and mixed mineral systems containing goethite.

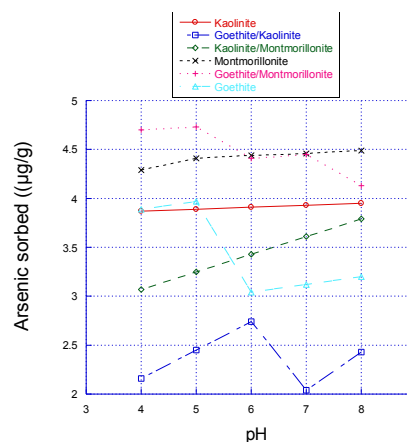


Fig. 1 Plots of arsenic sorbed versus pH for single and mixed mineral systems

Mixed mineral suspensions and Cp effects on arsenic (III) removal

A change in arsenic (III) sorption as particle concentration (C_p) increased was linear for goethite and mixed mineral systems containing goethite. Kaolinite demonstrated a step-

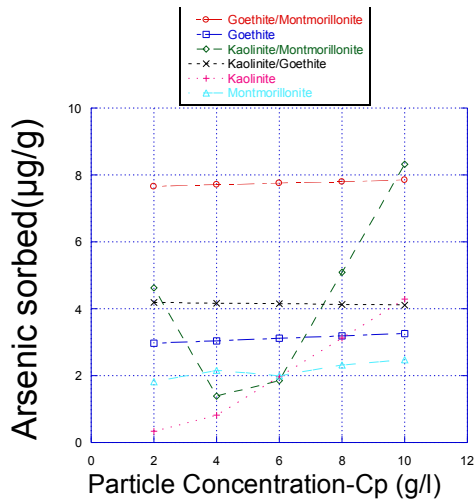


Fig. 2 Plots of arsenic sorbed versus particle concentration for single and mixed mineral systems

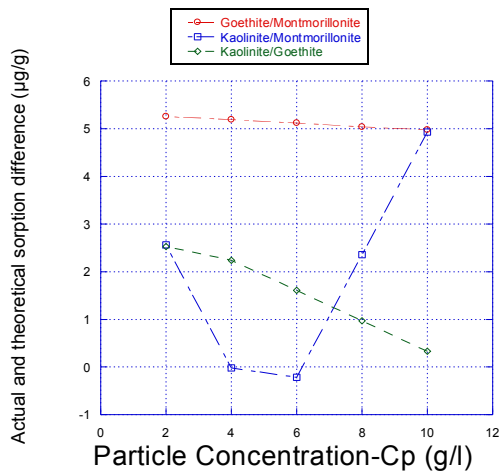


Fig. 3 Plots of actual and theoretical sorption differences versus particle concentration For arsenite sorbed on mixed mineral systems

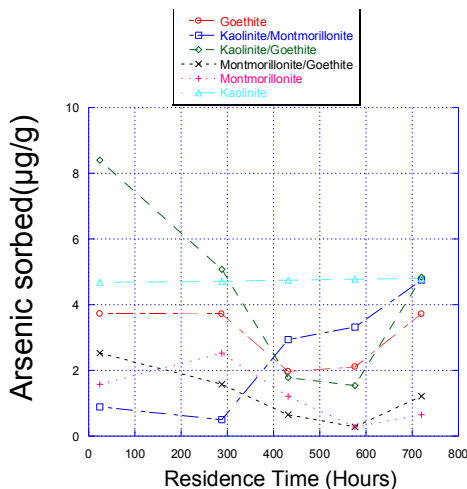


Fig. 4 Plots of arsenic sorbed versus residence time for single and mixed mineral systems

wise increase in arsenic (III) sorption as particle concentration was increased. Kaolinite/montmorillonite recorded a stepwise decrease in arsenite sorption upto pH 4, then increasing upto pH 8 (Fig. 2). Goethite in mixed suspensions may form separate (discrete) particles or it may form coatings on other mineral surfaces. Coatings of only a few atomic layers thickness are sufficient to influence sorption rates (Stipp *et al* 2002). This may account for differences in sorption behavior for arsenite sorbed on mixed suspensions containing goethite.

Decrease in arsenite sorption as Cp increases may be attributed to increase in particle size and aggregation of the mineral suspensions. The Cp effect is also related to effective surface area, pressure, and force at the mineral/water interface (20). Increase in Cp results in low pressure at the interface and a subsequent decrease in sorbing ion diffusion to reactive sites (Egirani *et al* 2005a, Egirani *et al* 2005b).

Arsenite sorbed difference (i.e., arsenite sorption obtained by experiments) and theoretical arsenite sorption (i.e., the predicted arsenite sorption obtained from the average summation of arsenite sorbed on the single mineral suspensions used in the mixing experiments) on kaolinite/montmorillonite showed negative sorption differences between the arsenite sorbed on the mixed mineral suspensions over the Cp range of 4 and pH 6, becoming positive as Cp increased to 8 and 10 (Fig.3). This means that mineral mixing reduced arsenite sorption within this range of Cp. However, differences in arsenite sorbed on the rest of the mixed mineral systems was positive indicating increased arsenite sorption due to mineral mixing with respect to Cp effect (Appel and Mao, 2002).

Mixed mineral suspensions and ageing effects on arsenic (III) removal

All single and mixed mineral systems except kaolinite demonstrated step-wise arsenite sorption (Figure 4). Kaolinite/goethite demonstrated a step down arsenite sorption for the first 288 hours, increasing arsenite sorption over time for the remaining residence time of the reaction. Goethite/montmorillonite demonstrated step down arsenite sorption for the first 576 hours, stepping up arsenite sorption for the remaining residence time of the reaction. Kaolinite/montmorillonite demonstrated a step-wise increase in arsenite sorption of the range of residence time in the reaction. Arsenite step-wise sorption probably indicated reaction phases attributed to outer sphere, inner sphere complexation and intra-particle diffusion as reported in paper I. The behavior of goethite as a single mineral or component of mixed mineral systems could be attributed to its high surface area when compared to the other minerals (Egirani *et al* 2005a, Egirani *et al* 2005b)). Differences between actual and theoretical arsenite sorption was positive for all mixed minerals, indicating increase in arsenite sorption. Increase in arsenite sorption as residence time increases may be attributed to increased hydroxylation of the mineral surfaces, resulting in the formation of new reactive sites (Schlegel, *et al* 2001).

CONCLUSIONS

The possibilities of using mixed sorbents of kaolinite, montmorillonite, and goethite to remove arsenite from simulated contaminated surface and ground water has been

investigated as a function of solution composition and ageing. Variability in arsenite sorption exists over the range of pH investigated. This variability in sorption may be attributed to increased deprotonation of reactive sites as pH was increased. Sorption pattern appeared to be controlled by outer sphere complexation, inner sphere complexation and intra-particle diffusion for arsenic sorption on goethite and mixed mineral systems containing goethite.

Single and mixed mineral systems exhibited different sorption patterns. Arsenic (III) sorption increased with increase in Cp with respect to goethite and mixed mineral systems containing goethite. Kaolinite/montmorillonite recorded a stepwise decrease in arsenite sorption upto pH 4, then increasing upto pH 5. While increase in arsenite sorption with increase in Cp may be attributed to increase in specific surface area, a decrease in arsenite sorption over the range of Cp investigated may be attributed to increase in particle size, flocculation and aggregation of mineral suspension.

All single and mixed mineral systems except kaolinite demonstrated step-wise arsenite sorption which may be attributed to inner sphere complexation, outer sphere complexation and intra-particle diffusion. The variable and complex behavior of mineral systems over the range of residence time investigated may be attributed to increased hydroxylation of the mineral surface resulting in the formation of new reactive sites.

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