RESEARCH ARTICLE

ARSENITE REMOVAL FROM AQUEOUS SOLUTION BY MIXED MINERAL SYSTEMS I. REACTIVITY AND REMOVAL KINETICS

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ARTICLE INFO

ABSTRACT

This study investigates the reactivity and removal kinetics of arsenite on mixed mineral systems from aqueous solution related to contaminated waters. The sorbents used were kaolinite, montmorillonite, goethite, and their mixtures. The effects of, proton coefficient, and sorption kinetics were studied at room temperature (23 ± 2°C). Reactivity studies demonstrate reduction in proton coefficient and the acidity of reactive sites by mixed mineral systems, thus impeding arsenite removal by proton exchange. Kinetic studies demonstrate three phase reactions attributed to outer sphere complexation, inner sphere complexation and intra-particle diffusion. Mineral mixing reduced the mass transfer rate of arsenite for kaolinite/montmorillonite in all reaction phases. The behaviors of the mixed mineral systems in arsenite sorption suggest that different reactive sites were involved at the onset of sorption, with reactions and sorption ending in intra particle diffusion over time. Mineral mixing increased % sorption when compared with the single mineral systems. % sorption was a function of the surface area of the mineral sorbent.

INTRODUCTION

Arsenic as an element remains near the top of the toxic list and its high level in drinking water is a problem in many countries (Pehlivan *et al.,* 2013, Farias *et al.,* 2003, Fazal and Kawaci, 2001). Arsenic is toxic to plants and animals, inorganic arsenic species are strong carcinogens to humans (Han *et al.,* 2013, Zhang *et al.,* 2011, Ng, 2005). Usually, arsenic is taken up and accumulated in the human body through drinking water. The human toxicity of arsenic ranges from skin lesions to cancer of the brain, liver, kidney, and stomach. Arsenic intake causes disturbance of nervous system functions and can lead to death (Awual *et al.,* 2013, Liu *et al.,* 2013, Jain and Ali, 2000, Boddu, Abburib, Talbottc, Smitha, and Haasch, 2008). Because of these effects, the World Health Organisation (WHO) and the United State Environmental Protection Agency (USEPA) reduced the arsenic standard concentration in drinking water from 50 to 10 mg/l (WHO 2006, USEPA 2001).

For successful treatment of water containing arsenic using mineral systems, a full understanding of the reactivity and the transport of reaction partners to the reactive sites of arsenic sorbents is required for environmental fate and managerial decisions (Dalmacija *et al.,*2011, Jain and Ali, 2000., Hatje *et al.,*2003, Pohlmeier and Lustfeld 2004).The removal of arsenic from water is controlled by the speciation, mobility, ionic size of the sorbing ions, sorbate composition, sorbent solubility, sorbent particle size, sorbent surface charge, surface area of the mineral sorbent, solution dilution and H+/ AsO_3 exchange stoichiometry (Kumaresan and Riyazuddin, 2001., Waeles *et al.,*2013., Pohlmeier and Lustfeld 2004, Kitano *et al.,*1980).

Arsenic ions occur in surface and ground waters in both organic and inorganic species, the inorganic forms being the predominant ones, e.g. arsenite (H_2AsO_3) and arsenate (H_2AsO_5) (Srivastava *et al.,*2013, Fazal and Kawaci, 2001).

Several methods have been established in the treatment of arsenic contaminated water. Some of these techniques include (Fe-electro-coagulation/co-precipitation, coagulation–microfiltration, oxidation/precipitation, coagulation/precipitation, reverse osmosis, filtration, nanofiltration, ion-exchange) and different adsorbents (cellulose beads loaded with iron oxyhydroxide, iron-oxide coated sand, granular ferric hydroxide, activated carbon, fly ash, zeolites, Calix(4)arenegrafted magnetite nanoparticles) have been used for the removal of arsenic (Guo and Chen, 2005; Gupta, Basu, and De, 2007; Leupin and Hug, 2005; Singh and Pant, 2004; Badruzzaman, Westerhoff, and Knappe, 2004; Mondal, Balomajumder, and Mohanty, 2007; Sayin *et al.,* 2010). However, some of these new techniques are rather expensive for limited size water treatment systems situated in rural communities. Consequently, innovative cost-effective treatment processes are urgently needed.One of such emerging method is the use of mixed mineral systems of clays and hydroxide(s) (Ahmad *et al.,* 2004).Mixed mineral systems that could be applied for arsenic removal from contaminated water are readily available locally.

Theoretical models and isotherms

To addresses the suitability of mixed mineral suspensions of clay and (hydr) oxides for arsenite i.e.Arsenic (III) removal, a theory is designed to explain and predict the behavior of mineral-arsenite interactions. Adsorption isotherms give a quantitative relationship between the solute concentration in the solution and the amount of solute adsorbed per unit mass

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of the adsorbent surface at equilibrium conditions. Langmuir, Freundlich, Dubinin–Radushkevich (D–R) are the commonly used isotherms. Selection of the type of isotherm depends upon number of factors such as environment, nature of adsorbent and adsorbate, their concentrations and types, and other environmental factors like pH and ionic strength (O¨zcan *et al.*, 2006; Saqiba *et al.*, 2013). In the present study, an empirical model derived from Freundlich isotherm model was chosen. Detailed system characterization and an empirical model involving the distribution coefficient (Kd) as used in this paper are provided in previous paper (Egirani *et al.*, 2005b). Kd was calculated from the Freundlich model equation,

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

where S is the sorbed concentration (μg/kg), Kd is the distribution coefficient, C is the equilibrium concentration (μg/l), 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:

$$K_{dtotal} = Kd_{total} = \frac{Kd_1 + Kd_2 + Kd_n}{n} \qquad 2$$

where Kd_{total}l is the theoretical distribution coefficient for a 1:1 mixed suspension, Kd_1 is the distribution coefficient for first single mineral suspension, and Kd_2 is the distribution coefficient for second single mineral suspension, Kd_n is the distribution coefficient for 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 Kd and the theoretical Kd (Kd_{total}) was used to clarify the effects of mineral mixing on arsenic removal. 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 the actual Kd and theoretical Kd:

$$\Delta Kd = Kd - Kd_{total} \qquad 3$$

For the reactivity and removal kinetic studies, the empirical model for the mixed mineral systems was related to α and Kf as follows:

$$\Delta \alpha = \alpha - \alpha_{total} \qquad 4$$
$$\Delta K_f = K_f - K_{f\,total} \qquad 5$$

where α, K_f, α_{total} and $K_{f\,total}$l are the proton coefficient, mass transfer rate, theoretical proton coefficient and

theoretical mass transfer coefficient, respectively. The main objective of this work is to determine the effects of mineral mixing on the reactivity and kinetics involved in arsenic removal from contaminated water. Mixed mineral suspensions of kaolinite, montmorillonite, and goethite used in this work were chosen to simulate natural minerals found in arsenic impacted areas.

The sorption kinetic model assumed that sorption rate was determined by sorption interaction between the sorbent reactive sites and the sorbate involving outer sphere complexation and inner sphere complexation (Tombacz *et al.*, 1999, Sherman and Randall 2003). Otherwise, the intra-particle diffusion involving the diffusion of the adsorbate in the pore of the adsorbent as a third sorption reaction step was involved (Blesa *et al.*, 1997). This is due to the fact that surfaces of clays and hydroxides have a high concentration of OH⁻ groups readily protonated at low pH, generating positive charge which retains anions by electrostatic attration (McBride 1982).

The mass balance of As(III) adsorbed per mass unit of the mixed mineral suspension (mg/g) was calculated by the following (Jiménez-Cedillo *et al.*,2011, Gile *et al.*,2013, Al-Degs *et al.*,2003., McLean and Bledsor, 1992., Altun and Pehlivan, 2012):

$$Q_e = \langle Ci - Ce \rangle \frac{V}{W} \qquad 6$$

where Ci and Ce are the initial and equilibrium As(III) concentrations in mg/l,. V is volume of the As(III) solution in ml, and W is the weight of adsorbent in mg respectively.

MATERIALS AND METHODS

System characterization

Clays used in this study provided by the Richard Baker Harrison Company and Acros Organics Ltd and (hydr)oxides provided by Iconofile Company Inc were nitrogen flushed and stored in airtight containers to avoid surface oxidation. Arsenic (III) stock solution was purchased from Merck. The AAS standard solution of 1000 mg/l Arsenic(III) was prepared by transferring the contents of a Titrisol ampule with As_2O_3 in H_2O (Merck, Germany) into a volumetric flask, which was filled up to the mark and stored at 20±2°C according to the instructions by Merck. The working solutions of different concentrations were prepared by diluting the stock solution immediately before starting the batch studies.

For sorbent characterization, the (a) Coulter laser method was used to determine the particle sizes; (b) % colloid was estimated from the particle size distribution curves; (c) equilibrium pH of the untreated mineral suspensions was determined using the Model 3340 Jenway ion meter; (d) the standard volumetric Brunauer, Emmett, and Teller (BET) method was used to determine the surface areas (Brunauer *et al.*, 1938. Hlavay and Polyak 2005) (e) the Na saturation method was used to determine cation exchange capacity (CEC) of the clay minerals (5) (Table 1). (f) Spectral analysis was performed using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) to confirm the mineral sorbent (Zhang *et al.*, 2011, Silva *et al.*, 2011, Egirani *et al.*, 2005a)

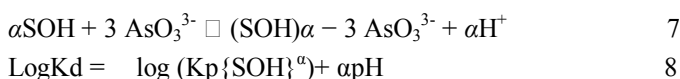**Table1** Characteristics of clays and hydrous oxides (Egirani *et al*, 2005a)

Mineral	Particle size (μm)	% (<1 μm) colloid	pH ± σ	Surface area(SSA±σ) (m2/g)
Kaolinite	20.01±0.5	3.00	6.05±0.05	47.01± 0.24
Montmorillonite	80.05±0.20	0.53	2.01±0.09	10.00± 0.00
Goethite	40.10±0.15	2.92	8.05±0.06	71.05± 0.17
Kaolinite/montmorillonite	80.05±50	0.97	5.01±0.02	88.05± 0.55
Montmorillonite/goethite	15.25±0.24	3.85	3.03± 0.04	147.10± 0.50
Kaolinite/goethite	140.35±55	0.73	3.05± 0.01	79.30± 0.59

Reactivity experiments

For reactivity studies to determine the proton coefficient as provided (Eqs. (8), (9), standard laboratory procedure was used (Sparks 2003, Cavallaro and McBride 1978). 1% single and 1:1 mixed mineral suspensions with no added electrolyte were reacted with solution containing 10ppm of arsenite regulated to the required pH at the start of experiments.

To validate the sorption mechanism involved in arsenite removal 1% single and 1:1 mixed mineral suspensions made up to 50 ml were reacted with solution containing 10 ppm of arsenite regulated to pH 4. 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).

Surface charge controls the reactivity of mineral surfaces and is dependent on the acid–base properties of surface hydroxyl groups, where H+ and OH− are the potential-determining ions (Blesa *et al.,* 1997). Sorption of arsenite on mineral surfaces requires proton exchange, the stoichiometry of this reaction is described (Egirani *et al.,* 2005a) and the proton consumption function is given by:

$$\alpha SOH + 3\ AsO_3^{3-} \ \square\ (SOH)\alpha - 3\ AsO_3^{3-} + \alpha H^+ \qquad 7$$

$$LogKd = \quad log\ (Kp\{SOH\}^{\alpha}) + \alpha pH \qquad 8$$

where SOH is the mineral surface-binding site, 3 AsO_3^{3-} is the soluble arsenic species, $(SOH)\alpha - 3\ AsO_3^{3-}$ is the surface bound arsenic, logKp is the apparent equilibrium binding constant, and α is the proton coefficient, representing the number of protons displaced when one mole of arsenite binds to the mineral surface (Kooner 1993). Proton coefficient was calculated from the slope of logKd versus pH plot provided (Table2, Fig. 2).

Kinetic experiments

For arsenic removal kinetics experiments, 1% single and 1:1 mixed mineral systems were reacted with solution containing 10ppm of arsenite regulated to pH 4. Amounts of Arsenite remaining in solution after 2, 4, 6, 8, 12, 18, and 24 h were determined using Hitachi Atomic Absorption Spectrophotometer (HG-AAS). Twenty-four hours was sufficient for kinetic studies because sorption reactions occur in milliseconds or minutes (Morton *et al.,* 2001, Raven *et al.,* 1998).

The transport of adsorbate from external layers to the mineral surface where sorption occurs is dependent on a mass transfer constant Kf obtained from the slopes of the curve derived from plotting $Ct/C0$ vs time (Hong *et al.,*2011, von Gunten 2006., Banerjee *et al.,*2008., Singh and Pant 2004., Oke *et al.,*2008., Egirani *et al.,*2005a),

$$\left[\frac{d(C_t/C_0)}{dt}\right]_{t=0} \cong -K_f\ Ss \qquad 9$$

where C_t and C_0 are the initial concentrations of Arsenite at time t , Ss is the exposed external surface area of the sorbent, and K_f is the mass transfer coefficient (Al-Degs 2003). The Freundlich isotherm was chosen to describe sorption of Arsenite because this is suitable for heterogeneous surfaces over a wide range of solute concentrations (Vitela-Rodriguez and Rangel-Mendez 2013, McLean and Bledsoe 1992).

At the end of equilibration, suspensions were shaken and centrifuged at 3000 rpm for 15 min and passed through a 0.2-μm filter to remove suspended solids. The amount of metal remaining in solution was then determined. In all experiments conducted, each treatment had three replicates and the differences in replicate runs were not statistically ($\chi2$) significant ($P \leq 0.01$).

RESULTS AND DISCUSSION

Mixed mineral systems and H+/ AsO₃³⁻ exchange stoichiometry

Although the proton coefficient (α) is not characteristic of a particular mineral (Table 2, derived from Figs.1), differences in α for mixed mineral systems   compared to each other and compared to single mineral systems   may be linked to differences in the availability of strongly acidic sites All proton coefficient for arsenite sorbed on single mineral systems except for goethite are greater than one. This indicates high level of protonation during the sorption process. Proton coefficient for arsenite-kaolinite interaction was higher than arsenite sorbed on goethite and montmorillonite. This may be attributed to the acidic sites present on kaolinite planar surface. Significant numbers of weakly acidic edge sites in goethite and montmorillonite may reduce the proton coefficient because of the limited exchange of protons for sorbing ions.

Table2 Proton coefficients (α) and regression coefficient (R^2) of Arsenite sorbed on mineral suspensions

Mineral suspensions	R^2	α	α_{total}
Kaolinite	0.99	1.50	$\otimes$
Goethite	0.99	0.96	$\otimes$
Montmorillonite	0.99	1.13	$\otimes$
Kaolinite/montmorillonite	0.99	1.14	1.32
Goethite/kaolinite	0.99	1.10	1.23
Goethite/montmorillonite	0.99	1.65	1.045

Note: $\otimes$ not applicable

Except for montmorillonite/goethite mixed suspension, α for arsenite sorbed on the remaining mixed suspensions were

lower than α_{total}, indicating increased potonation when montmorillonite was mixed with goethite. On the contrary, there was decreased protonation when kaolinite was mixed with either montmorillonite or goethite. The higher the acidity of sites the more protons are exchanged for arsenite. Therefore, mineral mixing reduces the acidity of reactive sites for kaolinite/montmorillonite and kaolinite/goethite mixed minerals interacted with arsenite. This may be due to the competition for the sorbing ion by the mixed mineral surfaces (Goldberg and Johnston 2001., Guo *et al.,* 2007., Zhang *et al.,* 2007., Tseng 2004., Barnett 1992). The $H+/ AsO_3^{3-}$ exchange stoichiometry of <2 (Table 2) for arsenite sorption on both the single and mixed mineral phases agrees with the findings of (Kooner 1993) for ions sorbed on (hydr) oxides. This suggests that surface charges become increasingly changed as arsenic sorption takes place. In addition, mineral surfaces with few displaceable H+ with limited pH-dependent sorption support lower $H+/ AsO_3^{3-}$ stoichiometry.

montmorillonite/goethite mineral system demonstrated a decrease in mass transfer rate for the mixed mineral systems in the order: KfI<KfII<KfIII. Goethite as a single mineral system or component of mixed mineral system behaved differently from the clay minerals in arsenite sorption. Mineral mixing reduced mass transfer rate for arsenite treated with kaolinite/montmorillonite and montmorillonite/goethite. On the other hand, mineral mixing increased the mass transfer rate in all reaction phases for arsenite treated with kaolinite/goethite. Differences in mass transfer rates of arsenite to the mineral reactive sites may be attributed (a) to different types of reactive sites on the single and mixed mineral systems (b) differences in surface area for the mineral systems and (c) differences in particle size distribution of these mineral systems (Yu et *al.,* 2013, Al-Degs *et al.,* 2003).
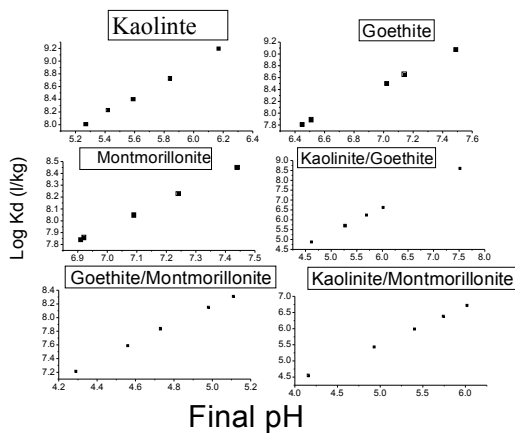

Fig. 1 Plots of logKd versus final pH for As (III) sorbed on mineral suspensions: (a) kaolinite, (b) montmorillonite, (c) goethite, (d) kaolinite/montmorillonite, (e) kaolinite/goethite, (f) montmorillonite/goethite
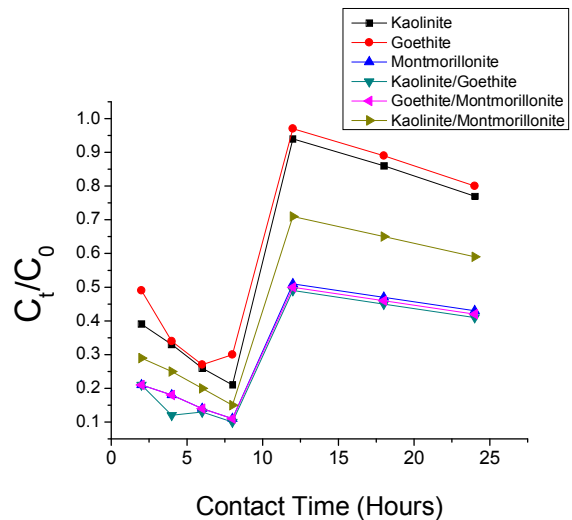

Fig. 2. Effects of arsenite sorption on mass transfer rates: (a) kaolinite; (b) montmorillonite; (c) goethite; (d) kaolinite/montmorillonite; (e) kaolinite/ goethite; (f) montmorillonite/goethite suspensions.

Mixed mineral systems and sorption kinetics

Sorption kinetics indicated a three phase reaction probably attributed to outer sphere, inner sphere complexation and intra-particle diffusion (Table 3, Fig 3).

Mixed mineral systems and arsenic removal

% sorption still indicated a three phase reaction probably attributed to outer sphere, inner sphere complexation and intra-particle diffusion (Table 3, Fig 3).

Table 3 Mass transfer rates for Arsenite sorbed on clay and (hydr) oxide mineral suspensions

Parameters/ Mineral	Kaolinite	Montmorillonite	Goethite	Kaolinite/ Montmorillonite	Kaolinite/ Goethite	Montmorillonite/ Goethite
slopeI(hr^{-1})	-0.92	-0.081	-0.036	-0.062	-0.082	-0.044
slopeII(hr^{-1})	-0.033	-0.064	-0.031	-0.058	-0.058	-0.031
Slope III(hr^{-1})	-0.025	-0.048	-0.026	-0.036	-0.48	-0.026
Exposed Surface Area(cm^{-1})	4700	1000	7100	8800	7900	14700
K_fI (cmhr^{-1})	0.00020	0.000081	0.00000051	0.0000070	0.000010	0.0000030
Theoretical K_fI (cmhr^{-1})				0.00014	0.00010	0.000041
K_fII (cmhr^{-1})	.0000070	0.000064	0.00000014	0.0000048	0.0000073	0.0000021
Theoretical K_fII (cmhr^{-1})				0.000064	0.0000036	0.000032
K_fIII (cmhr^{-1})	0.000005	0.000048	0.0000037	0.0000041	0.000061	0.000018
Theoretical K_fIII (cmhr^{-1})	*	*	*	0.000027	0.0000044	0.000026

Note: * Not applicable

Except for goethite, mass transfer rate decreased in the order $K_{fI}<K_{fII}<K_{fIII}$ for all single mineral systems. Only

All mineral systems demonstrated increase in % sorption at the onset of reaction, indicating a reaction dip after 6 hours of contact or residence time. Reaction dip ended after 12 hours of

residence or contact time, resulting in % sorption increase for the rest of reaction time. Goethite as a single mineral system or component of mixed mineral system behaved differently from the clay minerals in arsenite sorption recording highest % sorption. This could be attributed to the high surface area of goethite compared to the other minerals (Table 1). Differences between actual and theoretical % sorption was positive for all mixed minerals, indicating increase in % sorption.

Table 4 Arsenite sorbed (µg/g) on mineral suspensions at pH 4, zero ionic strength and 5ppm initial arsenic concentration

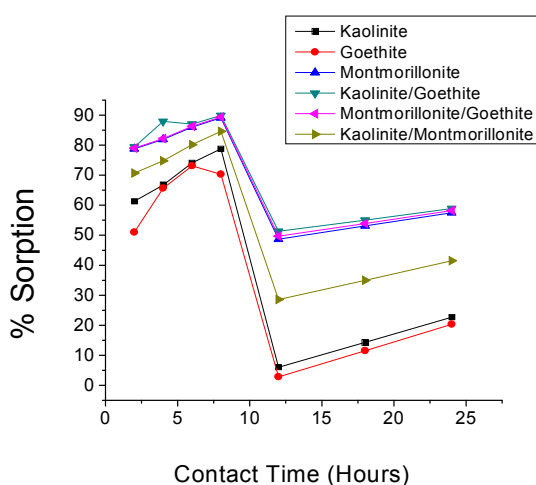| Mineral suspensions	Metal sorbed (µg/g)
Kaolinite	3.87
Goethite	3.89
Montmorillonite	4.29
Kaolinite/montmorillonite	3.07
Goethite/kaolinite	2.16
Goethite/montmorillonite	4.70

Fig.3. Plots of % sorption vs. centime time (hours): (a) kaolinite/montmorillonite;(b)kaolinite/goethite;(c) montmorillonite/goethite suspensions.
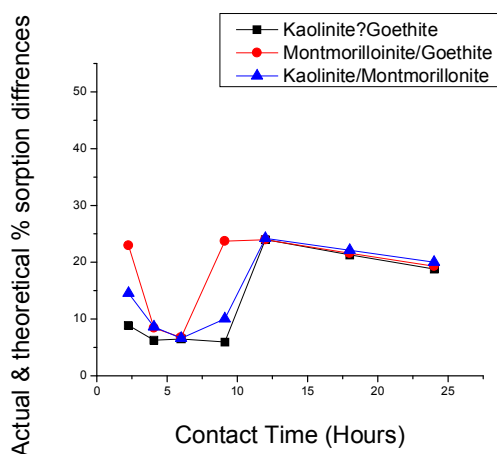

Fig.4 Plots of differences between actual percent of Arsenite removal and Theoretical percent vs. contact time (hours): (a) kaolinite/montmorillonite;(b)kaolinite/goethite;(c) montmorillonite/goethite suspensions.

CONCLUSIONS

The reactivity and removal kinetics of arsenite treated with single and mixed mineral systems of kaolinite, montmorillonite and goethite has been investigated. Using empirical models derived from Freundlich isotherm model, proton coefficient for arsenite sorbed on kaolinite and montmorillonite were greater than one, indicating high protonation during arsenite-mineral interactions. Whilst mineral mixing increased protonation for montmorillonite/goethite, kaolinite/montmorillonite and kaolinite/goethite mixed suspensions indicated decrease in protonation This means that mineral mixing reduces the exchange of protons for sorbing ions and the acidity of the reactive sites with respect to some of these mixed mineral systems. The H+/ AsO_3^{3-} exchange stoichiometry of <2 for arsenite sorbed on all mineral systems suggests that maximum protonation was not achieved in all reaction phases.

Kinetic studies demonstrated three phase reactions attributed to outer sphere complexation, inner sphere complexation and intra-particle diffusion. Except for goethite, mineral mixing reduced the transfer rate of arsenite to reactive sites of the single mineral systems in all reaction phases. The predicted mass transfer rates of arsenite to the mixed mineral reactive sites was higher (except for kaolinite/goethite) from the actual transfer rate during the reaction phases. This suggests that different reactive sites are involved in the removal kinetics of the sorbing ions as sorption progresses. Differences in sorption kinetics between the single and mixed mineral phases may be attributed to differences in the surface area and particle size distribution of single and mixed mineral systems.

Goethite as a single mineral system or component of mixed mineral system behaved differently from the clay minerals in arsenite sorption and recorded highest % sorption. This could be attributed to the surface area of goethite compared to the other minerals. Mineral mixing increased % sorption when compared with the single mineral systems. % sorption was a function of the surface area of the mineral sorbent.

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