

Arsenite Removal from Aqueous Solution using Mixed Mineral Systems Injected with Iron Sulfide under Sulfidic- Anoxic conditions 1: Reactivity and Removal Kinetics

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Abstract: The reactivity and removal kinetics of arsenite treated with single and mixed mineral systems of kaolinite, montmorillonite and goethite injected with iron sulfide under sulfidic- anoxic conditions has been investigated. Using empirical models derived from Freundlich isotherm model, injection of sulfidic-anoxic solution of iron sulfide onto the mixed mineral systems enhanced proton coefficient of all single minerals. Differences in sorption kinetics between the single and mixed mineral phases may be attributed to different types of reactive sites on the single and mixed mineral systems. Except for iron sulfide, kinetic studies demonstrated three phase reactions attributed to outer sphere complexation, inner sphere complexation and intra-particle diffusion. Injection of sulfidic-anoxic solution of iron sulfide could not change the three phase reaction trend.

Keywords: iron sulfide, kinetics, mixed minerals, reactivity, sulfidic-anoxic.

I. Introduction

Arsenic has caused human health problems world-wide. It is a naturally occurring toxic element having adverse effects on human health. Exposure of humans to elevated concentrations of arsenic in drinking water possess significant health risks, such as Blackfoot disease, skin, lung and bladder cancers, and disorders of the immune, nervous and reproductive systems [1-2]. Its sources are both natural and anthropogenic, occurring in soil, sediment, surface and groundwater. It is found naturally in the earth's crust, soil, sediment, and many kinds of rock and it may be transferred to water, groundwater, and air. Anthropogenic sources include wood preservatives, pesticides, insecticides and pigments. Most environmental arsenic problems are the result of mobilization under natural conditions, but man has had an important impact through mining activity, combustion of fossil fuels, the use of arsenical pesticides, herbicides and crop desiccants and the use of arsenic as an additive to livestock feed, particularly for poultry [3-5].

There is concern about removal of arsenic from water to the lower Maximum Contaminant Level (MCL) in drinking water because of its toxic nature [6]. Arsenic poisoning is a serious health concern worldwide and concentration above permissible limit in groundwater is one of the world's largest environmental calamities [7-8]. Groundwater enriched with arsenic species such as arsenite (As (III)) and organic arsenic has become one of the most serious problems in water environment [1, 9]. It is particularly worse when the groundwater is utilized as drinking water [10-11]. The As(III) is more difficult to remove from water at neutral pH by means of adsorption and co-precipitation due to the lack of electrostatic attraction [12-13].

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 [14-17]. Exposure of humans to high levels of arsenic in drinking water results in hyper-pigmentation, gangrene and gastrointestinal cancer [18]. Because of these effects, international agencies reduced the arsenic standard concentration in drinking water from 50 to 10 mg/L [19].

The availability and migration of arsenic, a toxic metalloid, is controlled largely through sorption processes [20-21]. Under oxic conditions, arsenic adsorbs strongly to iron oxide surfaces [22-26]. Surface-bound arsenic is released into solution under slightly reducing conditions through the reductive dissolution of the iron oxides [27-30]. Arsenate reduction to highly toxic trivalent arsenite, (As(OH)₃) may accompany its release into solution, potentially leading to widespread environmental contamination [31-34]. Arsenic concentrations typically decrease under anoxic conditions in ocean sediments [35-36], freshwater lakes [37-39], and rivers [40]. The uptake of arsenic in anoxic environments is strongly correlated with the formation of iron sulfide minerals including iron sulfide. The most important ores of arsenic are realgar (As₄S₄) and orpiment (As₂S₃). In the presence of sulfides, precipitation of realgar or orpiment can remove As(III) and have considerable control over arsenic concentrations. In addition, the quantity and speciation of arsenic depends on the local sorbent [41]. The most prevalent arsenic species depend on pH and the redox potential. As a general

rule, arsenite, As(III), is more likely to be found in anaerobic ground water, whilst arsenate, As(V), is found in aerobic surface water [42].

The valence states of arsenic include: As(-III), As(0), As(II), As(III), and As(V). It exists as sulfide minerals (e.g., As_2S_3), elemental As, arsenite (AsO_2^-), arsenate (AsO_4^{3-}), or various organic forms that include methylated arsenates and trimethyl arsine. Both anionic forms (arsenite and arsenate) and deprotonated groups of arsenic are highly soluble and toxic and the chemical and microbiological reactions of arsenic are complex [43].

Two oxidation states, As(III) (arsenite) and As(V) (arsenate), predominate in surface and subsurface environments, depending on the redox potential. Between these two, As(III) is more mobile and more difficult to remove from groundwater under acidic and neutral pH conditions [1]. Also, arsenic can exist as thioarsenic aqueous species often found in sulfidic environments. In general, charged anionic species tend to be more strongly sorbed to mineral surfaces than neutral species. Also, compared to metal cations, which usually form highly insoluble oxide and hydroxide phases, arsenic exhibits higher solubility and mobility as dissolved species in aqueous solution under both oxidizing and reducing conditions [44-45].

Sorption processes largely control the migration and fate of arsenic in natural systems. Its solubility in natural systems is strongly influenced by adsorption at iron oxide surfaces [46]. Natural sediments are heterogeneous and the overall sorption is the net result of the distinctly different sorption behavior on each constituent phase [47]. Arsenic mobilization in soils and acidic waters is controlled by sorption on newly formed precipitates (schwertmannite, jarosite and goethite), causing natural arsenic attenuation [48-51]. Therefore, successful treatment of water containing arsenic using mineral systems is dependent on a full understanding of the reactivity, fate and the transport of reaction partners to the reactive sites of arsenic-sorbents [52-56]. Dissolved arsenic is typically high for intermediate redox potential that results in dissolution of iron (hydr)oxides, in low oxic water when iron goethite are present [24, 46, 57-58] and also usually low when iron sulfide minerals are present [36, 59].

The removal of arsenic from water is controlled by the Redox potential (Eh) and pH, 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 [60-62]. Arsenic ions occur in surface and ground waters in both organic and inorganic species, the inorganic forms being the predominant ones [63-64]. Under oxidizing conditions, $H_2AsO_4^-$ is dominant at low pH, whilst at higher pH, $HAsO_4^{2-}$ becomes dominant. Also, $H_3AsO_4^0$ and AsO_4^{3-} may be present in extremely acidic and alkaline conditions respectively. Under reducing conditions at pH less than 9.2, the uncharged arsenite species H_3AsO_3 will predominate [65, 9]. Therefore high arsenic waters are not expected where there is a high concentration of free sulfide. Thioarsenite species will be more important at neutral and alkaline pH in the presence of very high sulfide concentrations [39].

Several methods have been established in the treatment of arsenic contaminated water. Some of these techniques include: synthetic iron sulfide [66], iron sulfide [67], troilite and iron sulfide [68-75], sorption on ferrihydrite [76], pristine iron sulfide and on surface-oxidized iron sulfide [77], vindhyan shales [8], iron monosulfides [78], natural siderite [79], iron precipitates [51], acid mine drainage [50], iron sediments [80], wood charcoal and fine sand filters [7], iron oxides [27], hydrous granular ferric oxide [81], activated alumina or bone char [18-82], engineered H_2S -rich wetland [83], natural zeolite and volcanic stone [84], natural iron ores [85], oxisol [86], red mud [87], and ferruginous manganese ore [88], deep sea sediments [89], synthesized iron sulfide [90].

Iron sulfide, is known to exist in ambient sulfidic environments and reactions of iron sulfide with environmental contaminants have been studied extensively [91] and it has been shown that iron sulfide affects the speciation and mobility of arsenic [70, 92, 93]. Several studies have focused on the reactions of As(III) or As(V) with iron sulfide and other iron sulfides [67, 68, 81, 90, 94-95]. These studies have reported that As(V)/As(III) formed outer-sphere surface complexes with iron sulfide. In addition, substantial adsorption of As(III) on pyritic shales and the extent of sorption were correlated with iron sulfide content. Furthermore, adsorption on troilite (FeS) and iron sulfide (FeS_2) and reported As(III) sorbs to FeS and FeS_2 through an inner-sphere mechanism distinct from those of surface hydroxyl exchange. Also, As(III) and As(V) were removed by synthetic iron sulfide due to formation of As_2S_3 or As_4S_4 surface phases. As(III) uptake by iron sulfide in a continuous-flow system and subsequent formation of arsenian iron sulfide has been reported [96] [Singer and Stumm 1970]. Metal sorption on Iron sulfide under sulfidic conditions has been studied [97-99]. Iron sulfide coated surfaces on substrate had degradation effects on garlic under anaerobic condition [100].

Application of sulfides in water treatment is largely dependent on understanding of fundamental studies into metal sulphide precipitation and sorption mechanism on sulfide [101]. In addition, understanding of groundwater chemistry in a chemically reducing environment is focused on mechanisms of the reactivity and removal kinetics of sorbent-sorbate interactions... there are some advantages to sulphide, including the lower solubility of metal sulphide precipitates, potential for selective metal removal and fast reaction rates, better

settling properties and potential for re-use of sulphide precipitates by smelting [79, 102-104]. However, some of these new techniques are rather expensive for limited size water treatment systems 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) injected with iron sulfide under sulfidic-anoxic conditions [80].

Nevertheless, information of arsenic sorption on mixed mineral systems is very limited [62] [Egirani et al 2013] and further testing using mixed mineral systems injected with iron sulfide under sulfidic-anoxic condition is needed. This study investigates the reactivity and removal kinetic component of arsenic sorption by mixed mineral systems clays and hydroxide(s) injected with iron sulfide under sulfidic-anoxic conditions [105] and to evaluate the effectiveness of these systems for arsenic removal. Mineral systems of clays, iron goethite and iron sulfide under sulfidic-anoxic conditions that could be applied for arsenic removal from contaminated water are readily available locally.

1.1. Theoretical models and isotherms

Sorption has been used as a technique for removal of arsenic. It is the process in which a chemical substance accumulates at the common boundary of two contiguous phases [106]. If one of the contiguous phases is a solid and the other a fluid, the solid phase is termed the adsorbent, and the matter that sticks to the solid phase is called the adsorbate. The adsorbent is the iron sulfide and the adsorbate is the arsenic in this study. A related process occurs when a chemical is detached from a solid phase and this process is called desorption or negative adsorption. Typical adsorption experiments are conducted in a sequence of three steps [66]. First, the reaction between adsorbent and adsorbate is allowed to proceed for a prescribed period of time. Second, the adsorbent is separated from the liquid phase after a sufficient time passes for the removal reaction to be completed. Last, the amount of adsorbate remaining in the liquid phase is measured and the amount of adsorbate attached to the solid phase is calculated. Removal of the adsorbate by the adsorbent can be the beginning of the process. After that, chemical processes such as precipitation can occur, which can affect the total amount of material removed. Sorption is characterized by several isotherm models [107].

To address the suitability of mixed mineral suspensions of clays and goethite injected with iron sulfide for arsenite i.e. Arsenic (III) removal, a theory is designed to explain and predict the behavior of mineral-arsenite interactions under sulfidic-anoxic conditions. Details of the empirical model derived from Freundlich isotherm model are provided [108-110].

Detailed system characterization and an empirical model involving the distribution coefficient (Kd) as used in this paper are provided in previous paper [110]. Kd was calculated from the Freundlich model as provided (1):

$$S = KdC^N \tag{1}$$

where S is the sorbed concentration ($\mu\text{g}/\text{kg}$), Kd is the distribution coefficient, C is the equilibrium concentration ($\mu\text{g}/\text{l}$), and $N = 1$ is a chemical-specific coefficient derived from the slope of the plot. The empirical model as provided [62] to address the mineral-arsenic interactions as provided (2):

$$Kd_{total} = \frac{Kd_1 + Kd_2 + Kd_n}{n} \tag{2}$$

where Kd_{total} 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 mercury contaminant between single mineral phases and mixed mineral phases is based on the assumptions that the following could account for differences between single and mixed mineral sorption:

- a. Secondary mineral phase developed during sorbate-sorbent interaction.
- b. Components of minerals in the mixed mineral suspension acted as chemisorbed species and not as individual networks.
- c. differential mass of mixed and single mineral phases.

The difference between the actual sorption and the theoretical sorption was used to clarify the effects of mineral mixing injected with iron sulfide under sulfidic-anoxic condition on As(III) sorption. Mineral mixing is said to (a) enhance As(III) removal where the difference is positive; (b) depresses or attenuate As(III) removal where the difference is negative; and (c) have no effect on As(III) removal where no difference exist between As(III)sorbed and theoretical As(III) sorption [108].

The difference between the actual K_d and the theoretical ($K_{d_{total}}$) was used to clarify the effects of mineral mixing on arsenic removal under sulfidic-anoxic conditions. Mineral mixing is said to (a) enhance arsenic removal where the difference is positive; (b) attenuate arsenic removal where the difference is negative; and (c) have no effect on arsenic removal where no difference exists between the actual K_d and theoretical K_d as provided (3):

$$\Delta K_d = K_d - K_{d_{total}} \tag{3}$$

For the reactivity and removal kinetic studies, the empirical model for the mixed mineral systems was related to α and K_f as provided (4-5):

$$\Delta \alpha = \alpha - \alpha_{total} \tag{4}$$

$$\Delta K_f = K_f - K_{f_{total}} \tag{5}$$

Where α , K_f , α_{total} and $K_{f_{total}}$ 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 under sulfidic-anoxic conditions. Mixed mineral suspensions of kaolinite, montmorillonite, goethite and iron sulfide used in this work were chosen to simulate natural minerals and sulfidic-anoxic conditions found in arsenic impacted groundwater aquifers [68].

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 [62, 111-112]. 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 [108, 113]. This is due to the fact that surfaces of clays, hydroxides and sulfides have a high concentration of OH^- and HS^- groups readily deprotonated at high pH, generating arsenic removal by precipitation [114-115].

The mass balance of As(III) adsorbed per mass unit of the mixed mineral suspension (mg/g) was calculated by the following equation as provided (6) [79, 62, 116-120]:

$$Q_e = \frac{(C_i - C_e)V}{W} \tag{6}$$

Where C_i and C_e are the initial and equilibrium metal concentrations in mg/l, V is volume of the metal solution in mL and W is the weight of adsorbent in mg respectively.

The main objective of this work is to determine the effects of mineral mixing on the reactivity and kinetics involved in arsenite removal from groundwater under sulfidic-anoxic condition. Mixed mineral suspensions of kaolinite, montmorillonite, and goethite used in this work were chosen to simulate natural minerals readily available.

II. Materials and methods

2.1. Preparation of sulfidic-anoxic iron sulfide suspension

Sulfidic-anoxic conditions are characterized by depletion of dissolved oxygen. These conditions will occur if the rate of oxidation is greater than the supply of dissolved oxygen [20]. In sulfidic-anoxic environment, hydrogen sulfide occurs as a product of sulfate and sulfide reduction [121]. In this study, 1% acidified iron sulfide sulfidic-anoxic suspension was prepared using deoxygenated deionized water. Purified nitrogen gas was bubbled through the iron sulfide suspension continuously for 24 hours. The content, securely sealed was stored in airtight containers in the anaerobic chamber in dark environment before use. The formation of hydrogen sulfide was prototypically characterized by a "rotten egg" odor [78].

2.2. System characterization

All solutions were prepared using de-aerated and deionized water. This water was prepared by bubbling purified nitrogen gas through deionized water for at least 24 hours. Deionized water was obtained from a Millipore Milli-Q system (18 M Ω). Then the water was purged overnight in an anaerobic chamber containing a mixture of 5% hydrogen and 95% nitrogen gases [90].

Clays and iron sulfide used in this study provided by the Richard Baker Harrison Company and Acros Organics Ltd and goethite provided by Iconofile Company Inc. were nitrogen flushed and stored in airtight

containers in the anaerobic chamber before use to avoid 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 As₂O₃ in H₂O (Merck, Germany) into a volumetric flask, which was filled up to the mark and stored at 20±2oC 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 [122]. 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 [123-124], (Table 1). (f) spectral analysis was performed using scanning electron microscopy, energy dispersive spectroscopy and x-ray diffraction to identify the mineral sorbent [62, 109125-126].

Table1: Characteristics of clays, goethite [109, 62] and Iron sulfide

Mineral	Particle size (µm)	% (<1 µm) colloid	pH ± σ	Surface area(SSA±σ) (m ² /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
Iron sulfide	80.0 ±0.20	4.729	4.02± 0.03	2.00± 0.00

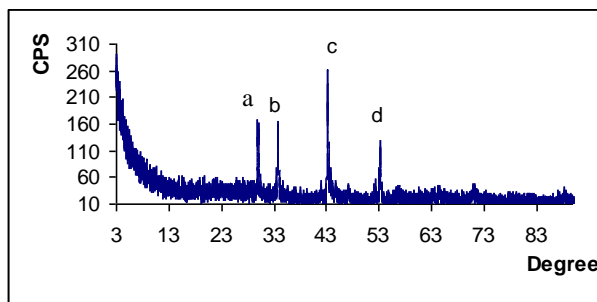


Figure 1 Untreated amorphous FeS showing peaks at a, b, c.

2.3. Reactivity experiments

For reactivity studies to determine the proton coefficient as provided (Eqs. (8-9), standard laboratory procedure was used [90, 127-128]. 1% sulfidic-anoxic suspension of iron sulfide was added to 1% single and 1:1 mixed mineral suspensions with no added electrolyte. The contents 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% sulfidic-anoxic suspension of iron sulfide was added to 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).

Spectroscopic studies have confirmed thiol (≡S-H) and hydroxyl (≡Me-OH) functional groups on surface of metal sulfides [93], [129-130]. These amphoteric reactive units are thought to undergo independent protonation and deprotonation reactions to produce reactive sites for sorption. Under acidic conditions, thiol groups are believed to play an important role in the reactivity of iron sulfide both in initial removal and subsequent surface reactions [62], [93]. The protonation of the iron sulfide surface makes it less negatively charged, at low pH. At high pH, the deprotonation of the surface makes it more negatively charged[113]. Sorption of arsenite on mineral surfaces requires proton exchange, the stoichiometry of this reaction is described [109, 62] and the proton consumption function is provided (7- 8):



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

where SOH is the mineral surface-binding site, 3AsO_3^{3-} is the soluble arsenic species, $(\text{SOH})\alpha - 3 \text{AsO}_3^{3-}$ is the surface bound arsenic, $\log K_p$ 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 [131]. Proton coefficient was calculated from the slope of $\log K_d$ versus pH plot provided (Table 2, Fig. 4). Arsenic reactions within the aquatic environment [81] under sulfidic-anoxic conditions are provided (9-10):

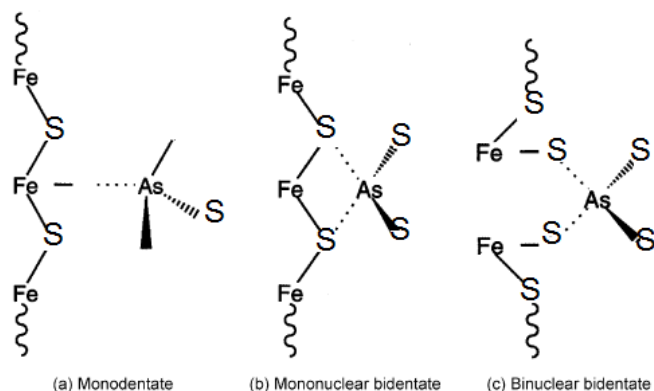


Figure 2: proposed arsenic surface complexes in sulfidic-anoxic environment [modified from [132, 81]

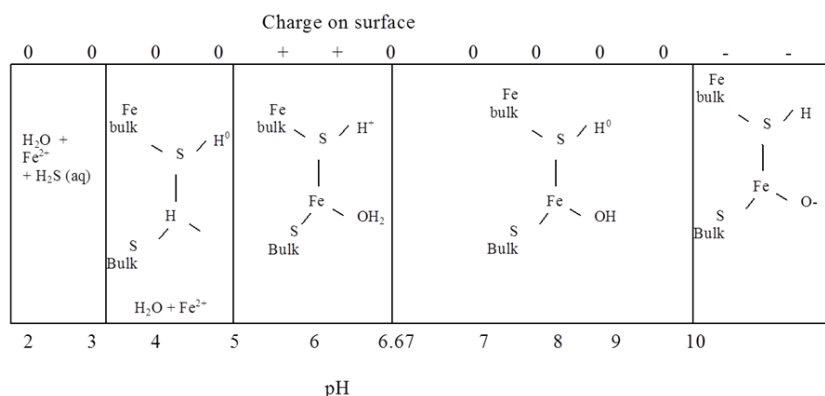


Figure 3: proposed surface species of iron sulfide at variable pH [134].

2.4. Kinetic experiments

For arsenic removal kinetics experiments, 1% sulfidic-anoxic suspension of iron sulfide was added to 1% single and 1:1 mixed mineral systems, 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 [62, 135, 46].

The transport of adsorbate from external layers to the mineral surface where sorption occurs is dependent on a mass transfer constant K_f obtained from the slopes of the curve derived from plotting C_t/C_0 vs time [66,136, 101, 137-139]., [109, 62] as provided (11):

$$\left[\frac{d(C_t/C_0)}{dt} \right]_{t=0} \cong -K_f S_s \tag{11}$$

where C_0 is initial arsenic concentration (mg/l) at time $t = 0$; C_t is arsenic concentrations (mg/l) at time t , S_s is the exposed external surface area of the sorbent, and K_f is the mass transfer coefficient [89, 117]. A higher inverse of K_f suggests greater sorption. The Freundlich isotherm was chosen to describe sorption of

arsenite because this is suitable for heterogeneous surfaces over a wide range of solute concentrations [140-142], [118].

At the end of equilibration, suspensions were shaken and centrifuged at 3000 rpm for 15 min and passed through a 0.2- μ m 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 (χ^2) significant ($P \leq 0.01$).

III. Results and discussion

3.1. Mixed mineral systems and H⁺/AsO₃³⁻ exchange stoichiometry

Although the proton coefficient (α) (Table 2, derived from Figs.4), may be linked to differences in the availability of strongly acidic sites. Previous study revealed proton coefficient for arsenite sorbed on single mineral systems greater than one except for goethite. Injection of sulfidic-anoxic solution of iron sulfide onto the mixed mineral systems enhanced proton coefficient of all single minerals. This indicates high level of protonation during the sorption process. Proton coefficient for arsenite-goethite interaction was higher than arsenite sorbed on kaolinite and iron sulfide. This could be attributed to amphoteric reactive units thought to undergo independent protonation and deprotonation reactions. In the presence of thiol (\equiv S-H) and hydroxyl (\equiv Me-OH) functional groups significant numbers of reactive sites in goethite and iron sulfide may increase the proton coefficient because of the enhanced exchange of protons for sorbing ions. Compared with previous study [62], injection of sulfidic –anoxic solution of iron sulfide did not change the trend of proton coefficient.

Table2: Proton coefficients (α) and regression coefficient (R) of arsenite sorbed on mineral suspensions injected with sulfidic-anoxic iron sulfide

Mineral suspensions	R	α	α_{total}	α_{-total}
Iron sulfide	0.99	1.15	⊗	⊗
Kaolinite	0.99	1.17	⊗	⊗
Goethite	0.99	1.204	⊗	⊗
Montmorillonite	0.99	1.243	⊗	⊗
Kaolinite/montmorillonite	0.99	1.146	1.2065	-0.0605
Goethite/kaolinite	0.99	1.095	1.187	-0.092
Goethite/montmorillonite	0.99	1.294	1.2235	0.0705

Note: ⊗ not applicable

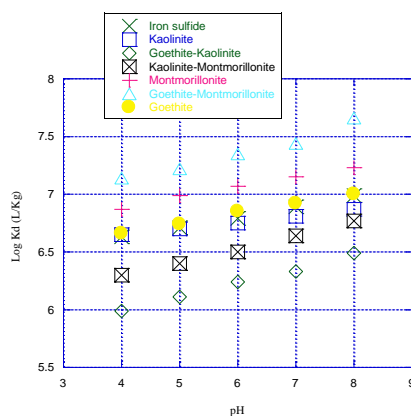


Figure 4: Plots of LogKd versus final pH for As (III) sorbed on iron sulfide, (b) goethite-kaolinite, (c) kaolinite-montmorillonite, (d) montmorillonite, (e) goethite-montmorillonite, (f) goethite, sulfidic-anoxic suspensions.

This is because except for montmorillonite/goethite mixed mineral system, α for arsenite sorbed on the remaining mixed suspensions were lower than α_{total} , indicating increased protonation when montmorillonite was mixed with goethite under sulfidic-anoxic conditions. The higher the acidity of sites the more protons are exchanged for arsenite. Therefore, mineral mixing under sulfidic-anoxic condition could not enhance the acidity of reactive sites for all but one mixed minerals interacted with arsenite under sulfidic-anoxic condition. This may be due to the inability of sulfidic-anoxic solution of iron sulfide to counteract the competition of sorbing ions when these minerals are mixed. The H⁺/AsO₃³⁻ exchange stoichiometry of <2 (Table 2) for arsenite sorbed on both the single and mixed mineral phases agrees with the findings of [62], for arsenic sorbed on clays and (hydr)oxides. This suggests that the presence of surface charges of thiol (\equiv S-H) and hydroxyl (\equiv Me-OH)

functional groups through injection of sulfidic-anoxic iron sulfide solution does not significantly change protonation of reactive sites for the mixed mineral systems.

3.2. Mixed mineral systems and sorption kinetics

Previous study [62], reported a three phase reaction probably attributed to outer sphere, inner sphere complexation and intra-particle diffusion (Table 3, Fig 5). Injection of sulfidic-anoxic solution of iron sulfide could not change the three phase reaction trend. However, iron sulfide-interacted with arsenic exhibited a single phase reaction process. Previous study [62], revealed a mass transfer rate decrease in the order $K_{fI} < K_{fII} < K_{fIII}$ for all single mineral systems but goethite. Under sulfidic-anoxic condition mass transfer rate for the single minerals is in the order montmorillonite<goethite< iron sulfide<kaolinite. For the mixed mineral systems, previous study [62], demonstrated a decrease in mass transfer rate for the mixed mineral systems in the order: $K_{fI} < K_{fII} < K_{fIII}$. Under sulfidic-anoxic condition, all K_{fI} values are greater than K_{fII} but montmorillonite/goethite. Furthermore, all K_{fII} values are greater than K_{fIII} but kaolinite/goethite. 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. Kaolinite/montmorillonite and montmorillonite goethite exhibited reduction in mass transfer rates due to mineral mixing but not necessarily due to injection of sulfidic-anoxic iron sulfide mineral solution. 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 as reported previously [62].

Table 3: Mass Transfer Rates for Arsenite Sorbed on Clay Minerals and Goethite sulfidic-anoxic suspensions

Parameters/ Mineral	Iron sulfide	Kaolinite	Montmorillonite	Goethite	Kaolinite/ Montmorillonite	Kaolinite/ Goethite	Montmorillonite/ Goethite
slopeI(hr ⁻¹)	-8.73e-4	-4.32e-2	-0.081	-2.42e-2	-3.35e-2	-1.78e-2	-2.42e-2
slopeII(hr ⁻¹)	*	-2.69e-2	-0.064	-4.06e-3	-0.02	-1.35e-2	-1.46e-2
Slope III(hr ⁻¹)	*	-0.02.70e-2	-0.048	-8.40e-3	-0.020	-1.43e-2	-1.47e-2
Exposed Surface Area (cm ²)	200	4700	1000	7100	8800	7900	14700
K _{fI} (cmhr ⁻¹)	4.36 e-6	9.19e-6	2.43e-4	3.40e-6	3.81e-6	2.26e-6	1.64e-6
Theoretical K _{fI} (cmhr ⁻¹)	*				1.26e-4	6.30e-6	1.23e-6
K _{fII} (cmhr ⁻¹)	*	5.72e-6	9.72e-5	5.72e-7	2.27e-6	1.71e-6	9.92e-7
Theoretical K _{fII} (cmhr ⁻¹)	*				5.15e-5	3.15e-6	4.89e-5
K _{fIII} (cmhr ⁻¹)	*	5.75e-6	2.02e-5	1.18e-6	2.30e-6	1.80e-6	1.00e-6
Theoretical K _{fIII} (cmhr ⁻¹)	*	*	*	*	3.89e-5	3.47e-6	1.07e-5

Note: * Not applicable

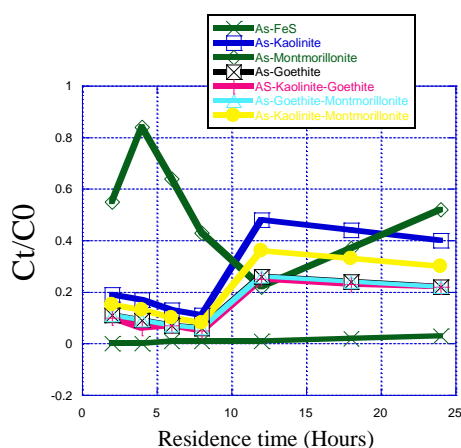


Figure 5: Effects of arsenite sorption on mass transfer rates: (a) iron sulfide, (b) kaolinite; (c) montmorillonite; (d) goethite; (e) kaolinite/goethite; (f) goethite/montmorillonite; (g) kaolinite/ montmorillonite sulfidic-anoxic suspensions.

3.3 Mixed mineral systems and arsenic removal

Previous study [62], revealed a % sorption still indicating a three phase reaction probably attributed to outer sphere, inner sphere complexation and intra-particle diffusion (Table 4, Fig 6). Except for arsenic sorbed on iron sulfide, 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 as previously reported [62]. This means that injection of sulfidic-anoxic mineral solution of iron sulfide could not significantly change the sorption characteristics of the single and mixed mineral systems. Iron sulfide as a single mineral system behaved differently from the clay minerals and hydroxides in arsenite sorption recording decrease in % sorption over time.

Table 4: Arsenite Sorbed ($\mu\text{g/g}$) on Mineral Suspensions at pH 4, Zero Ionic Strength and 10ppm Initial Arsenic Concentration

Mineral suspensions	Metal sorbed ($\mu\text{g/g}$)
Iron sulfide	8.83
Kaolinite	8.85
Goethite	8.86
Montmorillonite	9.06
Kaolinite/montmorillonite	8.45
Goethite/kaolinite	8.00
Goethite/montmorillonite	9.27

This could be attributed to decrease in reactive sites and surface area high surface area as reaction proceeds over time (Table 1). Differences between actual and theoretical % sorption was positive for all mixed minerals, indicating increase in % sorption and no effect of sulfidic-anoxic mineral solution injection onto the mineral systems..

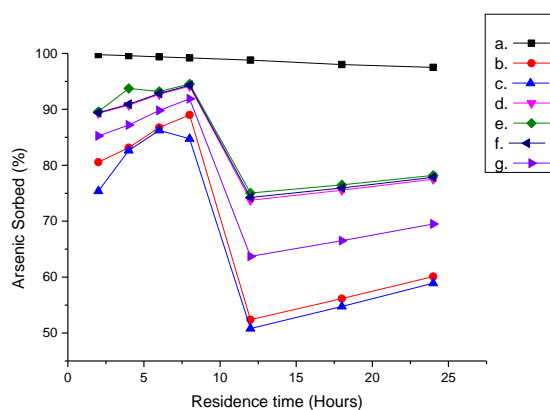


Figure 6: Plots of arsenic sorbed (%) vs. contact time (hours): (a) Iron sulfide, (b) kaolinite; (c) montmorillonite; (d) goethite; (e) kaolinite/goethite; (f) goethite/montmorillonite; (g) kaolinite/montmorillonite sulfidic-anoxic suspensions.

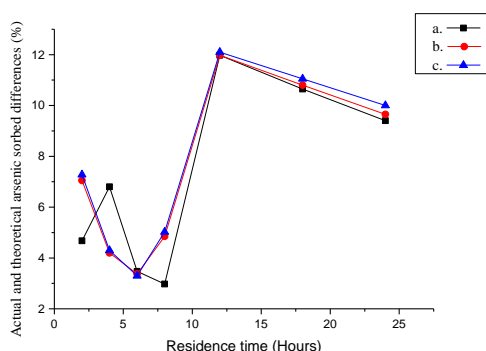


Figure 7: Plots of actual and theoretical arsenic sorbed differences(%) vs. contact time (hours): (a) kaolinite/goethite; (b) goethite/montmorillonite;(c) kaolinite/montmorillonite sulfidic-anoxic suspensions.

IV. Conclusions

The reactivity and removal kinetics of arsenite treated with single and mixed mineral systems of kaolinite, montmorillonite and goethite injected with iron sulfide under sulfidic- anoxic conditions has been investigated. Using empirical models derived from Freundlich isotherm model, injection of sulfidic-anoxic solution of iron sulfide onto the mixed mineral systems enhanced proton coefficient of all single minerals. This could be attributed to amphoteric reactive units thought to undergo independent protonation and deprotonation reactions. Proton coefficients in some cases are greater one, indicating high level of protonation during the sorption process.. The H^+/AsO_3^{3-} exchange stoichiometry of <2 for arsenite sorbed on all mineral systems injected with sulfidic-anoxic mineral solution of iron sulfide suggests that maximum protonation was not achieved in all reaction phases.

Except for iron sulfide, kinetic studies demonstrated three phase reactions attributed to outer sphere complexation, inner sphere complexation and intra-particle diffusion. Injection of sulfidic-anoxic solution of iron sulfide could not change the three phase reaction trend. However, iron sulfide-interacted with arsenic exhibited a single phase reaction process. Under sulfidic-anoxic condition, all KfI values are greater KfII but montmorillonite/goethite. Furthermore, all KfII values are greater than KfIII but kaolinite/goethite. Mineral mixing reduced mass transfer rate for arsenite treated with kaolinite/montmorillonite and montmorillonite/goethite. Kaolinite/montmorillonite and montmorillonite goethite exhibited reduction in mass transfer rates due to mineral mixing but not necessarily due to injection of sulfidic-anoxic iron sulfide mineral solution. Differences in sorption kinetics between the single and mixed mineral phases may be attributed to different types of reactive sites on the single and mixed mineral systems

Except for arsenic sorbed on iron sulfide, 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 as previously reported. This means that injection of sulfidic-anoxic mineral solution of iron sulfide could not significantly change the sorption characteristics of the single and mixed mineral systems.

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