

Arsenite Removal from Aqueous Solution using Mixed Mineral Systems Injected with Iron Sulfide under Sulfidic-Anoxic condition II. The role of solution composition and ageing

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Abstract: *The role of solution composition and ageing of arsenite treated with single and mixed mineral systems of kaolinite, montmorillonite and goethite injected with iron sulfide under sulfidic- anoxic conditions have been investigated. Variability in arsenite sorption exists over the range of pH investigated. This variability in sorption may be attributed to the presence of thiol ($\equiv S-H$) functional group contained in solution under sulfidic-anoxic condition. Arsenite sorption exhibits a non-promotive Cp effect (i.e. sorption decreases as Cp increases for all mineral systems. the nature of ionic species formed in solution is affected by changes in the mineral/ solution ratio. All mineral systems but kaolinite-goethite exhibits a step up arsenite sorption up to 288 hours residence time and flattens g out over the remaining residence time of the reactions.*

Keywords: *iron sulfide, solution composition, ageing, mixed minerals, sulfidic-anoxic.*

I. Introduction

Contamination of water by arsenic both as a result of natural and anthropogenic processes poses a major threat to human health and to the environment in general [1]. Arsenic has caused human health problems world-wide, notably in Bangladesh [2]. Arsenic is a naturally occurring element widely distributed through the Earth's crust. Most environmental arsenic problems are the result of mobilization under natural conditions. However, man has had an important additional impact through mining activity, combustion of fossil fuels, and the use of arsenical pesticides [3]. Elevated levels of arsenic can be present in the environment as a result of mineral weathering and dissolution [4]. It is mainly produced as a by-product of base metals smelting, in particular copper, lead, cobalt and nickel concentrates [5]. These two elements and other trace elements of environmental concern are released during coal mining, processing, or combustion [6]. Arsenic, a common constituent of the earth's crust, is a well-known carcinogen [7]. It is naturally present in water in different oxidation states and acid-base species depending on redox and pH conditions [7]. Arsenic can occur in the environment in several oxidation states (-3, 0, +3 and +5) but in natural waters is mostly found in inorganic form as oxyanions of trivalent arsenite [As(III)] or pentavalent arsenate [As(V)] [3]. Although organic Arsenic species can be presented as a result of in situ biomethylation, inorganic Arsenic as As(III) and As(V) are generally considered to be the dominant species in natural water. The oxidation state of arsenic depends primarily on pH and redox conditions, with As(V) being the most stable form under aerobic conditions [8]. While many metals form insoluble sulfides in sulfidic environments, arsenic is distinctive in being relatively soluble at lower pH, and mobile over a wide range of redox conditions [9].

Arsenic pollutants discharged by anthropogenic and natural sources could result in degraded surface and ground water chemistry. Pollutants infiltrate through surface runoff and drainage into the soil and can result in pollution of both the surrounding ecosystems and groundwater [10-13]. The need to reduce arsenic concentrations in water bodies remains a priority in both developed and most developing countries. Dissolved arsenic is typically high for intermediate redox potential that results in dissolution of iron (hydr)oxides, usually low in oxic surface or ground water when iron (hydr)oxides are present [14-17], and also usually low when iron sulfide minerals are present [18-19]. The removal of dissolved arsenic species can be hampered by the absence of reliable sorbents and solution chemistry adequate to understanding arsenic sorption. The removal of arsenic from contaminated water is controlled by the solution composition [20-22].

Arsenic removal from aqueous solution is controlled essentially by solution chemistry [23-24], namely, pH and solid concentration, besides the residence time (ageing) of the solid phase in the water. Iron sulfide ages to mackinawite in the presence of excess-sulfide [9]. Although arsenic is bound to the iron oxy-hydroxides under oxidizing conditions, the possibility exists that arsenic will be released under reducing conditions such as found in landfills [25-28]. Interactions between trace elements and FeS can decrease trace element availability in sediment porewaters [29]. 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 [30-31]. Solution pH controls (a) the solubilities of arsenic species; (b) hydrolysis behavior

of arsenic ions; and (c) surface charge of the sorbent As(III) adsorbed over a broader pH range on pristine pyrite than on surface-oxidized pyrite. Adsorption of As(III) on surface-oxidized pyrite was similar to reported adsorption on pyrite that had been prepared and stored in less-rigorously anoxic conditions than in our experiments or on iron oxides [2, 32].

The adsorption of arsenic and other anions have been reported to be dependent on the nature of the anion and the adsorbent surface [33]. Adsorption may decrease as particle concentration increases (outer sphere complexation) or not be significantly affected as particle concentration increases (inner sphere complexation) [34-37]. 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 [38-39]. 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 [40-41]. 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 [42-44].

Iron sulfide (FeS) is the most abundant metal sulfide at the surface of Earth. Application of iron sulfides in water treatment is largely dependent on understanding of fundamental studies into metal sulphide precipitation, and sorption mechanism on sulfide [45-46]. Mineral surface reactivity is ultimately dependent on three surface properties: chemical composition, atomic structure (which determines which atoms are exposed to the surface), and microtopography [47]. Highly reactive defect sites may also occur at Fe or S surface sites partially stabilized by disproportionation [48]. Limited surface oxidation may influence As(III) adsorption, potentially altering the extent of sorption or the redox state of sorbed arsenic [2]. Concerning heavy metals adsorption onto pyrite, it has been demonstrated that a surface-induced hydrolysis reaction mechanism may be more realistic than a simple ion exchange [49]. Pyrite surface charge can be governed by protonation–deprotonation reactions of the surface S groups as provided (1):



During surface hydration, water decomposition can occur either at S sites leading to hydroxyl release or at Fe sites, leading to release of protons in solution as provided (2-3) [50].



A complicating factor to sorption as a process for arsenic removal is that at higher pH values, the surfaces of oxide minerals are commonly negatively charged. Thus, sorption of negatively charged arsenic oxyanions may be minimal and an ineffective means of arsenic removal in the absence of thiol ($\equiv S-H$) functional group [51].

Pyrite dissolution and interaction with toxic elements have been studied under anoxic conditions by solution chemistry and spectroscopic techniques [52]. In addition, understanding of groundwater chemistry in a chemically reducing environment is focused on solution composition and ageing. In addition, there are some advantages to sulphide, including the lower solubility of metal sulphide and potential for selective metal removal [8, 53-55]. At a near-neutral pH, metastable FeS can be rapidly replaced by FeS₂ in the presence of excess sulfur such as dissolved hydrogen sulfide (HS⁻). Transformation of FeS to FeS₂ strongly influences the reactivity of trace elements in sulfidic sediments [56]. Sorption of arsenic in mixed mineral systems of clays and (oxyhydr)oxide towards sulfides revealed decrease in reaction rates, attributed to blocking of reactive sites for sulfide complexation. Slower stages of sorption are attributed to diffusion into micropores or aggregates [57]. Several techniques for removing arsenic from water are available; including adsorption with activated carbon (AC) or modified AC, ion exchange, adsorption (or precipitation) by iron and aluminum oxyhydroxides, and membrane separation [25]. Techniques for arsenic removal 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 methods is the use of mixed mineral systems of clays and hydroxide(s) injected with iron sulfide under sulfidic-anoxic conditions [58]. In addition, arsenic removal from ground water using direct kalshi filtration technique [layers of coarse sand, iron chips, wood charcoal and fine sand] has been reported [59].

Application of sulfides in water treatment is largely dependent on understanding of fundamental studies into metal sulphide reaction mechanism under selective solution composition and ageing [60]. Many

researchers have focused on the sorption characteristics of pure mineral phases, but the sorption behaviour of complex aquifer materials as mimicked by mixed mineral systems of different phases, including iron oxyhydroxides, clays and different aluminosilicates under sulfidic-anoxic condition has hardly been reported [60-61]. Nevertheless, information of arsenic sorption on mixed mineral systems at variable solution composition and ageing is limited [61] and further testing using mixed mineral systems injected with iron sulfide under sulfidic-anoxic condition at variable pH and residence time is required.

1.1. Theoretical models and isotherms

To address the suitability of mixed mineral systems of clays and goethite 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 [62-63]. Sorption of toxic metals proceeds through interaction on pyrite surface as provided (4) [64]:



Detailed system characterization and an empirical model involving the distribution coefficient (Kd) as used in previous paper [61,65]. Distribution coefficient used in calculating arsenic sorbed was derived from the Freundlich model as provided (5):

$$S = KdC^N \quad (5)$$

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 [61,65] to address the mineral-arsenic interactions are provided (6-7):

$$\text{Arsenic sorbed difference} = \text{arsenic sorbed} - \text{arsenic sorbed}_{\text{total}} \quad (6)$$

$$\text{Arsenic sorbed}_{\text{total}} = \frac{[S_1 + S_2 + S_n]}{n} \quad (7)$$

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 metal between mineral phases in mixed suspension is based on the following conditions reported previously [65]:

1. No significant secondary mineral phase is developed by the mixed mineral suspension except at alkaline pH
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

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 arsenite removal from aqueous solution using mixed mineral systems injected with iron sulfide under sulfidic- anoxic conditions, tested at variable solution composition and ageing was investigated.

II. Materials and methods

2.1. Preparation of sulfidic-anoxic iron sulfide suspension

As reported in companion paper I, Sulfidic-anoxic conditions are characterized by reduction of dissolved oxygen. These conditions will occur if the rate of oxidation is greater than dissolved oxygen supply [66]. In sulfidic-anoxic environment, hydrogen sulfide occurs as a product of sulfate and sulfide reduction [56]. 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 [1].

2.2. Sorption experiments

Batch mode experiments in this study was conducted using 1% sulfidic-anoxic suspension of iron sulfide added to 1% single (kaolinite, montmorillonite and goethite) and 1:1 mixed mineral suspensions (kaolinite/montmorillonite, goethite/kaolinite and goethite/montmorillonite) with no added electrolyte. 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, 1% sulfidic-anoxic suspension of iron sulfide was added to 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, 1% sulfidic-anoxic suspension of iron sulfide added to 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 conducted from 24 to 720 h, 1% sulfidic-anoxic suspension of iron sulfide was added to single and 1:1 aged mixed mineral suspensions containing 1% by mass and 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.

All solutions were prepared using deaerated 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 [67]. In all experimental studies samples were stored in the dark at room temperature (23±3 °C) for a maximum of 24 h before analysis [68]. 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).

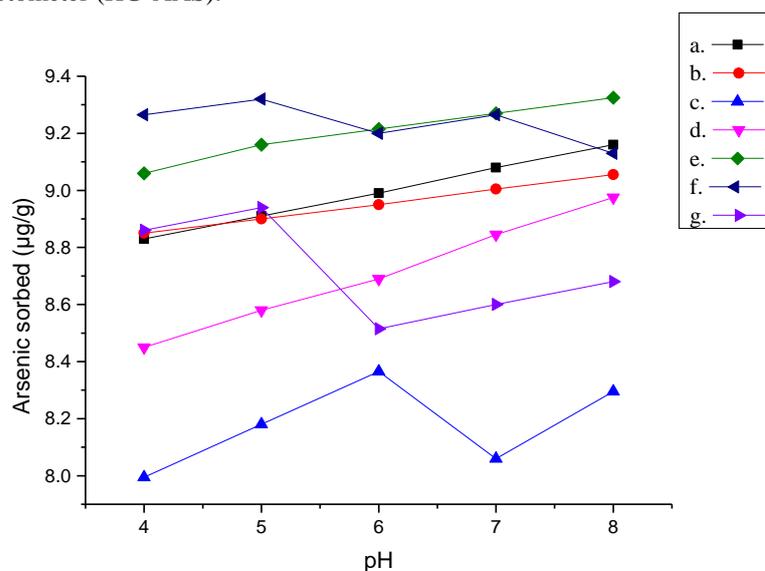


Figure 1: Plots of arsenic sorbed versus pH for (a) Iron sulfide, (b) kaolinite, (c) goethite/kaolinite, (d) kaolinite/montmorillonite, (e) montmorillonite, (f) goethite/montmorillonite, (g) goethite, sulfidic-anoxic mineral systems

III. Results and discussion

3.1. Mineral systems and pH effects on arsenic (III) removal

This is different from previous report [61] of arsenic sorbed on these mineral systems in the absence of sulfide under sulfidic anoxic condition (Fig. 1). In previous report, the behavior of goethite and mixed mineral systems containing goethite demonstrated a non-linear behaviour in arsenic(III) removal. Arsenic sorption by goethite and goethite/montmorillonite demonstrated a step-wise increase linearly between pH 5 and pH 6, dipping at pH 6 and 7 respectively before increasing over the remaining range of pH. This variability in sorption may be attributed to the presence of thiol ($\equiv\text{S-H}$) functional group contained in solution under sulfidic-anoxic condition. However, sorption pattern appears to be controlled by outer sphere complexation, inner sphere complexation and intra-particle diffusion for arsenic sorbed on goethite and mixed mineral systems containing goethite. Slower stages of sorption with increasing pH could be attributed to diffusion into micropores of mineral system framework.

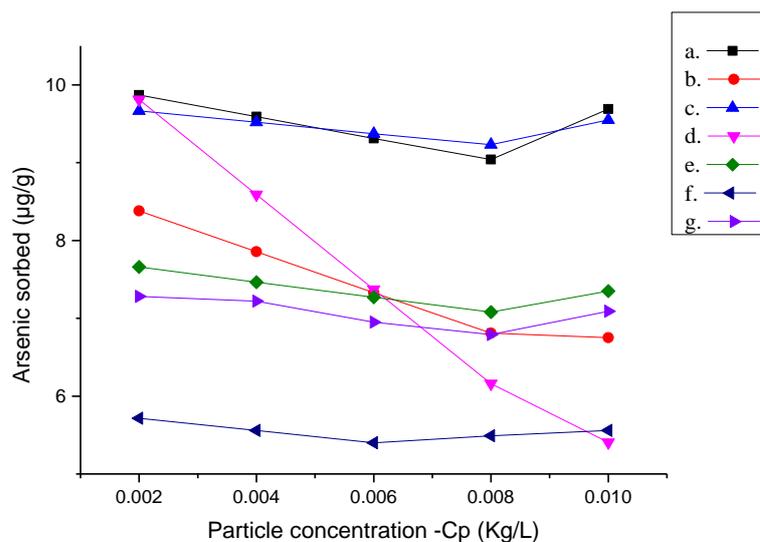


Figure 2: Plots of arsenic sorbed versus particle concentration for (a) Iron sulfide, (b) kaolinite, (c) kaolinite/goethite, (d) kaolinite/montmorillonite, (e) montmorillonite, (f) goethite/montmorillonite, (g) goethite, sulfidic-anoxic mineral systems

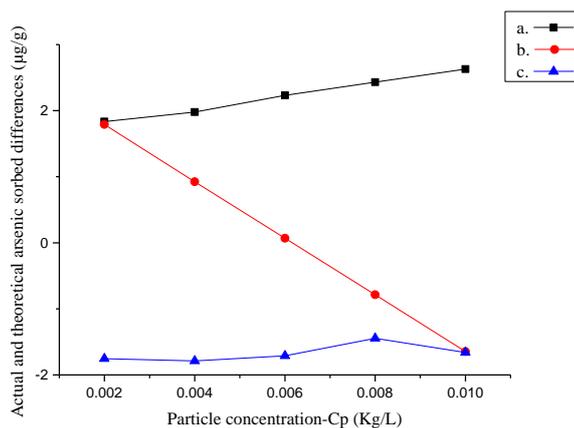


Fig. 3 Plots of actual and theoretical arsenic sorbed differences versus particle concentration for: (a) Kaolinite/goethite, (b) kaolinite/montmorillonite, (c) goethite/montmorillonite, sulfidic-anoxic mineral systems

3.2. Mineral systems and Cp effects on arsenic (III) removal

Previous report in the absence of iron sulfide exhibited linear increase in arsenite sorption as particle concentration (C_p) increases for goethite and mixed mineral systems containing goethite [61]. In a similar report, kaolinite demonstrated a step-wise increase in arsenite sorption as particle concentration was increased. In this report, arsenite sorption exhibited a non-promotive C_p effect (i.e. sorption decreases as C_p increases for all mineral systems (Fig. 2). This means that the nature of ionic species formed in solution is affected by changes in the mineral/ solution ratio. Sulfide minerals and mineral systems containing thiol ($\equiv S-H$) functional group may form coatings on other mineral surfaces. Coatings of only a few atomic layers thickness are sufficient to influence sorption rates [51, 69]. This may account for differences in sorption behavior for arsenite sorbed on mineral systems under sulfidic-anoxic conditions..

Decrease in arsenite sorption as C_p increases may be attributed to increase in particle size and aggregation of the mineral systems. The C_p effect is also related to effective surface area, pressure, and force at the mineral/water interface [70]. Increase in C_p results in low pressure at the interface and a subsequent decrease in sorbing ion diffusion to reactive sites [10-11].

Arsenite sorbed difference as reported previously (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) for kaolinite/montmorillonite was negative., becoming positive as C_p increased to 8 and 10. In this report, arsenite sorbed differences is

positive for kaolinite/goethite and negative for goethite/montmorillonite (Fig.3). This means that mineral mixing under sulfidic-anoxic condition increases arsenite sorption on the former while reducing arsenite sorption on the latter. However, differences in arsenite sorbed on kaolinite/montmorillonite started on the positive territory, becoming negative as Cp increases. This indicates that mineral mixing under sulfidic –anoxic condition initially enhanced arsenite sorption but reduces arsenite sorption over the remaining range of Cp [32].

3.3. Mineral systems and ageing effects on arsenic (III) removal

Previous study in the absence of iron sulfide demonstrated step-wise arsenite sorption [61]. Kaolinite/goethite in the same study demonstrated a step down arsenite sorption for the first 288 hours, increasing arsenite sorption over time for the remaining residence time of the reaction.. However, in this study under sulfidic-anoxic condition, all mineral systems but kaolinite/goethite exhibited a step up arsenite sorption up to 288 hours residence time, flattening out over the remaining residence of the reactions (Figure 4).. This decrease in reaction rates over time could be attributed to blocking of reactive sites for sulfide complexation under sulfidic-anoxic condition.

Also, this confirms previous report that the suite of available reactive sites for As(III) adsorption changes with time [7]. Arsenite step-wise sorption probably indicated reaction phases attributed to outer sphere, inner sphere complexation and intra-particle diffusion as reported in companion paper I. The behavior of kaolinite/goethite could be attributed to its high surface area when compared to the other minerals. Increase in arsenite sorption onto kaolinite/goethite over time may be attributed to increased hydroxylation of the mineral surfaces, resulting in the formation of new reactive sites [28].

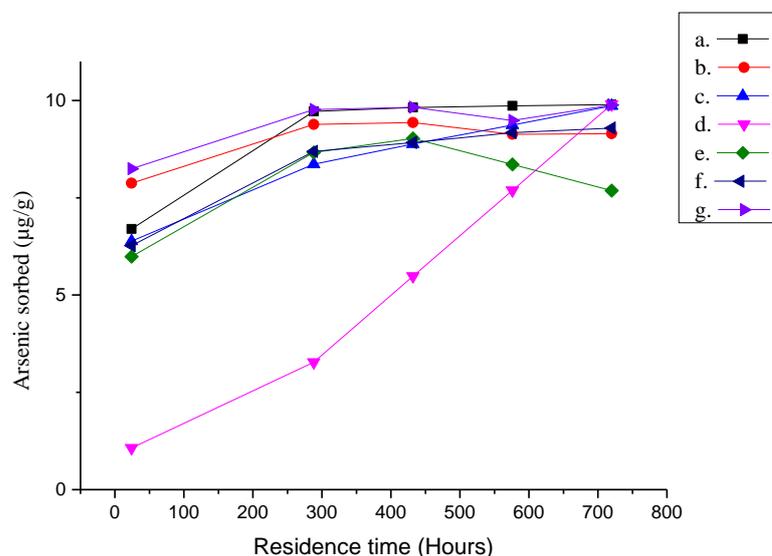


Fig. 4.: Plots of arsenic sorbed versus residence time for: (a) Iron sulfide, (b) goethite, (c) kaolinite/montmorillonite, (d) kaolinite/goethite, (e) montmorillonite/goethite, (f) montmorillonite, (g) kaolinite, sulfidic-anoxic mineral systems

IV. Conclusions

The possibilities of using mixed sorbents of kaolinite, montmorillonite, and goethite to remove arsenite from aqueous solution under sulfidic-anoxic condition 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 the presence of thiol ($\equiv\text{S-H}$) functional group contained in solution under sulfidic-anoxic condition. Sorption pattern appeared to be controlled by outer sphere complexation, inner sphere complexation and intra-particle diffusion for arsenite sorption on mineral systems containing.

Arsenite sorption exhibited a non-promotive Cp effect (i.e. sorption decreases as Cp increases for all mineral systems. the nature of ionic species formed in solution is affected by changes in the mineral/ solution ratio. arsenite sorbed differences is positive for kaolinite/goethite and negative for goethite/montmorillonite. This means that mineral mixing under sulfidic-anoxic condition increases arsenite sorption on the former while reducing arsenite sorption on the latter.

. All mineral systems but kaolinite/goethite exhibited a step up arsenite sorption up to 288 hours residence time, flattening out over the remaining residence of the reactions. Increase in arsenite sorption onto kaolinite/goethite

over time may be attributed to increased hydroxylation of the mineral surfaces, resulting in the formation of new reactive sites. Decrease in reaction rates over time could be attributed to blocking of reactive sites for sulfide complexation under sulfidic-anoxic condition.

References

- [1] R. T. Wilkin, R. T. Wilkin, R. T. and Barnes, H. L. Iron sulfide-arsenite interactions: adsorption behavior onto iron monosulfides and controls on arsenic *Geochimica et Cosmochimica Acta*, 60: 1996., 4167-4179.
- [2] F. Suna, B. A. Dempsey, K. A. Osseo-Asare, As(V) and As(III) reactions on pristine pyrite and on surface-oxidized pyrite, *Journal of Colloid and Interface Science* Volume 388, Issue 1, 2012, 170-175.
- [3] P.L. Smedley, D.G. Kinniburgh, A review of the source, behavior and distribution of arsenic in natural waters *Applied geochemistry*, 17, 2002, 517-568.
- [4] B. Manning, S. Fendorf, S. Goldberg, Surface Structures and Stability of Arsenic(III) on Goethite: Spectroscopic Evidence for Inner-Sphere Complexes, *Environ. Sci. Technol.* 32, 1998, 2383-2388.
- [5] G. Long, Y. Peng, D. Bradshaw, A review of copper-arsenic mineral removal from copper concentrates, *Minerals Engineering* 36-38, 2012, 179-186.
- [6] S.F. Diehl, M.B. Goldhaber, A.E. Koenig, H.A. Lowers, L.F. Ruppert, Distribution of arsenic, selenium, and other trace elements in high pyrite Appalachian coals: Evidence for multiple episodes of pyrite formation *International Journal of Coal Geology* 94, 2012, 238-249.
- [7] S.R. Ajakane, B. Manning, L. Charlet, H. Choi, Removal of Arsenic(III) from Groundwater by Nanoscale Zero-Valent Iron, *Environ. Sci. Technol.*, 39, 2005, 1291-1298.
- [8] H. Guo, D. Stüben, Z. Berner, Adsorption of arsenic(III) and arsenic(V) from groundwater using natural siderite as the adsorbent, *Journal of Colloid and Interface Science* 315, 2007, 47-53.
- [9] M. Wolthers a,*, I.B. Butler b, I, D. Rickard b, Influence of arsenic on iron sulfide transformations, *Chemical Geology* 236, 2007, 217-227.
- [10] V. González*, I. García, F. Del Moral, M. Simón, Effectiveness of amendments on the spread and phytotoxicity of contaminants in metal-arsenic polluted soil *Journal of Hazardous Materials* 205-206, 2012, 72-80.
- [11] L. Dupont, G. Jolly & M. Aplincourt, Arsenic adsorption on lignocellulosic substrate loaded with ferric ion. *Environmental Chemistry Letters*, 5, 2007, 125-129.
- [12] Ng J. C. Environmental contamination of arsenic and its toxicological impact on humans. *Environmental Chemistry*, 2, 2005, 146-160.
- [13] Ridge, A.S. Sedlak, D.L. copper and zinc complexes with edta during municipal wastewater treatment, *J. Water Res.* 38, 2004, 921-932.
- [14] B.A. Manning, S.E. Fendorf, S. Goldberg, surface structure and stability of arsenic(III) on goethite, spectroscopic evidence for inner-sphere complexes, *Environ. Technol.* 32,(16), 1998, 2383-2388.
- [15] C.P. Raven, A. Jain, R.H. Loepfert, Arsenite and arsenate adsorption on Ferrihydrite kinetics, equilibrium and adsorption envelopes, *Environ. Sci. Technol.*, 32, 1998, 344-349.
- [16] S. Dixit, J.G. Hering, 2003, comparison of arsenate and arsenite sorption onto iron oxides: Implications for arsenic mobility, *Environ. Sci. Technol.*, 37, 2003, 4182-4189.
- [17] J. Gimenez, J. de Pablo, M. Martinez, M. Rovira, C. Valderrama, Reactive transport of arsenic(III) and arsenic(V) on natural hematite: Experimental and modeling *J. Colloid Interface Sci.*, 348, 2010, 293-297.
- [18] A. Sullivan, R.C. Aller, Diagenetic cycling of arsenic in Amazon shelf sediments, *Geochim. Cosmochim. Acta*, 60, 1996, 1465-1468.
- [19] H.A. Lowers, G.N. Breit, A.L. Foster, J.Y. Whitney, J. Yount, M.N. Uddin, A.A. Muneem, Arsenic incorporation into authigenic pyrite, Bengal Basin sediment, Bangladesh, 2007, 2699-2717.
- [20] J. Giménez, M., Martínez, J., de Pablo, M. Rovira, L. Duro, Arsenic sorption onto natural hematite, magnetite, and goethite. *J. Hazard. Mater.* 141 (3), 2007, 575-580.
- [21] R. Nagar, D. Sarkar, K.C. Makris, R., Datta, Effect of solution chemistry on arsenic sorption by Fe- and Al-based drinking-water treatment residuals. *Chemosphere* 78, 2010, 1028-1035.
- [22] E.J.M. Terminghoff, S.A. Van Der Zee, M.G. Keizer, the desorption and speciation of copper in a sandy soil *J. Soil Sci.* 158, 1994, 398-407.
- [23] S.R., Chowdhury, E.K. Yanful, Arsenic and chromium removal by mixed magnetite-maghemite nanoparticles and the effect of phosphate on removal. *J. Environ. Manage.* 91 (11), 2010, 2238-2247.
- [24] O., Altin, H.Ö. Özbelge, and T. Dogu, Effect of pH in an Aqueous Medium on the Surface area, Pore Size Distribution, Density, and Porosity of Montmorillonite, *J. Colloid Interface Sci.* 217, 1999, 19-27.
- [25] J. Han, K. Song, B. Batchelor, A. Abdel-Wahab, Removal of arsenite(As(III)) and arsenate(As(V)) by synthetic pyrite (FeS₂): Synthesis, effect of contact time, and sorption/desorption envelopes *Journal of Colloid and Interface Science* 392, 2013, 311-318.
- [26] Y. Kitano, M. Okumura, M. Idogaki, Abnormal behaviour of Cu²⁺ and Zn ions in parent solution at the early stage of calcite formations. *Geochem. J.* 14, 1980, 167-175.
- [27] D. Banks, S.P. Burke, C.G. Gray, drainage and other ferruginous waters in north Derbyshire and south Yorkshire, U.K.. *J. Eng. Geol.* 30, 1997, 257-280.
- [28] M. Schlegel, L. A., Manceau, L. Charlet, D. Chateigner, J.-L. Hazemann, Sorption of metal ions on clay minerals. III. Nucleation and epitaxial growth of Zn on the edges of hectorite. *Geochimica et Cosmochimica Acta* 65, 2001, 4155-4170.
- [29] B. Morgan, A. W. Rate, E. D. Burton, Trace element reactivity in FeS-rich estuarine sediments: Influence of formation environment and acid sulfate soil drainage, *Science of the Total Environment* 438, 2012, 463-476.
- [30] V. Lenoble, O. Bouras, V. Deluchat, B. Serpaud, J.-C. Bollinger, Arsenic adsorption on pillared clays and iron oxides. *J. Colloid Interf. Sci.* 255, 2002, 52-58.
- [31] M.B. McBride, Organic anions adsorption on aluminum hydroxides: spin probe studies. *Clay and clay minerals*, 30(4), 1982, 438-444.
- [32] C Appel, L Ma, Concentration, pH, and surface charge effects on Cd and Pb sorption in tropical soils. *J. Environ. Qual.*, 31: 2002, 581-589.
- [33] K. Raven, A. Jain, R. Loepfert, Arsenite and Arsenate Adsorption on Ferrihydrite: Kinetics, Equilibrium, and Adsorption Envelopes, *Environ. Sci. Technol.* 32, 1998, 344-349.

- [34] D. M. Sherman, & S. R. Randall, Surface complexation of arsenic (V) to iron (III) hydroxides: Structural mechanism from ab initio molecular geometries and EXAFS spectroscopy. *Geochimica et Cosmochimica Acta*, 67, 2003, 4223–4230.
- [35] S., Goldberg, C.T., Johnston, Mechanisms of arsenic adsorption on amorphous oxides evaluated using macroscopic measurements, vibrational spectroscopy, and surface complexation modelling. *J. Colloid Interface Sci.* 234, 2001, 204-216.
- [36] G. Petruzzelli, B. Pezzarossa, Ionic strength influence on heavy metal sorption processes by soil, *J. Phys. IV Fr.* 107, 2003, 1061–1064.
- [37] D.M. Di Toro, J.D. Mahony, P.R. Kirchgraber, A.L O'Byrne, L.R Pasquale, D.C. Piccirilli, Effects of Nonreversibility, Particle Concentration, and Ionic Strength on heavy metal sorption, *Environ. Sci. Technol.* 20, 1986, 55–61.
- [38] D.A. Dzombak, F. Morel, *Surface Complexation Modeling: Hydrous Ferric Oxide*, Wiley, New York, 1990.
- [39] J. Lutzenkirchen, Ionic Strength Effects on Cation Sorption to Oxides: Macroscopic Observations and Their Significance in Microscopic Interpretation *J. Colloid Interface Sci.* 65, 2001, 149–155.
- [40] L. Lorenzen, J. S. J., van Deventer, & W. M. Landi, Factors affecting the mechanism of the sorption of As(V) species on activated carbon. *Minerals Engineering*, 8, 1995, 557–569.
- [41] A. Fotovat, R. Naidu, M.E. Sumner, Ionic-strength and pH effects on the sorption of cadmium and the surface-charge of soils, *European journal of soil science*, 45(4), 1994, 419-429.
- [42] K. A. Matis, M., Lehmann, & A. I Zouboulis, Modeling sorption of metals from aqueous solution onto mineral particles: The case of arsenic ions and goethite ore. In P. Misaelides, F. Macašek, T. J. Pinnavaia, & C. Colella (Eds.), *Natural microporous materials in environmental technology 1999*, 463–472.
- [43] W., Zhang, P., Singh, E., Paling, & S. Delides, Arsenic removal from contaminated water by natural iron ores. *Minerals Engineering*, 17, 2004, 517–524.
- [44] I.R. Philips, Copper, lead, cadmium and zinc sorption by waterlogged and air-dry soil *J. Soil Contam.* 8, 1999, 343–364.
- [45] P. Ebonnissel-Gissinger, M. Jean-Jacques Ehrhardt, and P. Behra, Surface Oxidation of Pyrite as a Function of pH, *Environ. Sci. Technol.*, 32, 1998, 2839-2845.
- [46] U. von Gunten, Kinetics and mechanistic aspects of As(III) oxidation by aqueous chlorine, chloramines, and ozone: Relevance to drinking water treatment. *Environ. Sci. Technol.* 40, 2006, 3285-3292.
- [47] A. S. Breitbach, *Nanoparticles in the Environment: A Study of Surface Reactivity of Pyrite and Arsenopyrite Materials • NNIN REU, Research Accomplishments*, 2006, 53-55.
- [48] B.C. Bostick, S. Fendorf *Geochim. Cosmochim. Acta*, 67 2003, 909.
- [49] J.B. Brower, R.L. Ryan and M. Pazirandeh, Comparison of ion exchange resins and biosorbings for the removal of heavy metals from plating factory wastewater. *Environmental Science & Technology*, 31, 1997, 2910-2914.
- [50] G. Kamei, and H. Ohmoto, The kinetics of reactions between pyrite and O₂-bearing water revealed from in situ monitoring DO, Eh and pH in a closed system. *Geochim. Cosmochim. Acta* 64, 2000, 2585–2601.
- [51] M. F. Lengkeel and R. N. TempeL, Reaction rates of natural orpiment oxidation at 25 to 40°C and pH 6.8 to 8.2 and comparison with amorphous As₂S₃ oxidation *Geochimica et Cosmochimica Acta*, Vol. 66, No. 18, 2002, 3281–3291.
- [52] M. Descostes, M.L. Schlegel, N. Eglizaud, F. Descamps, F. Miserque, E. Simoni, Uptake of uranium and trace elements in pyrite (FeS₂) suspensions, *Geochimica et Cosmochimica Acta* 74, 2010, 1551–1562.
- [53] N.; Belzile, A. Tessier, *Geochim. Cosmochim. Acta* 1990, 54, 103-109.
- [54] DC, Cooper, JW. Morse, Biogeochemical controls on trace metal cycling in anoxic marine sediments. *Environ Sci Technol* 32: 1998;327–30.
- [55] Holmes J. Fate of incorporated metals during mackinawite oxidation in seawater. *Appl. Geochem.* 14, 1999, 277–281.
- [56] Z. Gholami, M. Torabi Angaji, F. Gholami, and S. A. Razavi Alavi, Reactive Absorption of Hydrogen Sulfide in Aqueous Ferric Sulfate Solution *International Journal of Chemical and Biological Engineering* 2009, 2:2.
- [57] S.W. Poulton, and M.D. Kron, and R. Raiswell, revised scheme for the reactivity of iron (oxyhydr)oxide minerals towards dissolved sulfide, *Geochimica et Cosmochimica Acta*, 68, (18), 2004, 3703-3715.
- [58] R. A. Root, S. Dixit, K. M. Campbell, A. D. Jew, J. G. Hering, P. A. O'Day Arsenic sequestration by sorption processes in high-iron sediments, *Geochimica et Cosmochimica Acta* 71, 2007, 5782–5803.
- [59] A.H., Khan, S.B. Rasul, A.K.M. Munir, M., Habibuddowla, M. Alauddin, S.S., Hussam, Newazi, A., Appraisal of a simple arsenic removal method for groundwater of Bangladesh, *J. Environ. Sci. Health*, A35, (7), 2000, 1021-1041.
- [60] S. Paikaraj, S. Banerjee, S. Mukherji, sorption of arsenic onto Vindhyan shales, *Curr. Sci.*, 88 2005, 1580-1585.
- [61] D.E Egirani, A.R Baker, and J.E, Andrews, Arsenite Removal from Aqueous Solution by Mixed Mineral Systems II. The Role of Solution Composition and Ageing, *International Journal of Recent Scientific Research* 4 (4) 2013a, 439 - 443.
- [62] A. O' zcan; E.M.; O' ncu' A.S. O' zcan, Kinetics, isotherm and thermodynamic studies of adsorption of Acid Blue 193 from aqueous solutions onto natural sepiolite. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 277, 2006, 90–97.
- [63] M. Awual, S. A. REI-Safy A Jyo Removal of trace arsenic(V) and phosphate from water by a highly selective ligand exchange adsorbent *Spectrochimica Acta Part A* 100, 2013, 161–165.
- [64] S. Mustafa, A. Hamid, A. Naeem, Xanthate adsorption studies on chalcopyrite ore, *Int. J. Miner. Process.* 74, 2004, 317–325.
- [65] D.E, Egirani, J.E Andrews, and A.R, Baker, Characterization of Sorption and Quantitative Analysis of Hydroxyl Complexes of Cu and Zn in Aqueous Solution: The Interactive Effects of Mine Wastewater mixed Mineral Systems, *International Journal of Recent Scientific Research* Vol. 4, Issue, 4(4) 2013b, 69-475, 2013.
- [66] W.R., Cullen, K.J., Reimer, Arsenic speciation in the environment. *Chem. Rev.* 89, 1989. 713–764.
- [67] E.J. Kim, B. Batchelor, macroscopic and X-ray photoelectron spectroscopic investigations of arsenic with synthesized pyrite, *Environ. Eng. Sci.*, 26 2009, 1785.
- [68] J.D Morton, J.D Semaru, K.F. Hayes, An X-ray absorption spectroscopy study of the structure and reversibility of copper adsorbed to montmorillonite clay, *Geochim. Cosmochim. Acta* 65, 2001, 2709–2722.
- [69] S.L. Stipp, S M. Hansen, R. Kristensen, M.F Hochella, L Bennedsen, K. Dideriksen, T. Balic-Znic, D. Leonard, H.-J. Mathieu, *J. Chem. Geol.* 190, 2002, 321–337.
- [70] D. A. Dunnette, D. P. Chynoweth and K. H. Mancy, The Source of Hydrogen Sulfide in Anoxic Sediment, *Water Res.* 19, 1985, 875-884.