

Journal of Chemical, Biological and Physical Sciences



An International Peer Review E-3 Journal of Sciences

Available online at www.jcbpsc.org

Section A: Chemical Science

CODEN (USA): JCBPAT

Research Article

Mercury Removal from Aqueous Solution using Mixed Mineral Systems Injected with Iron Sulfide under Sulfidic- Anoxic Condition II. The Role of Solution Composition and Ageing

D.E. Egirani¹, J.E. Andrews², A.R. Baker²

¹Faculty of Science, Niger Delta University, Wilberforce Island, Nigeria

²School of Environmental Sciences, University of East Anglia, Norwich, UK

Received: 29 March 2014; **Revised:** 10 April 2014; **Accepted:** 14 April 2014

Abstract: This study investigates Hg (II) removal onto binary mixed mineral sorbents injected with iron sulfide under sulfidic-anoxic condition relevant to mercury contaminated water impacted environment. Batch mode studies at room temperature investigated the effects of solution composition and ageing. Variability in Hg(II) sorption exist over the range of pH investigated, exhibiting linear sorption for iron sulfide and some of the mixed mineral systems, Also, changes in Hg(II) sorption as particle concentration (Cp) increased exist, with iron sulfide and some mixed mineral systems exhibiting a linear decrease in Hg(II) sorption as Cp increases. All single and mixed mineral systems exhibit a near linear decrease in Hg(II) sorption over the range of residence time investigated. Hg(II) step-wise sorption probably indicates reaction phases attributed to outer sphere, inner sphere complexation and intra-particle diffusion.

Keywords: mercury, iron sulfide, solution, composition, ageing and mixed mineral systems.

INTRODUCTION

Mercury is well known as a toxic element in its most common forms, that is, elemental mercury, inorganic mercury, and methyl mercury. Much attention has been given to the toxic effects of elemental

mercury because of its presence in dental amalgams and to methyl mercury because of its ubiquity and tendency to bio-concentrate in fish¹. Mercury is one of the most toxic elements in the aqueous environment². The health of top predators, e.g. birds, fish, seals, and man, is thereby threatened^{3,4}. Three forms of non-biodegradable mercury contaminant namely elemental mercury (HgO), oxidized mercury (Hg²⁺) and particulate-bound mercury (Hg P) exist. The oxidized form of mercury is transformed into its toxic methylated species, transferred and bio-amplified as monomethyl mercury (MMHg) in the aquatic food chains⁵⁻¹⁵. The major sources of Hg emission worldwide come from coal combustion and Au amalgamation¹⁶⁻¹⁸.

Alluvial Au mining activities, using elemental Hg for Au-Hg amalgamation constitute biogeochemical reactors where dissolved organic matter (OM), SO₄ and Fe oxides favor bacterial activity¹⁹. The release of mercury into bodies of water is increasing, and non-admissible level of greater than 1 µg/L is found in surface, groundwater and the environment²⁰. Elevated concentrations can also be present in remedies not classified as *rasa shastra* [The deliberate addition of minerals, metals and metalloids to an herbal remedy is known as *rasa shastra*], presumably introduced in plant material or incidentally during manufacturing²¹⁻²³. Mercury is carcinogenic and its presence in humans results in severe chronic disease or death²⁴. In addition, elemental mercury exhibits high volatility and bioaccumulation in the environment, thus creating neurological health impact^{25, 26}. Specifically, methyl mercury induced by microbial bio-methylation of mercuric ions (Hg²⁺) can accumulate in the body and can cause brain damage and other chronic diseases^{27, 28}. Hence, testing the removal of Hg²⁺ from aqueous solution in the laboratory as a way of mimicking its removal from water bodies remains a current and relevant research topic.

The removal of aqueous mercury species (either in a positively charged Hg (II) or neutral HgO form) can be hampered by the absence of reliable sorbents and solution chemistry^{1, 29}. For HgO removal in liquid phase, the key point is to convert HgO to Hg²⁺ rapidly, the latter being easily dissolved in water as reported in literature³⁰⁻³². The removal of mercury from contaminated water bodies is controlled by the solution composition and ageing³³⁻³⁴. FeS(s) has been shown to readily exchange Fe²⁺ with Hg²⁺ to form HgS(s)³⁵⁻³⁷. HgS(s) is relatively insoluble and less volatile than other forms of mercury, and thus potentially less harmful³⁸⁻³⁹. It has also been suggested that HgS(s), due to its low solubility, may limit mercury cycling through the environment³⁸⁻⁴⁰. Thus, the formation of HgS(s) from mercury and sulfide interactions in water, soil, and sediments provides evidence that mercury pollution can be abated.

Solution pH controls (a) the solubility of mercury species; (b) hydrolysis behavior of mercury ions; and (c) surface charge of clays and hydroxides. pH variability is known to affect the charge density on sorbents due to de-protonation of reactive sites. Under sulfidic-anoxic condition, surfaces of metal sulfides have thiol (≡S-H) and hydroxyl (≡Me-OH) functional groups and reactive sites. In addition, clays and hydroxides have a high concentration of OH⁻ groups readily protonated at low pH, generating positive charge which retains anions by electrostatic attraction⁴¹⁻⁴⁴. The adsorption of heavy metals and metalloids and other anions have been reported to be dependent on the nature of the anion and the adsorbent surface⁴⁵. Adsorption may decrease as particle concentration increases (outer sphere complexation) or not be significantly affected as particle concentration increases (inner sphere complexation). 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 theory⁴⁶⁻⁴⁸.

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. 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 heavy metals and metalloids sorption^{16, 49-51}.

Theoretical models and isotherms: To address the suitability of mixed mineral suspensions of clay and (hydroxides) for Hg(II) removal, a theory derived from Freundlich isotherm model is designed to explain the predicted behavior of mineral-Hg(II) interactions as influenced by extraneous factors of pH, solid concentration and residence time or ageing⁵². Detailed system characterization and an empirical model involving the distribution coefficient (Kd) as used in previous paper⁵³⁻⁵⁴ and % sorption used in calculating Hg (II) sorbed are provided in equation 1⁵⁵⁻⁵⁸.

$$\% \text{Hg (II) sorbed} = \frac{(C_i - C_e)}{C_i} \times 100 \% \quad \dots (1)$$

Where C_i and C_e are the initial and equilibrium Hg (II) concentrations in mg/L. Distribution coefficient used in calculating Hg(II) sorbed was derived from the Freundlich model Equation 2,

$$S = KdC^N \quad \dots (2)$$

Where S is the sorbed concentration (μg/kg), Kd is the distribution coefficient, C is the equilibrium concentration (μg/g), and N = 1 is a chemical-specific coefficient derived from the slope of the plot. The empirical model^{16, 53}, to address the mineral-Hg interactions are provided in Equation 3 and 4,

$$\text{Hg (II) Sorbed difference} = \text{Hg (II) Sorbed actual} - \text{Hg (II) Sorbed total} \quad \dots (3)$$

$$\text{Hg (II) sorbed}_{\text{total}} = \frac{[S_1 + S_2 + S_n]}{n} \quad \dots (4)$$

Where Hg sorbed_{total} is the theoretical sorption for a 1:1 mixed mineral suspension, S_1 is the Hg(II) sorbed on first single mineral suspension, and S_2 is the Hg(II) sorbed on second single mineral suspension, S_n is the Hg(II) 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 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:

- Secondary mineral phase developed during sorbate-sorbent interaction.
- Components of minerals in the mixed mineral suspension acted as chemisorbed species and not as individual networks.
- 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 on Hg (II) sorption. Mineral mixing is said to (a) enhance Hg(II) removal where the difference is positive; (b) depresses or attenuate Hg(II) removal where the difference is negative; and (c)

have no effect on Hg(II) removal where no difference exist between Hg(II) sorbed and theoretical Hg(II) sorption¹⁶. Mercury treatment technologies are provided in companion paper I and include precipitation, membrane filtration, ion exchange, electro-deposition, adsorption and coagulation⁵⁹⁻⁶¹. Other researches focused on the removal of Hg (II) from water by sorption processes⁶²⁻⁶⁴.

However, the use of mixed mineral systems of clays and hydroxides as suitable sorbents in mercury removal is limited in literature^{1, 16}. Therefore, this paper addresses the sorption relationship between simulated mercury contaminated water and mixed mineral phases of kaolinite/montmorillonite, kaolinite/goethite and montmorillonite/ goethite injected with iron sulfide under sulfidic-anoxic condition. This is based on different solution composition such as pH, solid concentration and residence time (ageing).

Preparation of Sulfidic-Anoxic Zinc Sulfide Suspension: As reported in companion paper I, hydrogen sulfide occurs as a product of sulfate and sulfide reduction in sulfidic-anoxic environment^{28, 65}. In sulfidic-anoxic environment, hydrogen sulfide occurs as a product of sulfate and sulfide reduction⁶⁶. 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.

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. Then the water was purged overnight in an anaerobic chamber containing a mixture of 5% hydrogen and 95% nitrogen gases. 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.

Mercuric chloride (HgCl₂) provided by Iconofile Company Inc. was employed as the source of Hg (II). A standard solution containing variable concentrations of Hg (II) in ppm was prepared by dissolving HgCl₂ (Merck) in distilled water. In all experimental studies conducted in triplicates, samples were stored in the dark at room temperature (23±3 °C) not exceeding 24 h before analysis¹⁶. Supernatant was filtered through a cellulose acetate filter (pore size 0.2µm) and analyzed for Hg (II) using a Hitachi Atomic Absorption Spectrophotometer (HG-AAS). The working solutions of different concentrations were prepared by diluting the stock solution immediately before starting the batch studies.

EXPERIMENTAL METHODS

Sorption Experiments: Batch mode experiments in this study were conducted using single mineral suspensions of kaolinite, montmorillonite and goethite. Also, 1:1 mixed mineral suspensions of kaolinite/montmorillonite, kaolinite/goethite and montmorillonite/goethite were used to elucidate the differences in sorption behavior 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^{16, 54,55}. For batch mode pH investigation, 1% sulfidic-anoxic suspension of iron sulfide was added to 1% single and 1:1 mixed mineral systems made up to 50 ml containing 1% (by

mass) mineral suspension were reacted with solution containing 10 ppm of mercury 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 was added to 1% 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 10 ppm of mercury at zero electrolyte background. The treated suspensions were adjusted to pH 4 and equilibrated for 24 h. Batch mode ageing investigations was carried out from 24 to 720 h using 1% sulfidic-anoxic suspension of iron sulfide added to 1% single and 1:1 aged mixed mineral suspensions containing 1% (by mass) were reacted with solution containing 10 ppm of Hg(II) at zero electrolyte background. The treated suspensions, adjusted to pH 4 with no added electrolyte, were equilibrated for 24 h. Mercuric chloride (HgCl₂) provided by Iconofile Company Inc. was employed as the source of Hg (II). A standard solution containing variable concentrations of Hg (II) in ppm was prepared by dissolving HgCl₂ (Merck) in distilled water. In all experimental studies conducted in triplicates, samples were stored in the dark at room temperature (23±3 °C) not exceeding 24 h before analysis. Supernatant was filtered through a cellulose acetate filter (pore size 0.2µm) and analyzed for Hg(II) using a Hitachi Atomic Absorption Spectrophotometer (HG-AAS)⁶⁷.

RESULTS AND DISCUSSION

Mineral Systems and Ph Effects on Hg (II) Removal: In a previous study¹⁶, Hg (II) demonstrated a linear sorption increase with increasing pH for single mineral systems of kaolinite, montmorillonite, mixed mineral suspensions of kaolinite-montmorillonite and Goethite-Kaolinite. In this study, Hg (II) sorption under sulfidic-anoxic condition exhibited linear sorption for iron sulfide, montmorillonite, kaolinite and mixed mineral systems of kaolinite-montmorillonite and goethite-kaolinite as shown in **Figure 1 and Figure 2**. Goethite exhibits a stepwise increase in Hg (II) sorption as pH increases. Hg (II) sorption by goethite -montmorillonite decreased between pH 4 and pH 5, changing slope and increasing over the remaining range of pH.

This variability in sorption may be attributed to thiol (≡S-H) and hydroxyl (≡Me-OH) functional groups and reactive sites and increased de-protonation of reactive sites containing high concentration of OH-groups. However, sorption pattern appeared to be controlled by outer sphere complexation, inner sphere complexation and intra-particle diffusion for Hg (II) sorbed on goethite and mixed mineral system of goethite-montmorillonite with respect to pH. Differences in actual and theoretical Hg (II) sorbed goethite-kaolinite and kaolinite-montmorillonite is in the negative territory except goethite-montmorillonite. This indicates that mineral mixing under sulfidic-anoxic condition attenuated Hg (II) sorption for the former and enhanced Hg (II) sorption for the latter.

Mineral Systems and Cp Effects on Hg (II) Removal: In a previous study in the absence of iron sulfide¹⁶, Egirani *et al* indicated a linear decrease of Hg (II) sorbed on kaolinite/goethite, kaolinite-montmorillonite goethite-montmorillonite and montmorillonite over the range of Cp investigated. Kaolinite demonstrated an increase in Hg (II) sorption as particle concentration was increased. Goethite exhibited a sinusoidal behavior, decreasing up to 0.004g/L in Hg (II) sorption, then increasing up to 0.008g/L¹⁶. In this study under sulfidic-anoxic condition, iron sulfide, kaolinite/goethite, goethite/montmorillonite and kaolinite-montmorillonite exhibited a linear decrease in Hg (II) sorption as Cp increases.

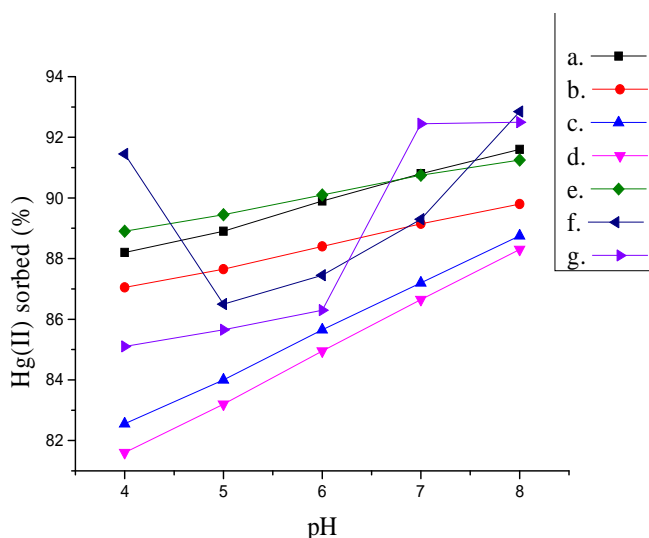


Figure 1: Plots of Hg (II) sorbed versus pH for (a) Iron sulfide, (b) kaolinite, (c) goethite/kaolinite, (d) kaolinite/montmorillonite, (e) montmorillonite, (f) goethite/montmorillonite, (g) goethite, sulfidic-anoxic mineral systems

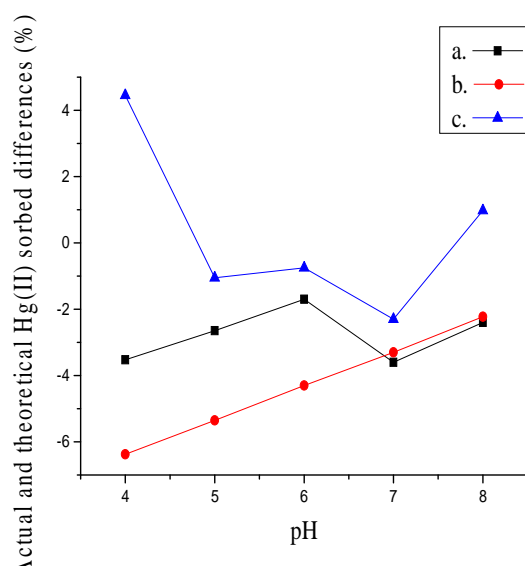


Figure 2: Plots of actual and theoretical Hg (II) sorbed differences vs, pH for (a) goethite/kaolinite, (b) kaolinite/montmorillonite, (c) goethite/montmorillonite, sulfidic-anoxic mineral systems

Differences in actual and theoretical Hg (II) sorbed on mineral systems is in the negative territory for kaolinite/montmorillonite and goethite/montmorillonite indicating non-promotive Hg (II) sorption as Cp increases. Kaolinite/goethite exhibits sinusoidal behavior in the positive territory indicating promotive Hg (II) sorption as Cp increases as shown in **Figure 3** and **Figure 4**. The behavior of these mineral systems under sulfidic-anoxic condition may reflect the formation of separate (discrete) particles or coatings on other mineral surfaces. Coatings and the presence of thiol ($\equiv\text{S-H}$) and hydroxyl ($\equiv\text{Me-OH}$) functional groups and reactive sites are sufficient to influence sorption rates and behavior⁶⁸.

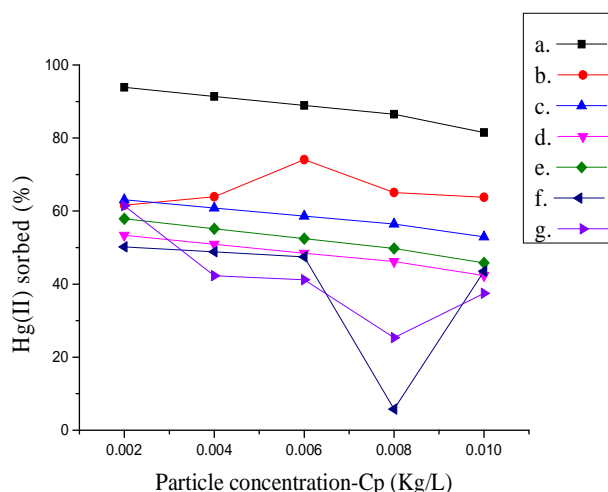


Figure 3: Plots of Hg (II) sorbed versus particle concentration-Cp for (a) Iron sulfide, (b) kaolinite, (c) kaolinite/goethite, (d) kaolinite/montmorillonite, (e) montmorillonite, (f) goethite/montmorillonite, (g) goethite, sulfidic-anoxic mineral systems

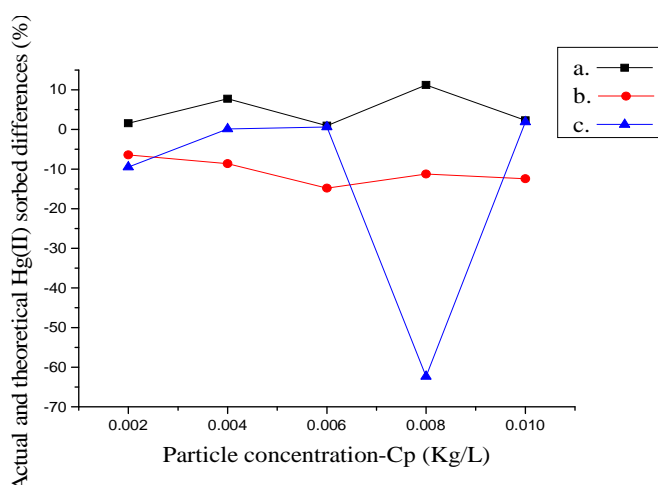


Figure 4: Plots of actual and theoretical Hg (II) sorbed differences versus particle concentration for Hg (II) sorbed on (a) kaolinite/goethite, (b) kaolinite/montmorillonite, (c) goethite/montmorillonite, sulfidic-anoxic mineral systems

Decrease in Hg (II) sorption as Cp was increased may be attributed to increase in particle size and aggregation of the mineral suspensions. The Cp effect is also related to effective surface area, pressure, and force at the mineral/water interface Egirani *et al.* Increase in Cp results in low pressure at the interface and a subsequent decrease in sorbing ion diffusion to reactive sites. Increase in Hg (II) uptake over the range of Cp investigated could also be attributed to the increased clays and hydroxide(s) surface area available for contact with the Hg (II) leading to increased number of surface-active groups.

Mineral Systems and Ageing Effects on Hg (II) Removal: In a previous study in the absence of iron sulfide ¹⁶, all single and mixed mineral systems exhibited a near linear decrease in Hg (II) sorption over the range of residence time investigated. The order of Hg (II) sorption on the mineral phases is in the order goethite> goethite-kaolinite>montmorillonite>goethite-montmorillonite>kaolinite-montmorillonite >

kaolinite. In the present study under sulfidic-anoxic condition exhibit Hg (II) sorption in the order: kaolinite > montmorillonite > iron sulfide > goethite for single mineral systems and the order: kaolinite-montmorillonite > goethite-montmorillonite > goethite-kaolinite. Hg (II) sorption on all mineral systems decrease over time increasing after 288 hours as shown in **Figure 5**. Differences in actual and theoretical sorption (**Figure 6**) for goethite-montmorillonite were in the positive territory indicating promotive Hg (II) sorption over time. Kaolinite-montmorillonite declined from the positive territory to the negative territory crossing over with goethite-kaolinite after 576 hours.

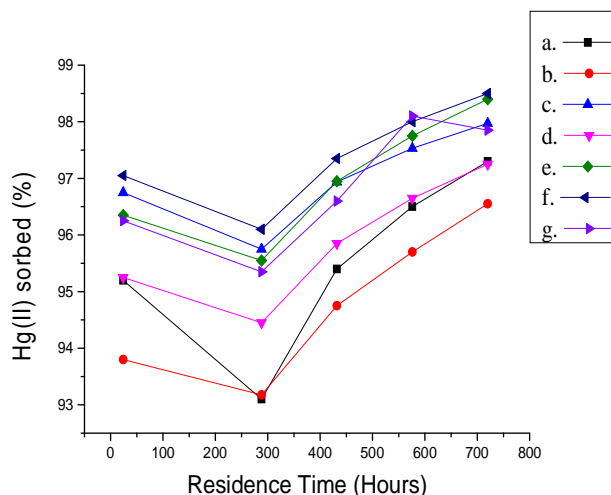


Figure 5: Plots of Hg (II) sorbed versus residence time for (a) Iron sulfide, (b) goethite, (c) kaolinite/montmorillonite, (d) goethite/kaolinite, (e) goethite/montmorillonite, (f) kaolinite, (g) montmorillonite, sulfidic-anoxic mineral systems

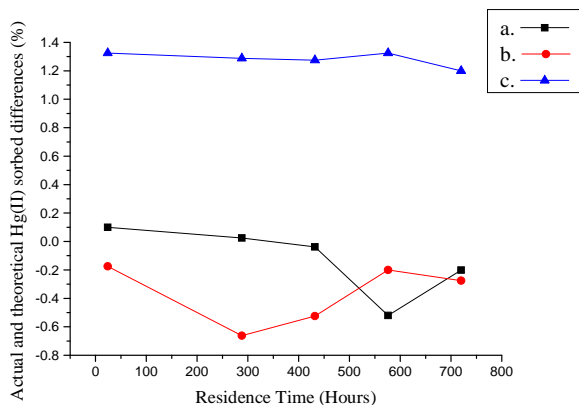


Figure 6: Plot of actual and theoretical Hg (II) sorbed differences vs. residence time for (a) kaolinite/montmorillonite, (b) goethite/kaolinite, (c) goethite/montmorillonite, sulfidic-anoxic mineral systems

This may suggest a decrease in Hg (II) removal due to mineral mixing for these two mixed mineral systems. The flat-linear pattern of sorption for goethite-kaolinite all in the positive territory may imply that mercury sorption onto goethite-kaolinite is essentially a surface phenomenon under sulfidic-anoxic

condition¹⁶. Hg (II) step-wise sorption probably indicated reaction phases attributed to outer sphere, inner sphere complexation and intra-particle diffusion as reported elsewhere¹⁶. Increase in Hg (II) sorption as residence time increases may be attributed to increased hydroxylation of the mineral surfaces and the unpredictable behavior of these minerals in the presence of thiol ($\equiv\text{S-H}$) and hydroxyl ($\equiv\text{Me-OH}$) functional groups and reactive sites, resulting in the formation of new reactive sites^{69, 70}.

CONCLUSIONS

The possibilities of using mixed mineral phases of kaolinite, montmorillonite, and goethite under to remove Hg (II) from simulated contaminated surface and ground water has been investigated as a function of solution composition and ageing. Variability in Hg (II) sorption exists over the range of pH investigated. Hg (II) sorption under sulfidic-anoxic condition exhibited linear sorption for iron sulfide, montmorillonite, kaolinite and mixed mineral systems of kaolinite-montmorillonite and goethite-kaolinite. Differences in actual and theoretical Hg (II) sorbed goethite-kaolinite and kaolinite-montmorillonite are in the negative territory except goethite-montmorillonite. This indicates that mineral mixing under sulfidic-anoxic condition attenuated Hg(II) sorption for the former and enhanced Hg(II) sorption for the latter. This variability in sorption may be attributed to the presence of thiol ($\equiv\text{S-H}$) and hydroxyl ($\equiv\text{Me-OH}$) functional groups and reactive sites and increased de-protonation of reactive sites as pH was increased. Sorption pattern appeared to be controlled by outer sphere complexation, inner sphere complexation and intra-particle diffusion for Hg (II) sorption some of the mineral phases.

Changes in Hg (II) sorption as particle concentration (Cp) increased exist. Iron sulfide, kaolinite/goethite, goethite/montmorillonite and kaolinite-montmorillonite exhibited a linear decrease in Hg (II) sorption as Cp increases. Differences in actual and theoretical Hg (II) sorbed on mineral systems is in the negative territory for kaolinite/montmorillonite and goethite/montmorillonite indicating non-promotive Hg(II) sorption as Cp increases. Kaolinite/goethite exhibits sinusoidal behavior in the positive territory indicating promotive Hg (II) sorption as Cp increases. Changes in Hg (II) sorption as ageing increases exist. Under sulfidic-anoxic condition Hg (II) sorption is in the order: kaolinite > montmorillonite > iron sulfide > goethite for single mineral systems and the order: kaolinite-montmorillonite > goethite-montmorillonite > goethite-kaolinite. Hg (II) sorption on all mineral systems decrease over time increasing after 288 hours. All single and mixed mineral systems exhibited a near linear decrease in Hg (II) sorption over the range of residence time investigated. Hg (II) step-wise sorption probably indicated reaction phases attributed to outer sphere, inner sphere complexation and intra-particle diffusion. Increase in Hg (II) sorption as residence time increases may be attributed to increased hydroxylation of the mineral surfaces and the unpredictable behavior of these minerals in the presence of thiol ($\equiv\text{S-H}$) and hydroxyl ($\equiv\text{Me-OH}$) functional groups and reactive sites, resulting in the formation of new reactive sites

REFERENCES

1. I. Koch, M. Moriarty, J. Sui, A. Rutter, R. B. Saper, K. J. Reimer, *Science of the Total Environ.* 2013, **454**–455, 9–15.
2. D. Quig, *Altern Med Rev.* 1998, **3**, 262-270.
3. B. Braune, D. Muir, B. DeMarch, M. Gamberg, K. Poole, R. Currie, M. Dodd, W. Dushenko, J. Eamer, B. Elkin, M. Evans, S. Grundy, C. Hebert, R. Johnstone, K. Kidd, B. Koenig, L. Lockhart, H. Marshall, K. Reimer, J. Sanderson, *Total Environ.* 1999, **230**, 145-207.

4. D. Muir, B. Braune, B. DeMarch, R. Norstrom, R. Wagemann, L. Lockhart, B. Hargrave, D. Bright, R. Addison, J. Payne, K. Reimer. *Total Environment*, 1999, **230**, 83-144.
5. L. Trasande, P.J. Landrigan, C. Schechter, *Envir. Health Perspec.* 2005, **113**:590–6.
6. H. Akagi, O. Malm, F.G.P. Branches, Y. Kinjo, Y. Kashima, J.R.D. Guimara, R.B. Oliveira, K. Haraguchi, W.C. Pfeiffer, Y. Takizava, *Wa Air Soil Pol.* 1995, **80**, 85–94.
7. A. Boudou, R. Maury-Brachet, M. Coquery, G. D. Durrieu, Cossa, *Environ Sci. Technol.* 2005, **39**, 2448–2454.
8. J.P. Carmouze, M. Lucotte, A. Boudou, Mercury in the Amazon. Human and Environmental Implications, Health Risks. IRD editions, Bondy. 2001, 20.
9. J. Dolbec, D. Mergler, P.C.J. Sousa, M.S. Sousa de, J. Lebel, *Int. Arch. Occup. Environ. Health*, 2000, **73**, 195–203.
10. N. Frery, R. Maury-Brachet, E. Maillot, M. Deheeger, B. Merona de, A. Boudou, *Environ Healt Perspect.* 2001, **109**, 449–456.
11. W.C. Pfeiffer, L.D. Lacerd, W. Salomon, O. Malm, *Environ. Rev.* 1993, **1**, 26–37.
12. M. M. Veiga, P. Maxson and L.D. Hylander, *J. of Cleaner Produc.* 2006, **14**: 436-447.
13. C. Watras, *Limnol. Oceanogr.* 1992, **37**, 1313–1318.
14. S. Lee, Y. Park, *Fuel Process Technol*; 2003, **84(1–3)**:197–206
15. D. Jaffe, S. Strode, *Environmental Chemistry*, 2008, **5**, 121–126.
16. D.E. Egirani, A.R. Baker, J.E. Andrews, *Journal of Environmental Science, Toxicology and Food Technology (IOSR-JESTFT)*, 2013, **4(2)**, 49-55.
17. UNEP, Global Atmospheric Mercury Assessment: Sources, Emissions and Transport, UNEP Chemicals Branch, Geneva, 2008, 42.
18. Y.Wu, S.Wang, D.G. Streets, J. Hao, M. Chan, J. Jiang, *Environmental Science and Technology*, 2006, **40**, 5312–5318.
19. B. Muresan, B. Pernet-Coudrier, D. Cossa, D. Varrault, *Applied Geochemistry*, 2011, **26**, 2057–2063.
20. J.W. Fitzpatrick, C.J., Lewis, D.O. Berninger, United States Patent, 1975, **3**, 873,581.
21. United States Environmental Protection (USEPA), National Primary Drinking Water Regulations; Arsenic and Clarifications to Compliance and New Source Contaminants Monitoring, Washington, DC. 2001.
22. R.B. Saper, R.S. Phillips, A. Sehgal, N. Khouri, R.B. Davis, J. Paquin, *JAMA*, 2008, **300**, 915–923.
23. I. Koch, M. Moriarty, K. House, J. Sui, W.R. Cullen, R. B. Saper, *Sci. Total Environ.* 2011, 409:4545–4552.
24. N. Langford, R. Ferner, *J. Hum. Hypertens.* 1999, **13**, 651-656.
25. J.H. Pavlish, M.J. Holmes, S.A. Benson, C.R. Crocker, K.C. Galbreath, *Fuel Process Technol.* 2004, **85**, 563–76.
26. A.P. Dastoora, Y. Larocpue, *Atmos Environ.* 2004, **38**, 147–61.
27. R. Qu, J. Liu, C. Sun, Y. Zhang, C. Ji, P. Yin, *J. Che. Eng. Da*, 2010, **55**, 4650–4659.
28. J. Wang, Y. Zhang, L. Han, L. Chang, W. Bao, *Fuel*, 2013, **103**, 73–79.
29. W.H. Schroeder, G. Yarwood, H. Niki, *Water, Air Soil Pollut.* 1991, **56**, 653–666.
30. E.G. Pacyna, J.M. Pacyna, *Water Air Soil Pollut.* 1995, **137**, 149–165.
31. Q.F. Ye, C.Y. Wang, D.H. Wang, G. Sun, X.H. Xu, *Journal of Zheijang University Science B - Biomedicine & Biotechnology*, 2006, **7(5)**, 404–410.
32. Xu, X.H. Ye, Q.F. Tang, T.M. Wang D.H. *Journal of Hazardous Materials*, 2008, **158**, 410–416.
33. K.F. Cen, Technical report of clean coal fired power generation, in: 2nd seminar for the clean coal technology of China, Coal Society, Hangzhou. 2001, 12-18.
34. A.M. Deshicar, S.S. Bokade, S.S. Dara, *Water Res.* 1990, **24**, 1011–1016

35. J. W. Morse, and G. W. Luther, *Geochimica Et Cosmochimica Acta*, 1999, **63**(19-20), 3373-3378.
36. H. Y. Jeong, Removal of Heavy Metals and Reductive Dechlorination of Chlorinated Organic Pollutants by Nanosized FeS. Civil and Environmental Engineering. Ann Arbor, University of Michigan. Published Ph.D.:2005. 217.
37. S. Allard and A. Duker, *Science of the Total Environment*, 2006, **36**, 8(1), 418-423.
38. K. L. Willet, R. R. Turner, and J. J. Beauchamp, *Hazardous Waste and Hazardous Material*, 1992, **9**, 275-288.
39. M. O. Barnett, R. R. Turner and P. C. Singer, *Applied Geochemistry*, 2001, **16**(13), 1499-1512.
40. D. P. Krabbenhoft, and C. L. Babiarz, *Water Resour Resea*, 1992, **28**(12), 3119-3128.
41. J.B. Brower, R.L. Ryan and M. Pazirande, *Environmental Science & Technology*, 1997, **31**, 2910-2914.
42. P. Bonnissel-Gissinger, M. Alnot, J.J. Ehrhardt, P. Behra, *Environ. Sci. Technol.* 1998, **32**, 2839-2845.
43. M.B. McBride, *Clay and clay minerals*, 1982, **30**(4), 438-444.
44. Y. Goksungur, S. Uren, U. Guvenc, *Bioresource Technol.* 2005, **96**, 103-109.
45. Z.R. Holan, B. Volesky, *Biotechnol. Bioengery*, 1994, **43**, 1001-1009.
46. T. Akar, Z. Kaynak, S. Ulusoy, D. Yuvaci, G. Ozsari, S.T. Akar, *J. Hazard. Mater.* 2009, **163**, 1134-1141.
47. W. Shao, L. Chen, L. Lu, F. Luo, *Desalination*, 2011, **265**, 177-183.
48. D.A. Dzombak, F. Morel, *Surface Complexation Modeling: Hydrous Ferric Oxide*, Wiley, New York, 1990.20.
49. J. Lutzenkirchen, *J. Colloid Interface Sci.* 2001, **65**, 149-155.
50. J. Devotta, R.A. Mashelkar, *Chem. Eng. Sci.* 1996, **51**, 561-569.
51. I.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*, The Netherlands: Kluwer, 1999, 463-472.
52. V.H. Hatje, D.M. Hill, G. McOrist, G.F. Birch, R. Szymczak, *J. Environ. Int.* 2003, **29**, 613-618.
53. D. E. Egirani, A. R. Baker, J. E. Andrews, *Journal of Colloid and Interface Science*, 2005a, **291**, 319-325.
54. D. E. Egirani, A.R. Baker, J. E. Andrews, *Journal of Colloid and Interface Science*, 2005b, **291**, 326-333.
55. T. Altun, & E. Pehlivan, *Food Chemistry*, 2012, **132**, 693-700.
56. D. E. Giles, M. Mohapatra, T. B. Issa, S. Anand, P. Singh, *Journal of Colloid and Interface Science*, 2013, **392**, 311-318.
57. Y.S. Al-Degs, M.F. Tutunji, H.M. Baker, *J. Clay Miner.* 2003, **38**, 501-509.
58. M. Horsfall Jnr and A. Spiff, *African Journal of Biotechnology*, 2005, **4**(2), 191-196.
59. I.Aguado, J.M. Arsuaga, A. Arencibia, *Mesopor. Mater.* 2008, **109**, 513-524.
60. R.S. Vieira, E. Guibal, E.A. Silva, M.M. Beppu, *Adsorption*, 2007, **13**, 603-611.
61. M.A. Uddin, *Energy Fuels*, 2008, **3**, 454-460.
62. F.S. Zhang, J.O. Nriagu, H. Itoh, *Water Res.* 2005, **39**, 389-395.
63. B.A.F. Mibeck, E.S. Olson, S.J. Miller, *Fuel Process. Technol.* 2009, **90**, 1364-1371.
64. E.A. Kim, A.L. Seyfferth, S. Fendorf, R.G. Luthy, *Water Res.* 2011, **45**, 453-460.
65. W. R. Cullen and K. J. Reimer, *Chem. Rev.* 1989, **89**, 713-764.
66. A.Velasco, M. Ramírez, T., Volke-Sepúlveda, A. González-Sánchez, S. Revah, *Journal of Hazardous Materials*, 2008, **151**(2-3), 407-413.
67. A. Morton, A. Semaru, A. A. Hayes, *Geochim. Cosmo Acta*, 2001, **65**, 2709-2722.

68. S. Cataldo A.Gianguzza, A.Pettignano, A. Villaescusa, *Reactive & Functional Polymers*, 2013, 73, 207–217.
69. I.L. Schlegel, A. Manceau, L. Charlet, D.Chateigner, J.L. Hazemann, *Geochimica et Cosmochimica Acta*, 2001, **65**, 4155-4170.
70. D. A. Dunnette, D. P. Chynoweth and K. H. Mancy, *Water Res.* 1985, **19** (7). 875-884.

***Corresponding author: D.E. Egirani;** Faculty of Science, Niger Delta University,
Wilberforce Island, Nigeria