

Mercury Removal from Aqueous Solution Using Mixed Mineral Systems Injected with Zinc Sulfide Under Sulfidic- Anoxic Conditions 1: Reactivity and Removal Kinetics

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Abstract : This study investigates the reactivity and removal kinetics of mercury on mixed mineral systems from aqueous solution related to contaminated waters. The sorbents used were zinc sulfide, kaolinite, montmorillonite, goethite, and their mixtures. Batch mode studies at room temperature (23 ± 2 °C). Reactivity studies demonstrate high level of protonation by some of the mineral systems during the sorption process. The complex behaviors of the mixed mineral systems in mercury sorption suggest that different reactive sites inclusive thiol ($\equiv S-H$) and hydroxyl ($\equiv Me-OH$) functional groups are involved at the onset of sorption, with reactions and sorption ending with inner-sphere complexation. Increase in contact time during mercury-mineral system interaction could help increase mercury removal by some mixed mineral systems.

Keywords: Zinc sulfide, mercury, sulfidic-anoxic, proton coefficient, mass transfer rate, mixed mineral systems.

1. INTRODUCTION

Mercury poses an environmental and human threat due to its toxicity at low concentrations. It occurs in three forms namely (Hg^0), (Hg^{2+}) and (HgP) and possesses high toxicity^[1] volatility. Due to the toxicity of mercury and the cost of its safe disposal, methods and reagents to either prevent its dissolution or to selectively remove it from the leaching solution are desirable for economic and safety reasons^[2-4]. Mercury bioaccumulates in the environment and creates neurological health impact^[5]. MeHg bioaccumulates up the aquatic food chain, causing increase in mercury concentrations in predatory fish^[6]. Moreover, it appeared as a critical and chronic problem because it can easily be transformed into methyl mercury, an organic form, by bacteria in bottom level sediments which is taken up by organisms more rapidly and is much more toxic and stable than inorganic form^[7].

Mercury promotes several health problems, tyrosinemia, paralysis, serious intestinal and urinary complications, dysfunction of the central nervous system and in more severe cases of intoxication, death. Mercury and its compounds recognized as dangerous and insidious poisons and can be adsorbed through the gastrointestinal tract and also through the skin and lungs^[8] which is stored in the liver, kidneys, brain, spleen and bone leading to development of carcinogenic, mutagenic, teratogenic and also promotes several health problems, tyrosinemia, paralysis, serious intestinal and urinary complications, dysfunction of the central nervous system and in more severe cases of intoxication, death. The severity of mercury toxicity was recognized in the late 1950s and 1960s because of an environmental tragedy in Minamata Bay, Japan, where hundreds of individuals suffered from mercury poisoning (Minamata disease)^[9-10].

As a common heavy metal, mercury has been used in medical treatment and industry, but its toxic properties for human health and ecosystem have attracted increasing attention^[11-13]. Concerning heavy metals adsorption onto pyrite,^[14] demonstrated that a surface-induced hydrolysis reaction mechanism may be more realistic than a simple ion exchange^[15]. Sorption is widely used for elimination of the heavy metal ions. Metal sorption through precipitation and complexation is a common approach to reduce metal toxicity in the environment^[16]. Sorption kinetic experiments revealed that mercury sorption is a relatively rapid process, where film diffusion and intra-particle diffusion play an important role. The United States Environmental Protection Agency (USEPA) prepared a list of pollutants found in wastewater that constitute serious health hazards^[17]. These include mercury as a priority pollutant^[18-20].

For successful treatment of water containing mercury using mineral systems, a full understanding of the reactivity and the kinetic reaction partners to the reactive sites of mercury sorbents is required^[21]. The removal of mercury from aquatic systems is controlled by the speciation, mobility, ionic size of the sorbing ions, sorbate composition, sorbent solubility, sorbent particle size, sorbent surface charge, surface area of the mineral sorbent, solution dilution and $H^+ / -M$ exchange stoichiometry^[9].

The sorption of a solute present in a solid-solution system is usually assumed to consist of four consecutive steps: external mass transfer of sorbate molecules across the boundary liquid film, binding of sorbate molecules on the active sites on the surface of the sorbent, intra-particle diffusion of sorbate molecules, and sorption of sorbate molecules on the active sites distributed within the sorbent particles. Reactivity of clay particles are associated with OM, Fe or Al oxides^[24-25] and combined with elevated temperatures and acidic pH (4–5) favor geochemical conditions and nutrient stocks favorable for Hg bacterial methylation. The rapid detection and removal of Hg²⁺ from pollutants are dependent on a full understanding of the reactivity and removal kinetics of mercury in aqueous solution^[25-32].

Enhancement of mercury(II) sorption from water by bituminous coal through chemical pretreatment was explored in the laboratory using batch sorption tests and down-flow column studies^[33]. Several other methods have been established in the treatment of mercury contaminated water. Some of these techniques include bamboo charcoal, apatite IITM, iron-based sorbents, diperiodatocuprate(III) coordination solution, malt spent rootlets, bacillus cereus, modified Fe₃O₄, flocculation method, complexation by dissolved organic matter, heterogeneous photocatalysis with TiO₂, alginate and pectate^[34-43]. Others have reviewed the technologies for removing mercury in aqueous solution^[44]. Chemofiltration through zinc sulfide collected on a membrane filter obtains a low detection limit of mercury^[45].

Application of sulfides in water treatment is largely dependent on understanding of fundamental studies into metal sulphide precipitation and sorption mechanism on sulfide^[46-47]. 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^[48-52].

However, some of these new techniques are rather expensive for limited size water treatment systems situated in rural communities and the reactivity and removal kinetics require further investigation. 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 zinc sulfide under sulfidic-anoxic condition. Mixed mineral systems that could be applied for mercury removal from contaminated water are readily available locally.

1.1. Theoretical models and isotherms

To address the reactivity and removal kinetics involved in sorbent-sorbate interaction, a theory is designed to explain and predict the behavior of mineral-Hg interactions. Adsorption isotherms give a quantitative relationship between the solute concentration in the solution and the amount of solute adsorbed per unit mass of the adsorbent surface at equilibrium conditions. Langmuir, Freundlich, Dubinin–Radushkevich (D–R) are the commonly used isotherms^[53]. In this study, an empirical model derived from Freundlich isotherm model was chosen.

Detailed system characterization and an empirical model involving the distribution coefficient (Kd) as used in this paper are provided elsewhere [54] Egirani et al 2013. Kd(L/kg) was calculated from the Freundlich model shown in **Equation 1**:

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

where S is the sorbed concentration (µg/kg), Kd is the distribution coefficient, C is the equilibrium concentration (µg/l), and N = 1 is a chemical-specific coefficient derived from the slope of the plot. The empirical model to address the mineral-Hg interactions is given by **Equation 2**:

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

where Kd_{total} is the theoretical distribution coefficient for a 1:1 mixed suspension, Kd₁ is the distribution coefficient for first single mineral suspension, and Kd₂ 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 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) sorption.

The difference between the actual Kd and the theoretical (Kd_{total}) was used to clarify the effects of mineral mixing on Hg removal. Mineral mixing is said to (a) enhances Hg removal where the difference is positive; (b) attenuate Hg removal where the difference is negative; and (c) have no effect on Hg removal where no difference exist between the actual Kd and theoretical Kd as shown in **Equation 3**:

$$\Delta Kd = Kd - Kd_{total} \quad (3)$$

For the reactivity and removal kinetic studies, the empirical model for the mixed mineral systems was related to α and Kf as provided in **Equations 4 and 5**:

$$\Delta \alpha = \alpha - \alpha_{total} \quad (4)$$

$$\Delta K_f = K_f - K_{f\ total}$$

$$\text{where } \alpha, K_f, \alpha_{total} \text{ and } K_{f\ total} \quad (5)$$

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 mercury removal from contaminated water. 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^[55]. 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^[56]. This is due to the fact that surfaces of clays and hydroxides have a high concentration of OH⁻ groups readily protonated at low pH, generating positive charge which retains anions by electrostatic attraction^[57].

Spectroscopic studies have confirmed thiol (\equiv S-H) and hydroxyl (\equiv Me-OH) functional groups on surface of metal sulfides.^[58-60] 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 sulfides both in initial removal and subsequent surface reactions^[54].

The mass balance of Hg(II) sorbed per unit mass of the mixed mineral suspension (mg/g) was calculated from **Equation 6**^[61-63],

$$Q_e = \langle Ci - Ce \rangle \frac{V}{W} \quad (6)$$

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

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^[15]. Pyrite surface charge can be governed by protonation–deprotonation reactions of the surface S groups as provided in **Equation 7**:



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 in **Equations 8 and 9**^[59],



II. MATERIALS AND METHODS

2.1 Preparation of sulfidic-anoxic zinc 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^[64]. In sulfidic-anoxic environment, hydrogen sulfide occurs as a product of sulfate and sulfide reduction^[65]. In this study, 1% acidified zinc sulfide sulfidic-anoxic suspension was prepared using deoxygenated deionized water. Purified nitrogen gas was bubbled through the zinc 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^[66].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^[67].

Clay minerals 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 analysis^[54]. 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

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 [68] [Anso et al 2004., [69] Brunauer et al 1938., [70] Hlavay and Polyak 2005] as shown in **Table 1**, . (f) spectral analysis was performed using scanning electron microscopy, energy dispersive spectroscopy and x-ray diffraction to identify the mineral sorbent^[54, 71-72].

2.3. Reactivity experiments

For reactivity studies to determine the proton coefficient, standard laboratory procedure was used^[73-74]. 1% sulfidic-anoxic suspension of zinc sulfide was added to 1% single and 1:1 mixed mineral suspensions with no added electrolyte were reacted with solution containing 10ppm of arsenite regulated to the required pH at the start of experiments.

To validate the sorption mechanism involved in mercury removal, 1% sulfidic-anoxic suspension of zinc 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 Hg(II) regulated to pH 4. Supernatant was filtered through a cellulose acetate filter (pore size 0.2 µm) and analyzed for Hg(II), using a Hitachi Atomic Absorption Spectrophotometer (HG-AAS). Surface charge controls the reactivity of mineral surfaces and is dependent on the acid–base properties of surface hydroxyl groups, where H⁺ and OH⁻ are the potential-determining ions^[56]. Sorption of Hg(II) on mineral surfaces requires proton exchange, the stoichiometry of this reaction is described^[54] and the proton consumption function is provided in **Equations 7 and 8**:



$$\log K_d = \log K_p \{ \text{SOH} \}^{\alpha} + \alpha \text{pH}, \quad (8)$$

where SOH is the mineral surface-binding site, M^{2+} is the soluble metal species, $(\text{SOH})\alpha - \text{M}$ is the surface bound metal, $\log K_p$ is the apparent equilibrium binding constant, and α is the proton coefficient, representing the number of protons displaced when one mole of metal binds to the mineral surface^[40]. Proton coefficient was calculated from the slope of $\log K_d$ versus pH plot as shown in Fig. 2.

Table1: Characteristics of Clays, Goethite^[54] and Zinc sulfide

Mineral	Particle size (μm)	% (<1 μm) colloid	pH $\pm \sigma$	Surface area(SSA $\pm\sigma$) (m^2/g)
Kaolinite	20.01 \pm 0.5	3.00	6.05 \pm 0.05	47.01 \pm 0.24
Montmorillonite	80.05 \pm 0.20	0.53	2.01 \pm 0.09	10.00 \pm 0.00
Goethite	40.10 \pm 0.15	2.92	8.05 \pm 0.06	71.05 \pm 0.17
Kaolinite/montmorillonite	80.05 \pm 50	0.97	5.01 \pm 0.02	88.05 \pm 0.55
Montmorillonite/goethite	15.25 \pm 0.24	3.85	3.03 \pm 0.04	147.10 \pm 0.50
Kaolinite/goethite	140.35 \pm 55	0.73	3.05 \pm 0.01	79.30 \pm 0.59
Zinc sulfide	6.297 \pm 0.20	8.143	5.02 \pm 0.03	4.00 \pm 0.00

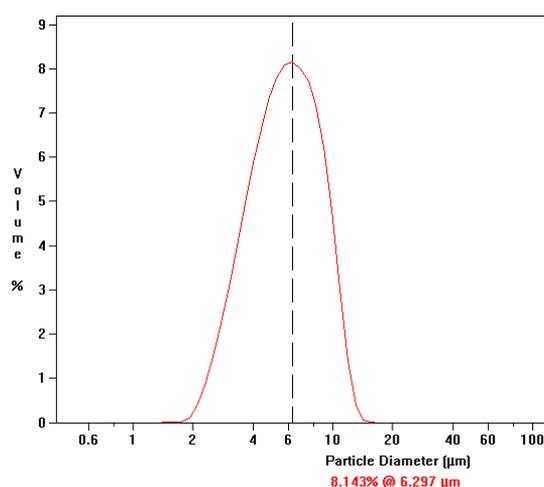


Figure 1: Particle size distribution of zinc sulfide

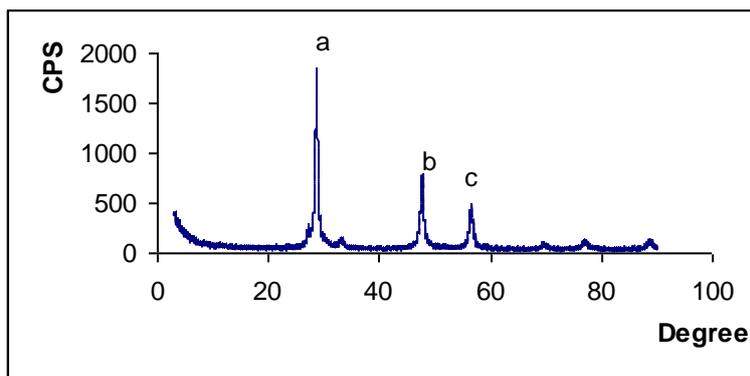


Figure 2: Untreated ZnS showing peaks at a, b, c.

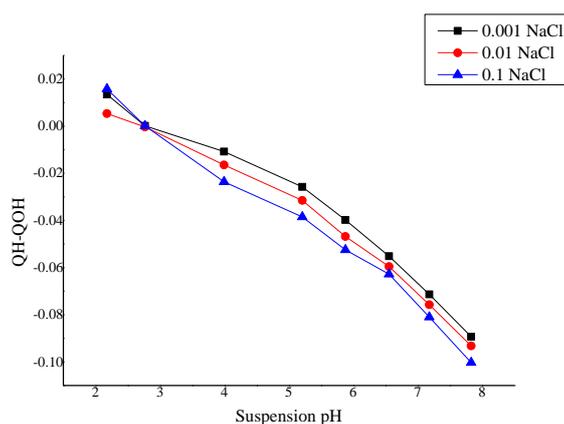


Figure 3: Potentiometric titration curves of Zinc sulfide as a function of pH at different ionic strengths. QH= concentrated acid and QOH= concentrated base [PZSE = 2.75]

2.4 Kinetic experiments

For Hg(II) removal kinetics experiments, 1% sulfidic-anoxic suspension of zinc sulfide was added to 1% single and 1:1 mixed mineral systems were reacted with solution containing 10ppm of Hg(II) regulated to pH 4. Amounts of Hg(II) 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^[75-76]. 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 from **Equation 9**.^[54]

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

where C_t and C_0 are the initial concentrations of Hg(II) at time t , S_s is the exposed external surface area of the sorbent, and K_f is the mass transfer coefficient^[42]. The Freundlich isotherm was chosen to describe sorption of Hg(II) because this is suitable for heterogeneous surfaces over a wide range of solute concentrations^[54].

III. RESULTS AND DISCUSSION

3.1. Mixed mineral systems and mercury reactivity

Although the proton coefficient (α) as shown in **Table 2**, derived from **Fig.4**, is not characteristic of a particular mineral, differences in α for mixed mineral systems compared to each other and compared to single mineral systems may be linked to differences in the availability of strongly acidic sites. In previous study^[54] in the absence of sulfidic-anoxic condition, all proton coefficient for Hg(II) sorbed on single mineral systems

except for goethite are greater than one. This indicated high level of protonation during the sorption process. In this study under sulfidic anoxic condition, all proton coefficient for Hg(II)-mineral system interaction are greater than one but kaolinite-montmorillonite and goethite-kaolinite. This may be attributed to the acidic and thiol reactive sites present on mineral planar surfaces. Significant numbers of weakly acidic edge sites in goethite and montmorillonite may reduce the proton coefficient because of the limited exchange of protons for sorbing ions. In addition, differences in protonation between sulfidic-anoxic solution and non-sulfidic –anoxic solution may be attributed to the presence of thiol ($\equiv\text{S-H}$) and hydroxyl ($\equiv\text{Me-OH}$) functional groups and reactive sites on surface of metal sulfides.

Actual proton coefficient α is higher than the theoretical proton coefficient α_{total} for all mixed mineral systems interacted with mercury under sulfidic-anoxic condition, indicating attenuated protonation for these mineral-mercury interaction. The higher the acidity of sites the more protons are exchanged for Hg(II). Therefore, mineral mixing reduced the acidity of reactive sites for these mixed mineral phases. This may be due to the competition for the sorbing ion by the mixed mineral surfaces^[54]. The H⁺/-M exchange stoichiometry of <2 is shown in **Table 2** for Hg(II) sorption on both the single and mixed mineral phases agreed with previous findings^[32]. This suggested that surface charges changes progressively as Hg(II) interacts with mineral systems. In addition, mineral surfaces with few displaceable H⁺ with limited pH-dependent sorption supported lower H⁺/-M stoichiometry.

Table 2: Proton Coefficients (α) and Regression Coefficient (R) of Mercury Sorbed on Sulfidic-Anoxic Mineral Systems

Mineral suspensions	R	α	α_{total}	
Zinc sulfide	0.99	1.26475	⊗	
Kaolinite	0.99	1.05326	⊗	
Goethite	0.99	1.06774	⊗	
Montmorillonite	0.99	1.08328	⊗	
Kaolinite/montmorillonite	0.99	0.95136	1.0605	-0.10914
Goethite/kaolinite	0.99	0.96748	1.0605	-0.09302
Goethite/montmorillonite	0.99	1.02719	1.07551	-0.04832

Note: ⊗ not applicable

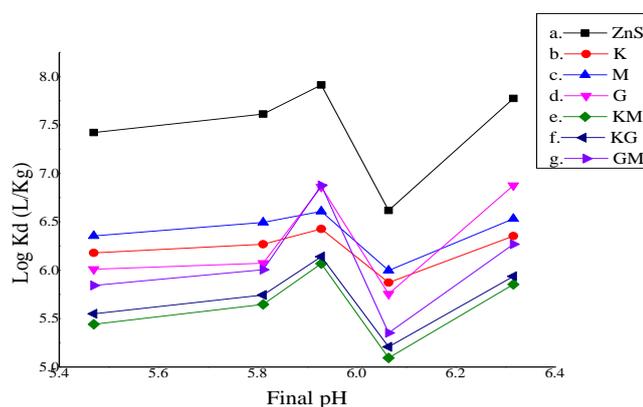


Figure 4: Plots of logKd versus final pH for Hg(II) sorbed on: (a) Zinc sulfide, (b) kaolinite, (c) montmorillonite., (d) goethite., (e) kaolinite/montmorillonite, (f) kaolinite/goethite., (g) goethite/montmorillonite, sulfidic-anoxic mineral systems.

3.2. Mixed mineral systems and mercury removal kinetics

In previous study in the absence of zinc sulfide^[54], sorption kinetics indicated a two- phase reaction probably attributed to outer sphere and inner sphere complexation with minimal intra-particle diffusion. Also, mass transfer rate for the first-phase reaction (K_{f1}) decreased in the order goethite<kaolinite<montmorillonite for all single mineral systems. In this study under sulfidic-anoxic condition, sorption kinetics indicates a two phase reaction steps as shown in **Table 3 and Fig 5**. Mass transfer rates for the first reaction phase K_{f1} are in

the order montmorillonite > zinc sulfide > kaolinite > goethite for the single mineral system and the order: kaolinite-montmorillonite > kaolinite-goethite > montmorillonite-goethite. Theoretical K_{pI} is lower for kaolinite-montmorillonite and kaolinite-goethite but higher for montmorillonite-goethite, indicating increase in mass transfer rate for mixed minerals containing kaolinite and attenuation of mass transfer rate for montmorillonite-goethite-mercury interaction.

Mass transfer rate for the second phase reaction K_{pII} is in the order: zinc sulfide > montmorillonite > goethite > kaolinite for the single mineral systems interacted with mercury and the order: kaolinite-montmorillonite > kaolinite-goethite > montmorillonite-goethite for the mixed mineral systems. Theoretical K_{pII} is lower for kaolinite-montmorillonite and higher for the rest of the mixed mineral systems indicating that mineral mixing attenuated the mass transfer rates for the latter. Differences in mass transfer rates for Hg(II) ions transferred to the mineral reactive sites may be attributed (a) to different types of hydroxyl and thiol reactive sites in solution (b) differences in BET surface area for the mineral systems and (c) differences in particle size distribution of these mineral systems are shown in **Table 1**.

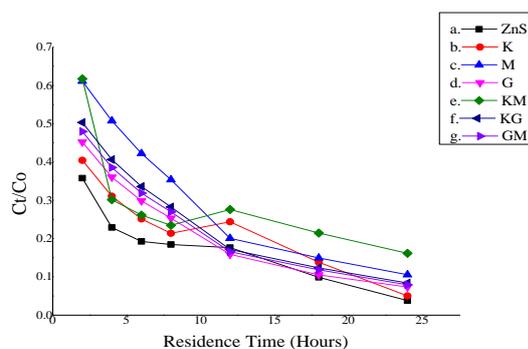


Figure 5: Plots of C_t/C_o vs. residence time for mercury sorbed on (a) Zinc sulfide, (b) kaolinite, (c) montmorillonite, (d) goethite., (e) kaolinite/montmorillonite, (f) kaolinite/goethite, (g) goethite/montmorillonite sulfidic-anoxic mineral systems.

Table 3: Mass Transfer Rates for Mercury Zinc Sulfide Treated Sulfidic-Anoxic Mineral Systems.

Parameters/ Mineral	Zinc sulfide	Kaolinite	Montmorill onite	Goethite	Kaolinite/ Montmorill onite	Kaolinite/ Goethite	Montmorill onite/ Goethite
slopeI(hr ⁻¹)	- 0.07283	-0.08711	- 0.13674	-0.09936	-0.11418	-0.1111	-0.10574
slopeII(hr ⁻¹)	- 0.01121	-0.0142	- 0.01841	-0.04981	-0.01774	-0.015	-0.01198
Exposed Surface Area (cm ⁻¹)	400	4700	1000	7100	8800	7900	14700
K_{pI} (cmhr ⁻¹)	1.821e- 4	1.853e-5	1.367e-4	1.399e-5	1.2975e-5	1.406e-5	7.193e-6
Theoretical K_{pI} (cmhr ⁻¹)	⊗		⊗	⊗	1.272e-5	1.180e-5	8.0306e-6
K_{pII} (cmhr ⁻¹)	2.803e- 5	3.0213e- 6	1.841e-5	7.015e-6	2.016e-6	1.899e-6	8.150e-7
Theoretical K_{pII} (cmhr ⁻¹)	⊗	⊗	⊗	⊗	1.853e-6	4.0506e-6	2.320e-6

Note: ⊗ Not applicable

3.3 Mixed mineral systems and Hg(II) removal

In previous study in the absence of sulfidic-anoxic zinc sulfide mineral system^[54], mercury uptake decreased as BET surface area increased for all single and mixed mineral systems within the range of pH studied. Furthermore, the mercury uptake does not appear to be linearly correlated with BET surface area, implying that mercury sorption onto single and mixed mineral systems was not strictly a surface phenomenon^[54].

In this study under sulfidic-anoxic condition, mercury removal increases overtime up to 12h contact time for all mineral systems but kaolinite-montmorillonite. After the reaction kink at 12 hour contact, mercury removal increased over the rest of the reaction time investigated is shown in **Fig 6**. Differences between actual and theoretical % sorption progresses from negative to positive territory for kaolinite-montmorillonite interacted with mercury in solution as shown in **Fig 7**. Mercury removal progressed from the positive to negative territory for goethite-montmorillonite-interacted with mercury. Kaolinite-goethite interacted with mercury was in the negative territory over the range of contact time investigated. Cross-over time exists for kaolinite-montmorillonite and goethite-montmorillonite interacted with mercury. At the cross-over point, mineral systems affected possess similar sorption %, indicating similar sorption characteristics as shown in **Fig 6**. This complex behavior of mercury-mineral interaction under sulfidic-anoxic condition may be attributed to the presence of thiol reactive sites in solution. It could be suggested that increase in contact time during mercury-mineral system interaction could help increase mercury removal by some mixed mineral systems as shown in **Fig 6**.

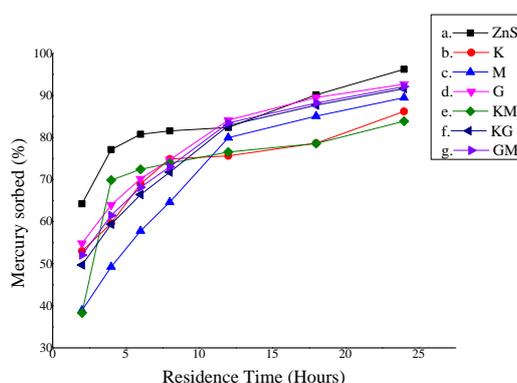


Figure 6: Plots of mercury sorbed vs. residence time for : (a) zinc sulfide, (b) kaolinite, (c) montmorillonite, (d) goethite, (e) kaolinite/montmorillonite, (f) kaolinite/goethite, (g) montmorillonite/goethite., zinc sulfide sulfidic-anoxic mineral systems.

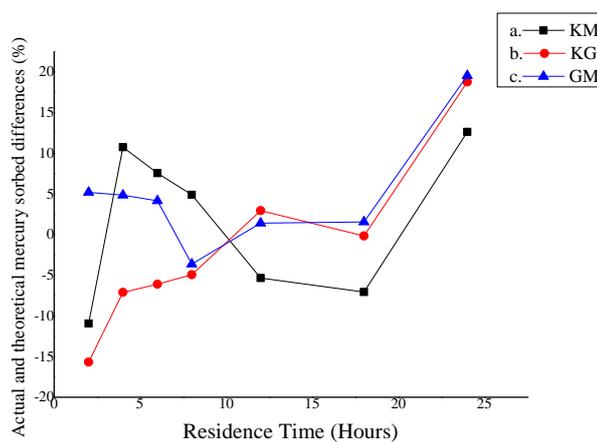


Figure 7: Plots of actual and theoretical Hg(II) sorbed difference(%) vs. residence time for (a) kaolinite/montmorillonite, (b) kaolinite/goethite, (c) montmorillonite/goethite zinc sulfide sulfidic-anoxic mineral systems.

IV. CONCLUSIONS

The reactivity and removal kinetics of Hg(II) treated with zinc sulfide, single and mixed mineral systems of kaolinite, montmorillonite and goethite under sulfidic-anoxic condition have been investigated. Using empirical models derived from Freundlich isotherm model. In this study under sulfidic anoxic condition,

all proton coefficient for Hg(II)-mineral system interaction are greater than one except kaolinite-montmorillonite and goethite-kaolinite. This indicated high level of protonation during the sorption process. This may be attributed to the acidic and thiol reactive sites present on mineral planar surfaces

Mass transfer rates for the first reaction phase K_1 are in the order montmorillonite > zinc sulfide > kaolinite > goethite for the single mineral system and the order: kaolinite-montmorillonite > kaolinite-goethite > montmorillonite-goethite. Mass transfer rate for the second phase reaction K_2 is in the order: zinc sulfide > montmorillonite > goethite > kaolinite for the single mineral systems interacted with mercury and the order: kaolinite-montmorillonite > kaolinite-goethite > montmorillonite-goethite for the mixed mineral systems. This suggested that different reactive sites were involved in the removal kinetics of the sorbing ions as sorption progressed. Differences in sorption kinetics between the single and mixed mineral phases may be attributed to differences in the BET surface area of single and mixed mineral systems.

Mercury removal increases overtime up to 12h contact time for all mineral systems but kaolinite-montmorillonite. After the reaction kink at 12 hour contact, mercury removal increased over the rest of the reaction time investigated. Differences between actual and theoretical % sorption progresses from negative to positive territory for kaolinite-montmorillonite interacted with mercury in solution. Mercury removal progressed from the positive to negative territory for goethite-montmorillonite-interacted with mercury. This complex behavior of mercury-mineral interaction under sulfidic-anoxic condition may be attributed to the presence of thiol reactive sites in solution. It could be suggested that increase in contact time during mercury-mineral system interaction could help increase mercury removal by some mixed mineral systems.

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