

Mercury Removal from Aqueous Solution Using Mixed Mineral Systems Injected with Zinc Sulfide in Sulfidic- Anoxic Conditions II. The role of solution composition and Ageing

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Abstract : This study investigates Hg(II) removal onto binary mixed mineral sorbents from simulated mercury contaminated water, in zinc sulfide related sulfidic-anoxic condition. The sorbents used were zinc sulfide, kaolinite, montmorillonite, goethite, and their mixtures. Batch mode studies at room temperature demonstrate a linear increase in mercury sorption with increase in pH up to pH 4, gradually flattening for the rest of pH investigated. Increase in Cp-particle concentration does not reveal a corresponding increase in sorption of mercury. Except for zinc sulfide, kaolinite and montmorillonite, increase in residence time could not lead to a corresponding increase in mercury removal. The complex behavior of mineral-mercury interaction under sulfidic-anoxic condition may be attributed to increased hydroxylation of the mineral surface and the presence of thiol ($\equiv S-H$) and hydroxyl ($\equiv Me-OH$) functional groups and reactive sites on surface of metal sulfides.

Keywords: mercury, mixed mineral systems, particle concentration, residence time, sulfidic-anoxic, zinc sulfide.

I. INTRODUCTION

Mercury is well known as a toxic element in its most common forms, that is, elemental mercury, inorganic mercury, and methyl mercury^[1]. 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 fish^[2]. 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 (Hg⁰), oxidized mercury (Hg²⁺) and particulate-bound mercury (HgP) exist. Due to the great harm it does to the environment and human health, mercury pollution is considered as the top of the list of environmental pollutants by the World Health Organization^[5]. The oxidized form of mercury is transformed into its toxic methylated species, transferred and bioamplified as monomethyl mercury (MMHg) in the aquatic food chains^[6-15],

The major sources of Hg emission worldwide come from coal combustion and Au amalgamation^[16-18]. 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 activity^[19]. The release of mercury into bodies of water is increasing, and non-admissible level of greater than 1µg/L is found in surface and groundwater^[20]. Mercury is carcinogenic and its poisoning results in severe chronic disease or death^[21]. In addition, elemental mercury exhibits high volatility and bioaccumulation in the environment and neurological health impact^[22-23]. 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^[24-25]. 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 dissolved mercury species can be hampered by the absence of reliable sorbents and solution chemistry. For Hg⁰ removal in liquid phase, the key point is to convert Hg⁰ to Hg²⁺ rapidly, the latter being easily dissolved in water as reported in literature^[26-30].

Solution pH controls (a) the solubilities 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 deprotonation of active sites^[31-32]. Application of sulfides in water treatment is largely dependent on understanding of fundamental studies into metal supplied precipitation and sorption mechanism on sulfide.^[3-34]. 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^[35-36]. There are some advantages to be supplied, 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^[37-43].

As in companion paper I, spectroscopic studies have confirmed thiol ($\equiv\text{S-H}$) and hydroxyl ($\equiv\text{Me-OH}$) functional groups on surface of metal sulfides.^[44-46] These amphoteric reactive units are thought to undergo independent protonation and deprotonation reactions to produce reactive sites for sorption^[47-48]. 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^[49].

Sorbate sorption may decrease as particle concentration increases (outer sphere complexation) or not be significantly affected as particle concentration increases (inner sphere complexation)^[50]. Mercury uptake is associated with surface area availability and number of surface-active groups. Also, 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^[51-54]. Prolonging the residence time of solid mineral phase in the absence of a sorbate could results in much mineral surface reorganization. This is due to the fact that high and new reactive sites are formed. Mercury sorption by porous sorbents is known to exhibit variable behavior over time^[55-57]

1.1. Theoretical models and isotherms

To addresses the suitability of mixed mineral suspensions of clay and (hydr)oxides for Hg(II) 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 residence time or ageing^[58].

Detailed system characterization and an empirical model involving the distribution coefficient (Kd) as used in previous paper [49] Egirani et al 2013, % sorption used in calculating Hg(II) sorbed is provided in **Equation 1**^[59-62],

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

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**,

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

where S is the sorbed concentration ($\mu\text{g/kg}$), Kd is the distribution coefficient, C is the equilibrium concentration ($\mu\text{g/g}$), and N = 1 is a chemical-specific coefficient derived from the slope of the plot. The empirical model as provided [49] Egirani et al 2013, to address the mineral-Hg interactions is given in **Equation 3 and 4**:

$$\text{Hg(II) sorbed difference} = \text{Hg(II) sorbed} - \text{Hg(II) sorbed}_{\text{total}} \quad (3)$$

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

where Hg sorbed_{total} is the theoretical sorption for a 1:1 mixed mineral suspension, S₁ is the Hg(II) sorbed on first single mineral suspension, and S₂ 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:

- 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. there exist differential masses 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 differences exist between Hg(II) sorbed and theoretical Hg(II) sorption.

Currently available technologies for the treatment of mercury-polluted aqueous solutions include precipitation, membrane filtration, ion exchange, electrodeposition, adsorption and coagulation [63-64]. Other researches focused on the removal of Hg(II) from water by sorption processes are provided [65-67]. However, the use of mixed mineral systems of clays and hydroxides as suitable sorbents in mercury removal is lacking in literature. 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 zinc sulfide in sulfidic-anoxic condition. This is based on different solution composition such as pH, solid concentration and residence time (ageing).

1.2 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. In sulfidic-anoxic environment, hydrogen sulfide occurs as a product of sulfate and sulfide reduction [68]. 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.

1.3 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. Clays and iron sulfide used in this study provided by the Richard Baker Harrison Company and Acros Organics Ltd and goethite provided by Iconofile Company Inc. were nitrogen flushed and stored in airtight containers in the anaerobic chamber before use to avoid oxidation. Arsenic(III) stock solution was purchased from Merck. The AAS standard solution of 1000 mg/l Arsenic(III) was prepared by transferring the contents of a Titrisol ampule with As₂O₃ in H₂O (Merck, Germany) into a volumetric flask, which was filled up to the mark and stored at 20±2°C according to the instructions by Merck. The working solutions of different concentrations were prepared by diluting the stock solution immediately before starting the batch studies.

For sorbent characterization as provided in paper I, 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 [69-70], (f) spectral analysis was performed using scanning electron microscopy, energy dispersive spectroscopy and x-ray diffraction to identify the mineral sorbent [49, 71-72]

II. EXPERIMENTAL METHODS

2.1. Sorption experiments

Batch mode experiments in this study were conducted using 1% single mineral suspensions of kaolinite, montmorillonite and goethite and 1:1 mixed mineral systems of kaolinite/montmorillonite, kaolinite/goethite and montmorillonite/goethite. The mixed mineral systems were used to elucidate the differences in sorption behaviour 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 paper 1 [49, 59].

For batch mode pH investigation, 1% sulfidic-anoxic suspension of zinc sulfide was added to 1% single and 1:1 mixed mineral suspensions 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 mineral 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 zinc sulfide was 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 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. 1% sulfidic-anoxic suspension of zinc sulfide was added to 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^[51]. 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).

III. RESULTS AND DISCUSSION

3.1. Mineral systems and pH effects on Hg(II) removal

In previous study, in the absence of zinc sulfide sulfidic-anoxic condition^[49], Hg(II) demonstrated a linear sorption increase with increasing pH for single mineral system of kaolinite, montmorillonite and mixed mineral systems of kaolinite-montmorillonite and Goethite-Kaolinite. In the present study under sulfidic-anoxic condition, all mineral systems demonstrated a linear increase with increasing pH up to pH 4, gradually flattening for the rest of pH investigated. Cross-over pH exists between zinc sulfide and montmorillonite and between goethite and goethite-montmorillonite. At this cross-over points sorption capacity for these mineral systems are the same as shown in Fig.1. Differences between the actual and predicted sorption capacity are all in the negative territory for all mixed mineral systems, indicating that mineral mixing attenuated sorption for these mineral systems as shown in Fig 2. This variability in sorption may be attributed to increased deprotonation of reactive sites as pH was increased. However, sorption pattern appeared to be controlled by outer sphere complexation, inner sphere complexation and intra-particle diffusion for Hg(II) sorbed on these mineral systems.

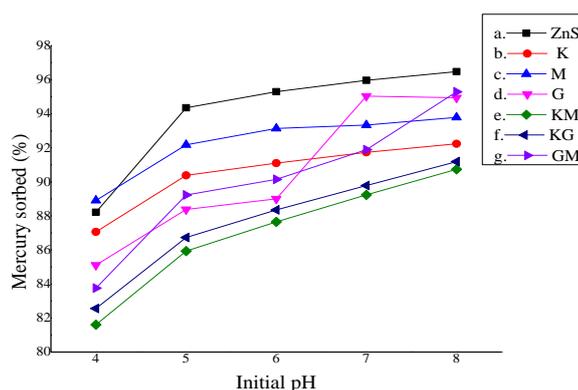


Figure 1: Plots of mercury sorbed versus pH for (Zinc sulfide., (b) kaolinite., (c) montmorillonite., (d) goethite., (e) kaolinite/montmorillonite., (f) kaolinite/goethite., (g) goethite/montmorillonite., sulfidic-anoxic mineral systems.

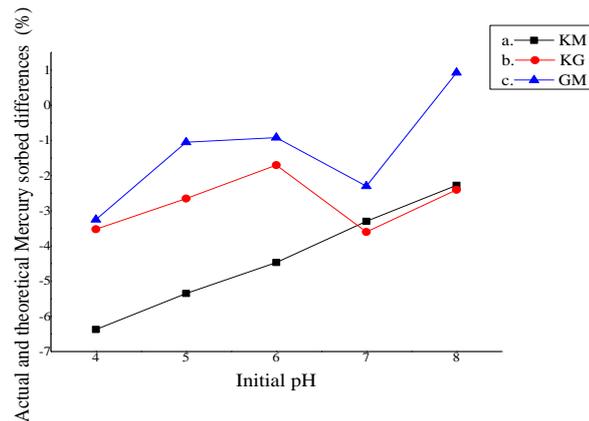


Figure 2: Plots of actual and theoretical mercury sorbed differences versus pH for (a) kaolinite/montmorillonite., (b) kaolinite/goethite., (c) goethite/montmorillonite., zinc sulfide sulfidic-anoxic mineral systems.

3.2. Mineral systems and Cp effects on Hg(II) removal

Previous study in the absence of zinc sulfide^[49] revealed a linear decrease of Hg(II) sorbed on kaolinite/goethite, kaolinite-montmorillonite goethite-montmorillonite and montmorillonite as Cp increased over the range of Cp investigated. In the presence of zinc sulfide under sulfidic-anoxic condition, all mineral systems demonstrate a near flat sorption as Cp increases indicating that increase in Cp has no significant effect on the sorption of Hg(II) removal. This phenomenon is neither non-promotive nor promotive Cp effect. Zinc sulfide demonstrate a sinusoidal behavior, decreasing up to 0.004g/L in Hg(II) sorption, then increasing up to 0.008g/L as shown in Fig.3. The behavior of zinc sulfide 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. Mineral surface coatings of only a few atomic layers thickness are sufficient to influence sorption rates and behaviour^[73].

In previous study^[49], Hg(II) sorbed difference (i.e., Hg(II) sorption obtained by experiments) and theoretical Hg(II) sorption (i.e., the predicted mercury sorption obtained from the average summation of Hg(II) sorbed on the single mineral suspensions used in the mixing experiments) exhibited positive sorption differences for kaolinite/goethite over the Cp range investigated. This meant that mineral mixing decreased (Hg(II) sorption for kaolinite/goethite. In the present study under sulfidic condition differences between actual and theoretical sorption of mercury as Cp increases was complex. Kaolinite-goethite is on the positive territory with decreasing sorption as Cp increases as shown in Fig 4. Kaolinite-montmorillonite and goethite-montmorillonite are on the negative territory as Cp increase. This means that in the former, mineral mixing enhance sorption, attenuating sorption in the latter^[74],

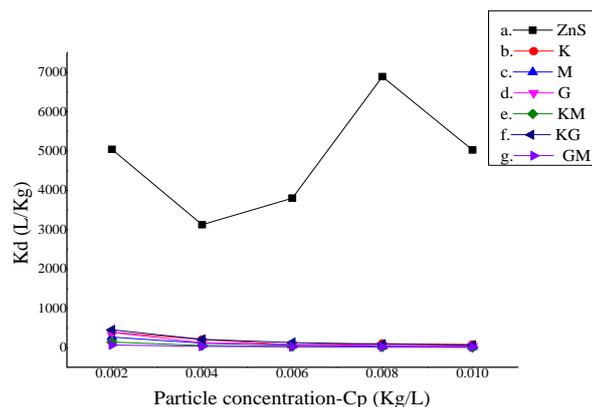


Figure 3: Plots of Hg(II) sorbed versus particle concentration-Cp for (a) ZnS sulfide, (b) kaolinite, (c) montmorillonite, (d) goethite, (e) kaolinite/montmorillonite, (e) (f) kaolinite/goethite, (g) goethite/montmorillonite, sulfidic-anoxic mineral systems.

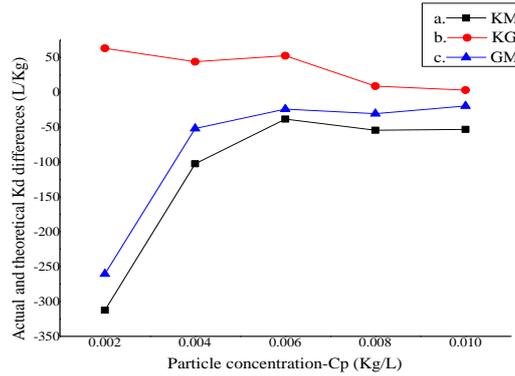


Fig. 4: Plots of actual and theoretical Kd differences versus particle concentration for Hg(II) sorbed on (a) kaolinite/montmorillonite, (b) kaolinite/goethite, (c) goethite/montmorillonite, zinc sulfide sulfidic-anoxic mineral systems

3.3. Mineral systems and ageing effects on Hg (II) removal

In previous study in the absence of zinc sulfide [49] [Egirani et al 2913], all single and mixed mineral systems exhibited a near linear decrease in Hg(II) sorption over the range of residence time investigated. This was in the order goethite>goethite-kaolinite>montmorillonite>goethite-montmorillonite>kaolite-montmorillonite>kaolinite-Goethite/montmorillonite. In this study under sulfidic-anoxic condition, zinc sulfide, kaolinite and montmorillonite exhibit increase in Kd over the range of residence time investigated. Mercury removal by zinc sulfide exhibits a linear relationship. All other mineral systems exhibit a near flat sorption characteristic indicating that increase in residence time could not significantly change sorption characteristic as shown in Fig 5.

In previous investigation without zinc sulfide [49] differences in actual and theoretical sorption exhibited a linear increase all in the negative territory for kaolinite-montmorillonite and goethite-montmorillonite. This may suggest a decrease in Hg(II) removal due to mineral mixing for these two mixed mineral systems. In this study under sulfidic-anoxic condition, differences between actual and predicted Kd started at zero point (i.e. no difference at the start of ageing), becoming positive for goethite-montmorillonite and decreasing into the negative territory for the rest of the mixed mineral systems. This suggests that Hg(II) sorption for the former is enhanced by mineral mixing and is attenuated in the latter case. It also implies that mercury sorption by these mineral systems is not strictly a surface phenomenon [50]. Hg(II) step-wise sorption probably indicated reaction phases attributed to outer sphere, inner sphere complexation and intra-particle diffusion as reported elsewhere [49].

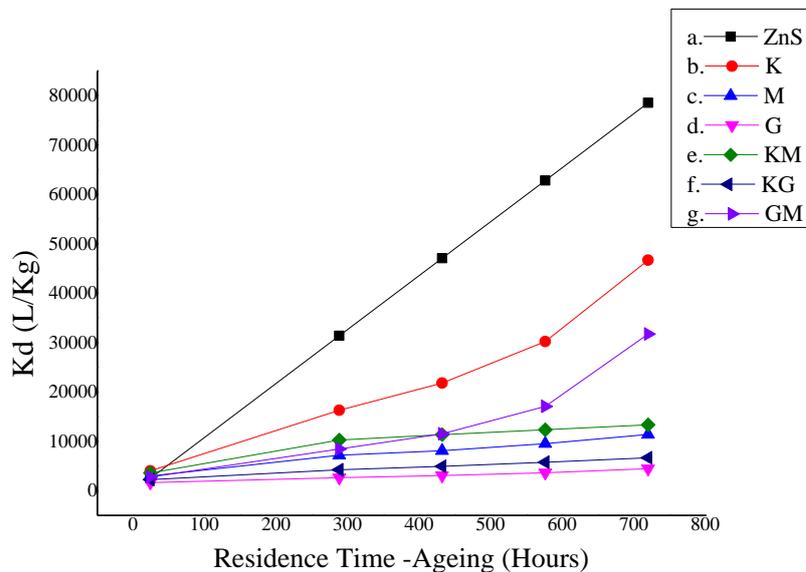


Fig. 5: Plots of Kd versus ageing for (a) Zinc sulfide, (b) kaolinite, (c) montmorillonite, (d) goethite, (e) kaolinite/montmorillonite, (f) kaolinite/goethite, (g) goethite/montmorillonite, sulfidic-anoxic mineral systems

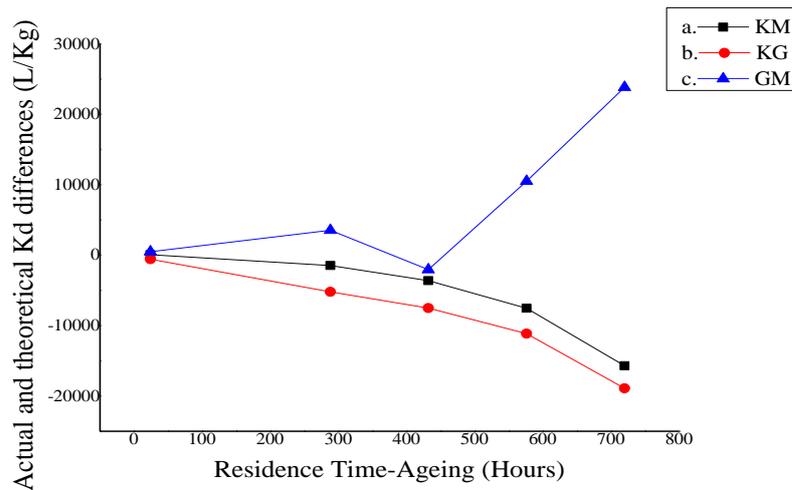


Figure 6: Plot of actual and theoretical K_d differences vs. ageing for Hg(II) sorbed on (a) kaolinite/montmorillonite, (b) kaolinite/goethite, (c) goethite/montmorillonite, zinc sulfide sulfidic-anoxic mineral systems

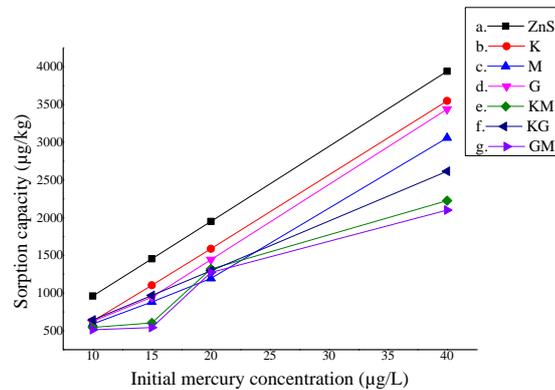


Figure 3: Plots of sorption capacity versus initial ion concentration for (a) Zinc sulfide., (b) kaolinite., (c) montmorillonite., (d) goethite., (e) kaolinite/montmorillonite., (f) kaolinite/goethite., (g) goethite/montmorillonite., sulfidic-anoxic mineral systems.

3.4. Mineral systems and Initial mercury concentration effects on Hg (II) removal

In previous study using activated carbon^[75], mercury removal increased with increase in initial metal concentration at the onset of investigation, flattening out as initial metal concentration was increased. In this study under sulfidic-anoxic condition, mercury removal increased with increase in initial metal concentration over the range of concentration investigated. This may be attributed to the low range of initial metal concentration used in this study and the presence of thiol ($\equiv\text{S-H}$) and hydroxyl ($\equiv\text{Me-OH}$) functional groups and reactive sites on surface of metal sulfides.

IV. CONCLUSIONS

All mineral systems demonstrated a linear increase with increasing pH up to pH 4, gradually flattening for the rest of pH investigated. Cross-over pH exists between zinc sulfide and montmorillonite and between goethite and goethite-montmorillonite. At these cross-over points sorption capacity for these mineral systems are the same (Fig.1) Differences between the actual and predicted sorption capacity are all in the negative territory for all mixed mineral systems, indicating that mineral mixing attenuated sorption for these mineral systems. This variability in sorption may be attributed to increased deprotonation 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.

All mineral systems demonstrate a near flat sorption as Cp increases indicating that increase in Cp has no significant effect on the sorption of mercury. This phenomenon is neither non-promotive nor promotive Cp effect. Differences between actual and theoretical sorption of mercury as Cp increases was complex. Kaolinite-goethite is on the positive territory with decreasing sorption as Cp increases. The behavior of zinc sulfide 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. Mineral surface coatings of only a few atomic layers thickness are sufficient to influence sorption rates and behavior.

Zinc sulfide, kaolinite and montmorillonite exhibit increase in Kd over the range of residence time investigated. Mercury removal by zinc sulfide exhibits a linear relationship. All other mineral systems exhibit a near flat sorption characteristic indicating that increase in residence time could not significantly change sorption characteristic. Differences between actual and predicted Kd started at zero point (i.e. no difference at the start of ageing), becoming positive for goethite-montmorillonite and decreasing into the negative territory for the rest of the mixed mineral systems. This suggests that Hg(II) sorption for the former is enhanced by mineral mixing and is attenuated in the latter case. It also implies that mercury sorption by these mineral systems is not strictly a surface phenomenon. The variable and complex behavior of mineral systems over the range of residence time investigated may be attributed to increased hydroxylation of the mineral surface resulting in the formation of new reactive sites.

Mercury removal increased with increase in initial metal concentration over the range of concentration investigated. This 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.

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