

Mercury Removal from Aqueous Solution by Mixed Mineral Systems 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, relevant to surface and groundwater impacted environment. 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. 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 The 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.*

Keywords: *mercury, removal, reaction, kinetics, mixed mineral systems.*

I. Introduction

Mercury is one of the most toxic elements in the aqueous environment [1] The health of top predators, e.g. birds, fish, seals, and man, is thereby threatened [2-3] Three forms of non-biodegradable mercury contaminant namely elemental mercury (Hg₀), oxidized mercury (Hg²⁺) and particulate-bound mercury (HgP) exist. The oxidized form of mercury is transformed into its toxic methylated species, transferred and bioamplified as monomethyl mercury (MMHg) in the aquatic food chains [4-13]

The major sources of Hg emission worldwide comes from coal combustion and Au amalgamation [14-16]. 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 [17].

The release of mercury into bodies of water is increasing, and non-admissible level of greater than 1µg/L are found in surface and groundwater [18]. Mercury is carcinogenic and its poisoning results in severe chronic disease or death [19]. In addition, elemental mercury exhibits high volatility and bioaccumulation in the environment and neurological health impact [20, 21]. Specifically, methyl mercury induced by microbial biomethylation of mercuric ions (Hg²⁺) can accumulate in the body and can cause brain damage and other chronic diseases [22-24]. 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 [25-27]. The removal of mercury from contaminated water bodies is controlled by the solution composition and ageing [28, 29].

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 [30, 31].

Sorbate sorption may decrease as particle concentration increases (outer sphere complexation) or not be significantly affected as particle concentration increases (inner sphere complexation) [32]. 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 [33-35].

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. Mercury sorption by porous sorbents is known to exhibit variable behavior over time [36-38].

1.1. Theoretical models and isotherms

To address 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 [39].

Detailed system characterization and an empirical model involving the distribution coefficient (Kd) as used in previous paper [40-41]. % sorption used in calculating Hg(II) sorbed is provided [42-45]

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

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,

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

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 as provided [40] to address the mineral-Hg interactions is given:

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

$$\text{Hg(II) sorbed}_{\text{total}} = \frac{(S_1 + S_2 + S_n)}{n} \quad 3$$

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:

1. Secondary mineral phase developed during sorbate-sorbent interaction .
2. Components of minerals in the mixed mineral suspension acted as chemisorbed species and not as individual networks.
3. 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.

Currently available technologies for the treatment of mercury-polluted aqueous solutions include precipitation, membrane filtration, ion exchange, electrodeposition, adsorption and coagulation [46-47]. Other researches focused on the removal of Hg(II) from water by sorption processes are provided [48- 50] . 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. This is based on different solution composition such as pH, solid concentration and residence time (ageing).

II. Experimental methods

2.1. 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 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 [41-42].

For batch mode pH investigation, 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 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, 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 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 ($HgCl_2$) 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 $HgCl_2$ (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 $0.2 \mu m$) and analyzed for $Hg(II)$ using a Hitachi Atomic Absorption Spectrophotometer (HG-AAS).

III. Results and discussion

3.1. Mixed mineral suspensions and pH effects on $Hg(II)$ removal

$Hg(II)$ demonstrated a linear sorption increase with increasing pH for single mineral suspensions of kaolinite, montmorillonite, mixed mineral suspensions of kaolinite-montmorillonite and Goethite-Kaolinite (Fig.1 and Fig 2). The behavior of kaolinite and mixed mineral systems containing kaolinite demonstrated a linear behaviour in $Hg(II)$ removal. Goethite and goethite/montmorillonite demonstrated a stepwise decrease in $Hg(II)$ sorption as pH was increased. $Hg(II)$ sorption by goethite -montmorillonite decreased between pH 4 and pH 5, changing slope and dipping up to pH 7 before increasing over the remaining range of pH. 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 goethite and mixed mineral system of goethite-montmorillonite with respect to pH.

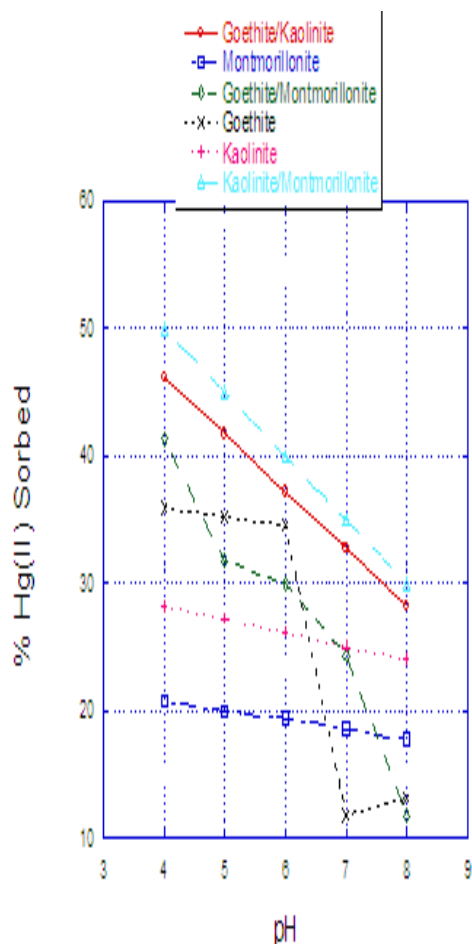


Figure 1: Plots of % $Hg(II)$ sorbed versus pH sorption difference vs, pH for $Hg(II)$ sorbed single and mixed mineral systems

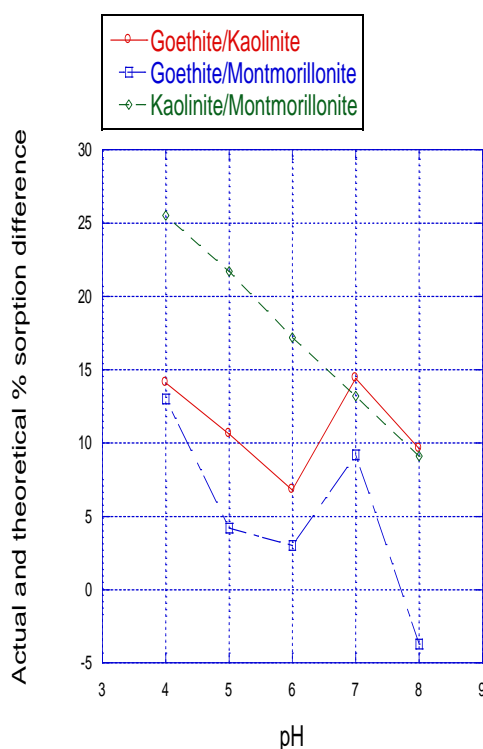


Figure 2: Plots of actual and theoretical % for single and mixed mineral systems for on mixed mineral systems

3.2. Mixed mineral suspensions and Cp effects on Hg(II) removal

Changes in Hg(II) sorption as particle concentration (Cp) increased, exhibiting a linear decrease of Hg(II) sorbed on kaolinite/goethite, kaolinite-montmorillonite goethite-montmorillonite and montmorillonite over the range of pH 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/L (Fig.3 and Fig 4). The behavior of montmorillonite containing aluminium and mixed mineral phases containing Al-montmorillonite may form separate (discrete) particles or it may form coatings on other mineral surfaces. Coatings of only a few atomic layers thickness are sufficient to influence sorption rates and behaviour [52]. This may account for differences in sorption behavior for Hg(II) sorbed on mixed mineral suspensions containing montmorillonite.

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 [Matis et al 1999]. Increase in Cp results in low pressure at the interface and a subsequent decrease in sorbing ion diffusion to reactive sites [32, 34]. 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.

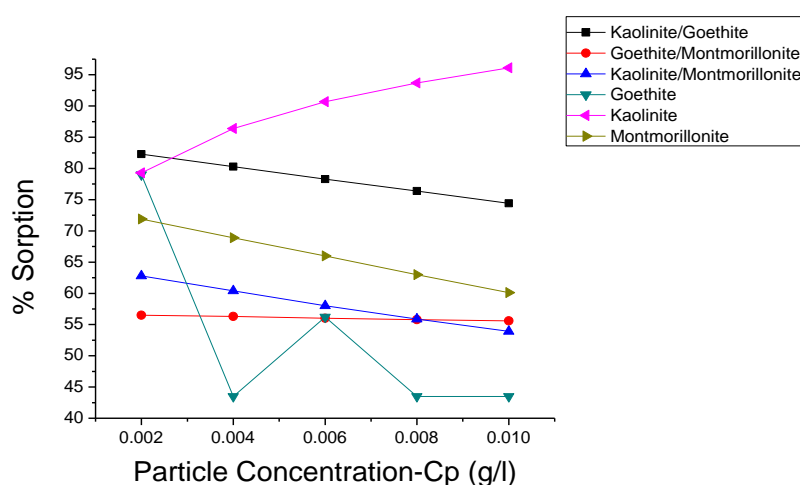


Figure 3: Plots of Hg(II) sorbed versus particle concentration for single and mixed mineral systems

Hg(II) sorbed difference (i.e., Hg(II) sorption obtained by experiments) and theoretical Hg(II) sorption (i.e., the predicted arsenite 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 means that mineral mixing decreased (Hg(II) sorption for kaolinite/goethite. On the other hand, sorption differences started on a negative territory and exhibited a step-wise increase for goethite/montmorillonite, becoming positive as Cp increased to 0.01 g/L (Fig.3). This means that mineral mixing based on the empirical model, reduced Hg(II) sorption at the onset and increased Hg(II) removal as the Cp was increased for goethite/montmorillonite. However, differences in actual and theoretical sorption for Hg(II) sorbed on kaolinite/montmorillonite exhibited a decrease as Cp was increased. This decrease was on the negative territory indicating that mineral mixing reduced Hg(II) uptake for this mixed mineral phase [53].

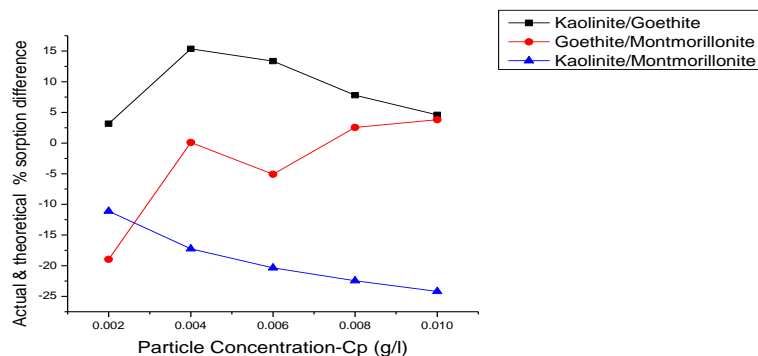


Fig. 4: Plots of actual and theoretical sorption differences versus particle concentration for Hg(II) sorbed on mixed mineral systems

3.3. Mixed mineral suspensions and ageing effects on Hg (II) removal

All single and mixed mineral systems exhibited a near linear decrease in Hg(II) sorption over the range of residence time investigated (Figure 5 and Fig 6). The order of Hg(II) sorption on the mineral phases is in the order goethite> goethite-kaolinite>montmorillonite>goethite-montmorillonite>kaolinite-montmorillonite>kaolinite. Goethite/montmorillonite exhibited a cross-over sorption with kaolinite/montmorillonite at 432 hours contact time. This means that Hg(II) uptake for these two mixed mineral phases are the same at this residence time.

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. The sinusoidal and non-linear pattern of sorption for goethite-kaolinite beginning in the positive territory and ending in the negative territory suggest that Hg(II) sorption for this mixed mineral phase implies that mercury sorption onto goethite-kaolinite is not strictly a surface phenomenon [32]. Hg(II) step-wise sorption probably indicated reaction phases attributed to outer sphere, inner sphere complexation and intra-particle diffusion as reported elsewhere [40-41]. Increase in Hg(II) sorption as residence time increased between 432 and 476 hours of contact for goethite-kaolinite may be attributed to increased hydroxylation of the mineral surfaces, resulting in the formation of new reactive sites [54]

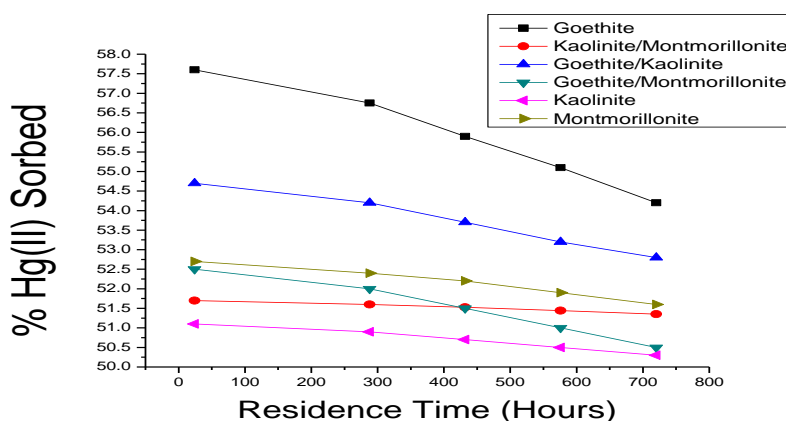


Fig. 5: Plots of % Hg (II) sorbed versus residence time for single and mixed mineral systems

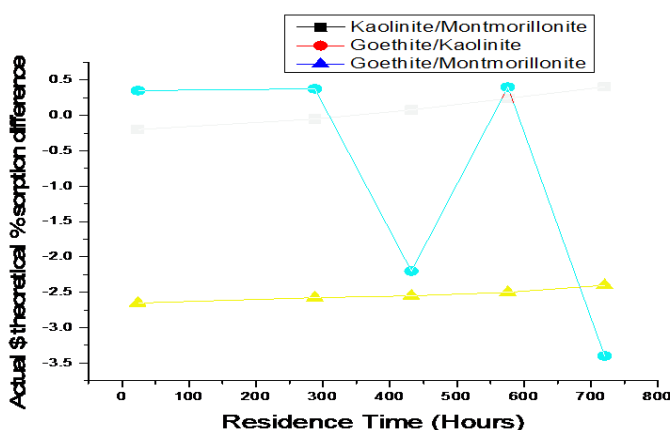


Figure 6: Plot of actual and theoretical % sorption difference vs. residence time for Hg(II) sorbed on mixed mineral systems

IV. Conclusions

The possibilities of using mixed mineral phases of kaolinite, montmorillonite, and goethite 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 exist over the range of pH investigated. The behavior of kaolinite and mixed mineral systems containing kaolinite demonstrated a linear behaviour in Hg(II) removal.

Goethite and goethite/montmorillonite demonstrated a stepwise decrease in Hg(II) sorption as pH increases. 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.

Changes in Hg(II) sorption as particle concentration (C_p) increased, exhibiting a linear decrease of Hg(II) sorbed on kaolinite/goethite, kaolinite-montmorillonite goethite-montmorillonite and montmorillonite over the range of pH investigated. However, differences in actual and theoretical sorption for Hg(II) sorbed on kaolinite/montmorillonite exhibited a decrease as C_p was increased. This decrease was on the negative territory indicating that mineral mixing reduced Hg(II) uptake for this mixed mineral phase.

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. 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.

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