EFFECT OF CLAY AND GOETHITE MINERAL SYSTEMS ON LEAD REMOVAL FROM AQUEOUS SOLUTION- PAPER II

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ABSTRACT

Mineral systems have been investigated to determine their effect on lead removal. This study was in relation to pH, ionic strength, and particle concentration and residence time. These are related to simulated contaminated waters inclusive effluent discharge. Sorption isotherms indicated that sorption capacities of the different clay minerals, goethite and their mixtures were dependent on the particle size. Mixed mineral systems of kaolinite/montmorillonite and kaolinite/goethite exhibited different sorption behavior from the single mineral components, reducing lead removal over the range of pH investigated. Increased ionic strength and solid concentration, showed a complex response leading to lower lead sorption. Enhanced lead sorption on some of the mixed mineral systems as ageing increased may be linked to increased hydroxylation of the mineral surface resulting in the formation of new reactive sites.

Keywords: Particle size, Lead, Mineral systems, Adsorption, pH; ionic strength.

INTRODUCTION

There is need to remove heavy metal ions from sewages, before their release to the environment [Bystrzejewski and Pyrzyn 2011]. Heavy metals present in these effluents, when discharged untreated, pollute water bodies and pose threat to ecosystem [García-Lorenzo et al 2010]. Heavy metals are non-biodegradable and tend to accumulate in living organisms, causing various life threatening disorders [Bystrzejewski and Pyrzyn 2011]. Metals can be distinguished from other toxic pollutants, since they are non-biodegradable and can accumulate in living tissues, thus becoming concentrated throughout the food chain [Maleki et al., 2011]. Lead is one of the major pollutant in the effluents discharged from industries working in the field of electroplating, electrical & electronic, hydrometallurgical processing, ore beneficiation, tanneries, [Randhawa et al., 2012, Terminghoff et al., 1994], The need to reduce metal concentrations discharged into water bodies remains a priority in both developed and most developing countries. The removal of dissolved metal species can be hampered by the absence of reliable sorbents and solution chemistry adequate to understanding metal sorption [Terminghoff et al., 1994]. Sorption to natural solids especially clay minerals is an underlying process affecting the transport, degradation, and biological activity of organic compounds in the environment [Joseph and Baoshan, 1996].The aim of this study is to explore the effect of mineral systems of kaolinite-montmorillonite, kaolinite-goethite and montmorillonite-goethite on sorption behavior of lead in relation to pH, ionic strength, solid concentration and residence time.

LITERATURE REVIEW

The removal of lead ions from wastewater is controlled by several variables [Kołodyńska, 2011]]. These include: pH, ionic strength, and solid concentration, besides the residence time (ageing) of the solid phase in the wastewater [Kitano et al., 1980, Helios-Rybick and Wójcik 2012, Schlegel et al., 2001]. However, the particle size of mineral systems could change the sorption characteristics involved in the study [André et al., 2009, Brdar et al., 2014, Al-Degs et al., 2003]. Solubilities of metal hydroxides; hydrolysis behavior of metals; and surface charge of the sorbent are pH dependent [Appel and Ma 2002]. Ionic strength effects on heavy metal adsorption depend on the predominant sorption mechanism [Kołodyńska, 2011], Ghayaza et al., 201, Egirani et al., 2013a]. The adsorption isotherm declines as particle concentration increases is an anomalous adsorption phenomenon [Egirani et al., 2005b]. Increase in evidence time could enhances new reactive sites formation [Gubbuk, 2011].

METHODOLOGY

Characterization

Table1: Characteristics of Mineral Systems

Mineral systems	Particle size range (µm)			% (<1 µm) Colloid	pH ± σ	Surface area(SSA±σ) (m2/g)
K	15-30	30-45	45-60	3.00	6.05±0.05	47.01± 0.24
M	15-30	30-45	45-60	0.53	.01±0.09	10.00± 0.00
G	25-50	50-75	75-100	2.92	8.05±0.06	71.05± 0.17
K M	15-30	30-45	45-60	0.97	5.01±0.02	88.05± 0.55
MG	1-4	4-8	8-12	3.85	3.03± 0.04	147.10± 0.50
KG	25-50	50-75	75-100	0.73	3.05± 0.01	79.30± 0.59

In this section of the report, K, M, G, KM, MG and KG represents kaolinite, montmorillonite, goethite, kaolinite-montmorillonite, montmorilloniye-goethite and kaolinite-goethite. Characterization of sorbents used in this study included (a) particle size; (b) pH; and (c) specific surface area (SSA) (Table 1). In all batch mode experiments two components of the batch mode reactions (lead and the electrolyte solutions) were added at the same time to the mineral suspension (t = 0) and equilibrated for 24 h at the desired pH. Particle size was determined using LS 13 320 coulter laser diffraction particle size analyzer. In this study, 1% mineral suspension was prepared using drops of sodium hexa-metaphosphate (calgon solution) and deionized water. The content was placed on ultrasonic bath and stirred for 5 minutes. The content was removed from ultrasonic bath, a magnetic base inserted and content stirred for another 5 minutes. Sample was pipetted into the analyzer and run at 8%.

Batch Mode Experiments

This study was conducted using 1:1 single mineral systems of kaolinite, montmorillonite and goethite. Also, 1:1 mixed mineral systems of kaolinite/montmorillonite, kaolinite/goethite and montmorillonite/goethite were used to elucidate the difference in sorption between the single and mixed mineral phases. For batch mode pH investigation, single and 1:1 mixed mineral systems made up to 50 ml containing 1% (by mass) mineral suspension and 5 mg/L initial metal concentration of lead as single sorbates at zero electrolyte background were adjusted to the required pH (ranging from pH 4 to 8) using 0.1 M HNO_3 and 0.1 M NaOH. The treated systems were equilibrated for 24 h and pH measured using a Model 3340 Jenway ion meter. For batch mode ionic strength investigation, single and 1:1 mixed mineral systems made up to 50 ml containing 1% (by mass) mineral suspension of the required mineral(s) and 10, 15, 20, and 40 mg/l of lead as single sorbates at pH 4 were adjusted to the required ionic strength, ranging from 0.0M (i.e., no electrolyte solution was added to the mineral system) to 0.1 M $NaNO_3$. Based on preliminary experiments, difference in molar concentration between lead over the range of metal concentration (mg/L) was not statistically (χ2) significant ($P \leq 0.01$). The treated mineral systems were equilibrated for 24 h. For batch mode solid or particle concentration investigation, single and 1:1 mixed mineral systems were made up to 50 ml containing solid concentrations (kg/L) of 0.002 to 0.01 and 10, 15, 20, and 40 mg/l of lead metals. The treated systems adjusted to pH 4 and 0.01 M ionic strength was equilibrated for 24 h. Batch mode aging investigations were carried out from 24 to 720 h using single and 1:1 aged mixed mineral systems containing 1% (by mass). These mineral systems made up to 50 ml contained 10, 15, 20, and 40 mg/l initial concentrations of lead sorbates. The treated systems, adjusted to pH 8 with no added electrolyte, were equilibrated for 24 h. In all experimental studies samples were stored in the dark at room temperature (23±3 ◦C) for a maximum of 24 h before analysis.

Twenty-four hours was sufficient to establish equilibrium between the solid and liquid phases because metal ion sorption reactions occur in milliseconds or minutes [Morton, et al., 2001]. Kinetic experiments conducted at shorter equilibration times (i.e., beginning at 18 h) showed the same sorption behavior as at 24 h. Three replicates were used for each treatment, and metal concentration sorbed (S) in mgkg−1 was calculated from difference between the initial metal concentration C0 (metal concentration before sorption) and the equilibrium concentration C (the metal concentration in solution after sorption equilibrium),

$$S = \frac{(C_0 - C) \times V_{\text{total}}}{W_{\text{solid}}}, \qquad (1)$$

Where Vtotal is the suspension volume and W is the mass of mineral solid. The effect of polycarbonate tubes on the sorption of metal ions is so small that it can be neglected [Javaid et al., 2011]. The amount of metal remaining in solution was determined using Hitachi Atomic Absorption Spectrophotometer (HG-AAS). Detailed system characterization and an empirical model involving the solid-phase to solution-phase distribution coefficients (*K*d) as used in this paper are provided in I. Due to the low range of metal concentration used in this study, adsorption isotherms were of the C type, resulting in linear isotherms. Therefore, Kd was calculated from the Freundlich model equation,

$$S = \mathrm{Kd}C^{N}, \qquad (2)$$

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.

RESULTS

Distribution Coefficient (Kd) Increased With Increase In Ph As Provided (Figure 1)

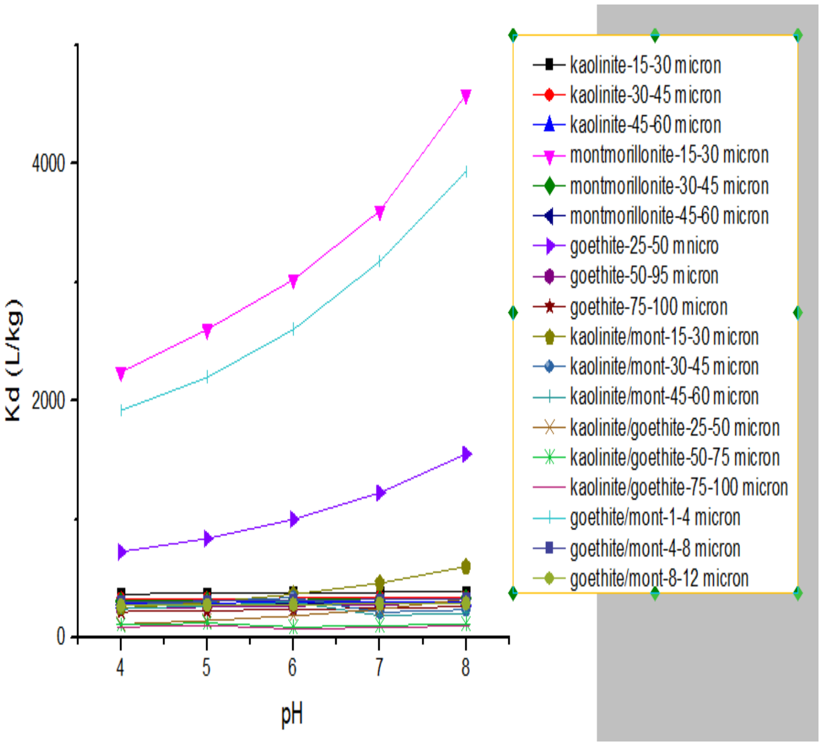

Fig. 1: plot of coefficient of distribution Kd versus initial pH

Sorption capacity of the mineral systems decreased with increase in solid concentration as provided (Figure 2). This was between 0.003kg/L to 0.008kg/L. There was promotive Cp effect over the rest of the solid concentration for some of the mineral systems.

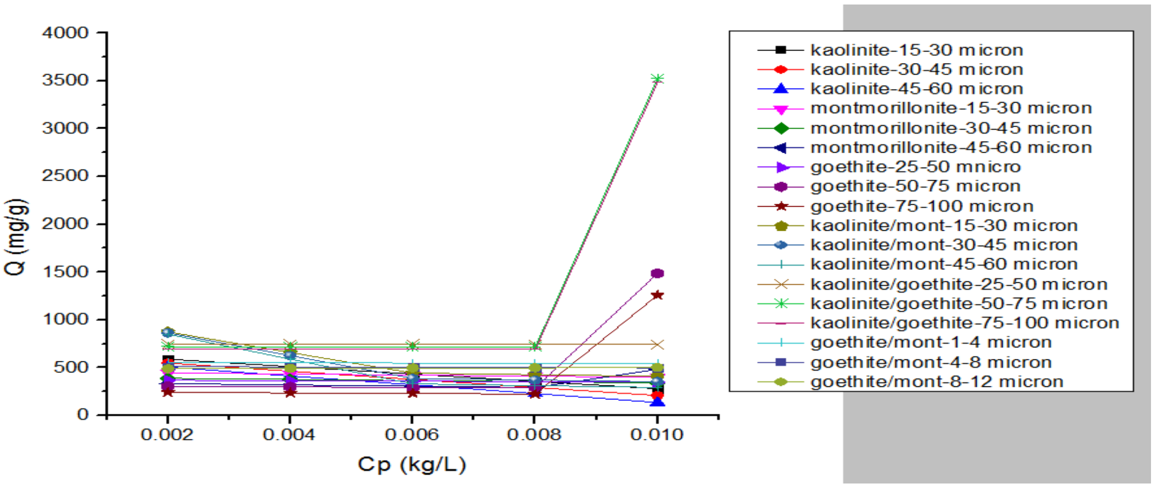

Fig. 2: Plot of Sorption Capacity-Q versus Solid Concentration-Cp

Sorption capacity of the mineral systems over the range of ionic strength investigated was complex. These included non- promotive ionic strength (i.e sorption capacity decrease with increase in ionic strength) at some ionic strength concentration. There was promotive ionic strength for some of the mineral systems. This means that there was increase in sorption as ionic strength was increased (Figure 3).

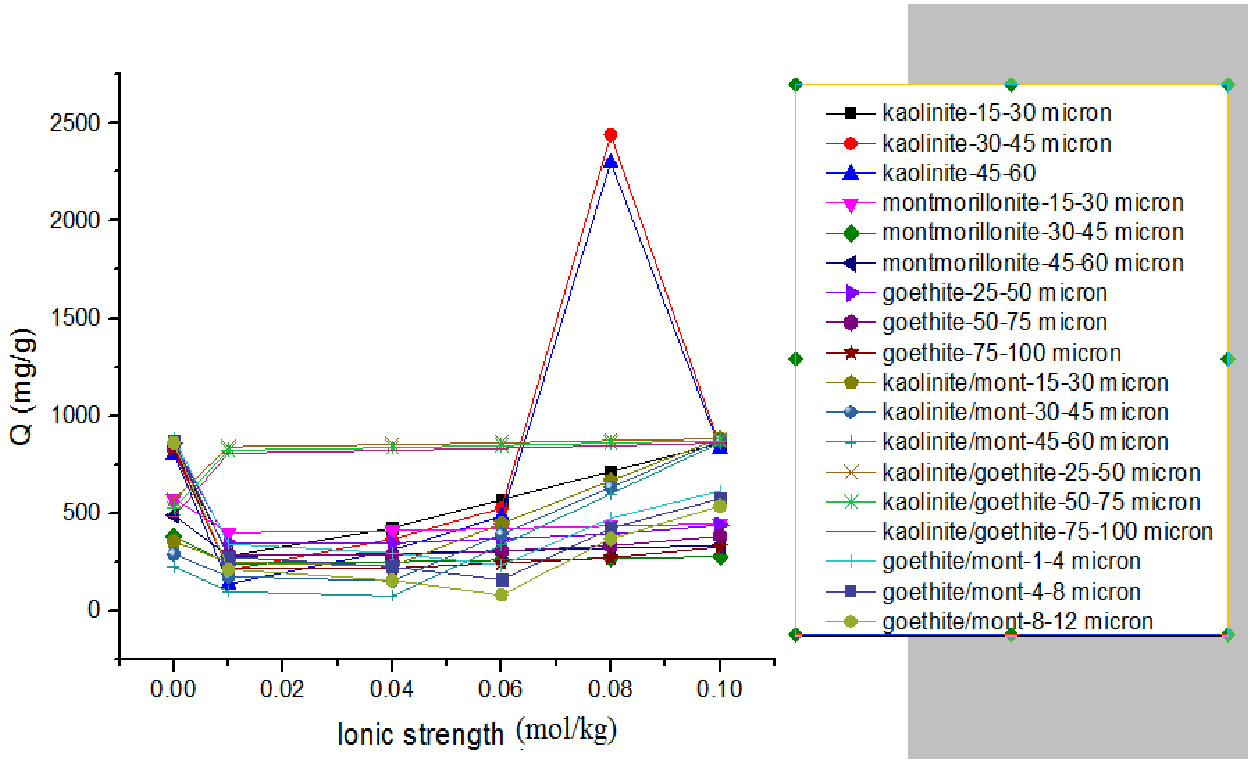

Fig. 3: Plot of Sorption Capacity Q versus Ionic Strength of Mineral Systems

Ageing of mineral systems did not significantly affect lead removal (Figure 4). This was different in the case of kaolinite-goethite and goethite over the range of particle size investigated.

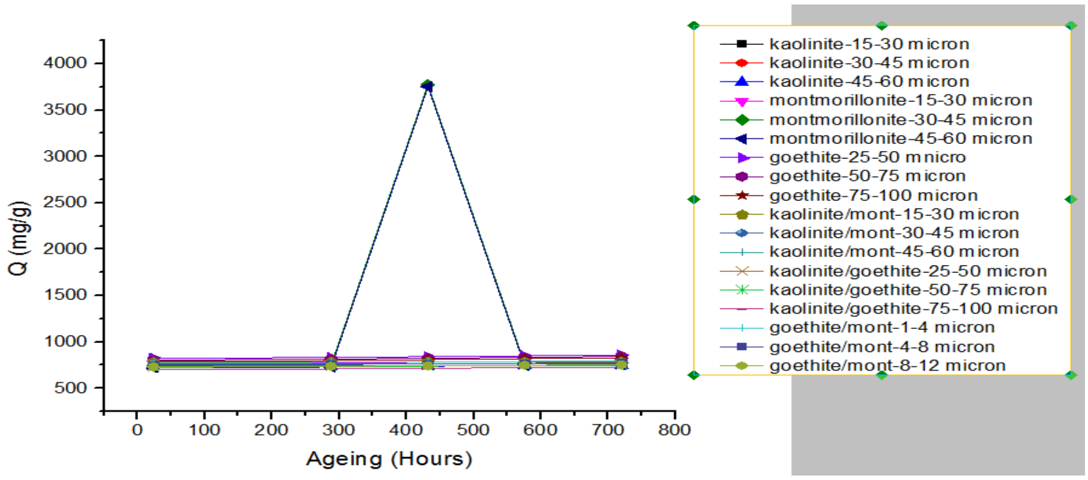

Fig. 4: Plot of Sorption Capacity-Q versus Residence Time –Ageing For Mineral Systems

All mineral systems demonstrated decrease in lead removal as particle size was increased (Figure 5a and 5b).

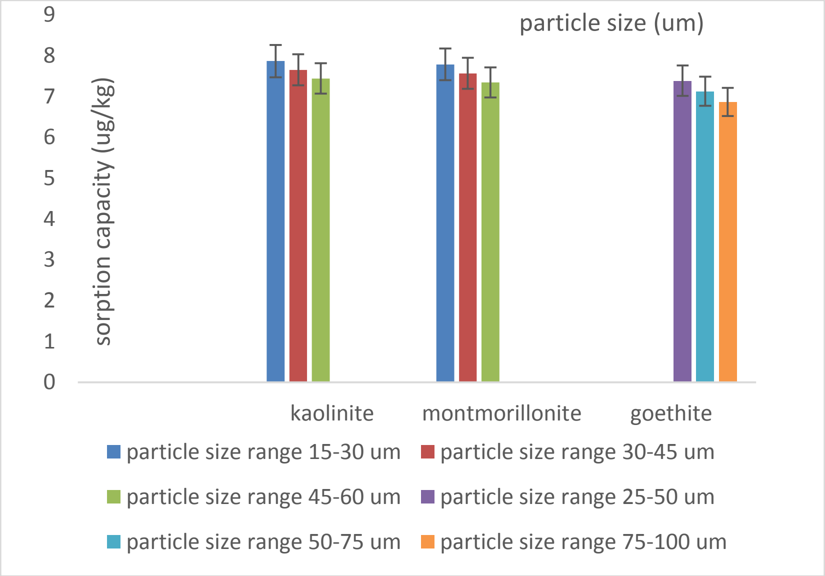

Figure 5a: Plot of Sorption Capacity versus Particle Size for Single Mineral Systems

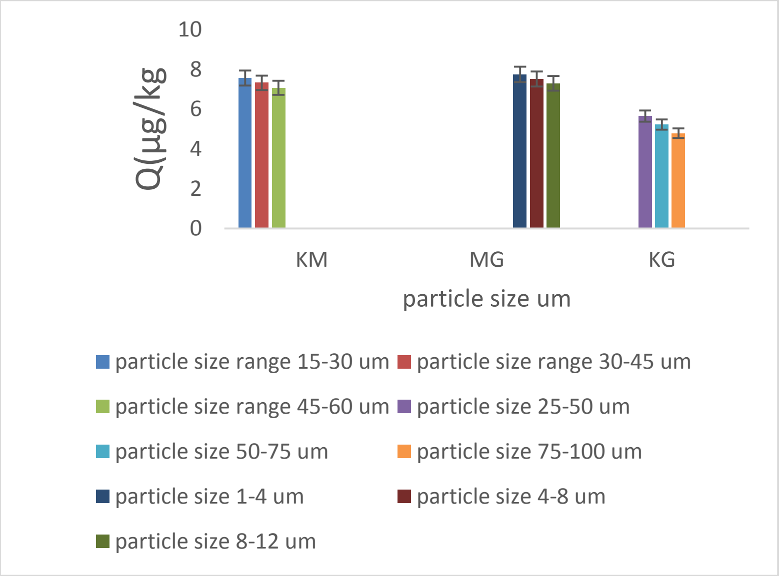

Figure 5b: Plot of Sorption Capacity versus Particle Size for Mixed Mineral Systems

DISCUSSION

Mineral Systems and ph Effect Derived from Freundlich Isotherm

Lead sorption increased with increasing pH and decreased with increasing particle size of the mineral systems (Fig. 1). Goethite and kaolinite/goethite behaved differently in the sorption of lead, displaying a cross-over Kd (i.e. Kd at which mineral systems of different particle sizes exhibit similar sorption pattern at a particular pH) (Fig. 1). However, Increase in Pb sorption as pH increases may be linked to deprotonation of reactive sites Kitano et al., 1980. Mixed mineral systems of kaolinite/montmorillonite and kaolinite/goethite exhibited different sorption behavior from the single mineral components, reducing Pb removal because particle size of the mixed mineral systems was increased relative to the single mineral systems, thus altering the specific surface area (Figs. 1).

Mineral mixing results in greater aggregation of flocs impeding Pb diffusion and can account for the low efficiency of the mixed systems to sorb metals by ion exchange [Tombacz et al., 1999]. In addition, reactive sites of the mineral surfaces are masked by mineral mixing thus impeding sorption. These findings do not completely agree with the view of [Pauwels, et al., 1999] that mineral mixing does not significantly affect heavy metal sorption on the birnessite/montmorillonite mixed suspension. Although montmorillonite/goethite and kaolinite/montmorillonite exhibited similar sorption behavior. The magnitude of Pb sorption was greater for montmorillonite/goethite relative to kaolinite/montmorillonite. This reflects the high colloidal fraction and specific surface area of montmorillonite/goethite relative to kaolinite/montmorillonite. A possible mechanistic explanation for the behavior of Pb sorption mechanism may be due to the higher efficiency of –Al–OH+ 2 type sites to sequester Pb, while the reversal of sorption on the montmorillonite/ goethite and kaolinite/montmorillonite mineral systems may be due to the higher efficiency of reactive sites created by isomorphic substitution to sequester Pb.

Mineral Systems and Ionic Strength

Pb sorption on single and mixed mineral systems (a) decreased after electrolyte was added as the ionic strength increased from 0.01 to 0.02 mol/kg, increasing steadily up to 0.08 mol/kg and dipping over the rest of ionic strength (Fig. 2). Several Crossover Kd (Fig. 2) exist and suggests a progressive change in the mode of particle association to favor Pb sorption as the ionic strength was increased. Also, this indicates that Pb sorption on the mixed mineral systems was not different from the single mineral systems. The decrease in Pb sorption with increase in ionic strength is linked to outer sphere complexation. Kaolinite/montmorillonite and kaolinite/goethite exhibited similar behaviors for Pb sorption and is linked to specific adsorption of Pb on the mixed mineral systems. Pb sorption on kaolinite/goethite increased as the ionic strength increased, suggesting a progressive expansion of reactive sites and formation of doubly charged species.Differences in Pb sorption on electrolyzed kaolinite/goethite mixed mineral systems and crossover of Kd for the montmorillonite suspension are linked to differences in the modes of particle association such as (a) edge-to-edge (EE); (b) edge-to-face (EF); and (c) face-to-face (FF) . As the electrolyte concentration increases in the kaolinite/ goethite suspension, it is likely that the particle association changes from EE to EF mode, thus blocking and reducing the amount of faces available for Pb sorption. [Rao and Khan, 2009]. This presumably accounts for the observed variability in Pb sorption on the mixed systems.

Mineral Systems and Particle Concentration Effect

Pb sorption decreased with increase in solid concentration for mineral systems, except for kaolinite-goethite and goethite over the range of particle size investigated. Kaolinite-goethite and goethite exhibited higher sorption capacity than the rest of the mineral systems (Fig. 3). There was no significant ($\chi 2$) sorption differences between the single and mixed mineral systems at $P \leq 0.01$ level of significance (Fig. 3). Therefore, promotive and non-promotive Cp effect exist over the range of particle size and solid concentration investigated. Increase in particle size and aggregation of the mineral systems may be responsible for the decrease in metal sorption as Cp increases. The Cp effect is also related to effective surface area, pressure, and force at the mineral/water interface. Increase in Cp results in low pressure at the interface and a subsequent decrease in sorbing ion diffusion to reactive sites. Enhancement of Pb sorption as Cp increased may be linked to increased number of reactive sites over-riding aggregation of mineral particles. Suppression of Pb sorption (Fig. 3) may be linked to reduction in the availability of reactive sites for Pb sorption due to mineral mixing. Goethite in mixed systems 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. This may account for differences in Pb sorption on mixed mineral systems containing goethite.

Mineral Systems and Ageing

Pb removal from simulated wastewater by the aged mineral systems increased minimally with increasing ageing or residence time over the range of particle size investigated (Fig.4). Goethite within the particle range of 75-100 micron exhibited a different behavior plateauing over the first 288 hours of contact with lead, increasing in sorption over the next 576 hours and dipping over the remaining residence time investigated. These may be linked to increased hydroxylation of the mineral surfaces, resulting in the formation of new reactive sites [Joseph and Baoshan 1996]. Previous investigation using Cu and Zn revealed similarity in Kd indicating similar sorption characterization of these two metals at some point in the sorption process. Similarity in Kds were absent in this investigation indicating non-similarity in the sorption characterization of Pb. Also differences in the behavior of Pb sorption over the range of mineral particle size in the aged mineral suspension may be linked to differences in the hydrolysis behavior of the sorbing ion.

Particle Size Effect on Lead Removal

Decrease in sorption capacity as particle size was increased was in the order kaolinite>montmorillonite>goethite (Figure 5a) for the single mineral systems. This was in the order kaolinite-montmorillonite>montmorillonite-goethite>kaolinite-goethite (Figure 5b) for the mixed mineral systems Differences in lead removal as exhibited by these mineral systems could be linked to differences in BET surface area. However, for the mixed mineral systems, lead removal behavior may be linked to the particle size characteristics and surface area of the mineral systems (Table 1).

CONCLUSIONS

Pb was investigated to determine particle size effect on its sorption. This study was in relation to solution composition and ageing of Pb by mixed mineral systems related to simulated contaminated waters. Sorption isotherms indicated that sorption capacities of the different clay minerals, goethite and their mixtures were dependent on the particle size. Lead sorption increased with increasing pH and decreased with increasing particle size of the mineral systems Furthermore, lead sorption increased with increasing pH and decreased with increasing particle size of the mineral systems. Also, lead sorption increased with increasing pH and decreased with increasing particle size of the mineral systems. Its sorption decreased with increase in solid concentration for mineral systems, except for kaolinite-goethite and goethite over the range of particle size investigated. Promotive and non-promotive Cp effect exist over the range of particle size and solid concentration investigated. Mineral system of goethite at particle size range of 75-100 micron exhibited sorption behavior different from the rest of the mineral systems .Different characteristics of sorption exhibited by these systems may be influenced by the masking of the reactive sites of the mineral systems, thus impeding Pb diffusion at some point and the creation of new reactive sites resulting in increased sorption behavior of these mineral systems.

Suppression of Pb sorption as Cp increases may be linked to increased particle size and aggregation of the mineral systems. Increase in Pb sorption by the aged mineral systems as ageing was increased may be linked to increased hydroxylation of the mineral surface resulting in the formation of new reactive sites. Decrease in lead removal as particle size was increased may be linked to decrease in surface area of the mineral systems.

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