

Heavy Metal Sorption Behaviour of Suspended Materials Kaolinite and Iron Oxide (Goethite)

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Abstract : The retention studies of Cu, Pb and Zn on (kaolinite and iron oxide) mixed samples in the laboratory to understanding metal adsorption between solid phase and solution show most of the adsorbent materials were recovered and most of the metal was accounted for. The K_d value of the mixture of kaolinite and iron oxide (goethite) was low. This may be due to iron oxide coating the kaolinite, and an increase the adsorption sites on the kaolinite surface. That may be because of changes to the negative charges on the surface of kaolinite occurring when iron oxides accumulate on the surface.

I. INTRODUCTION

The suspended sediment system in the water is contains of clay and other silicate minerals as well as organic microorganisms, diatoms and plant (Hart et al, 1982). Clay sediment plays a very important role in suspended sediment concentration of watercourses and lakes (Walling and Morehead, 1989). In addition, the nature of the soil controls the composition and physical and geochemical properties of the suspended sediment in the river. The availability of metals in the fluvial system is controlled by a mixture of factors such as natural efficiency, soil, flora, water cycle (Jain and Sharma 2001; Zhang and Huang 1993; Aurada et al.,1983; Warren et al.,1981). The metals load in river system environments is held and distributed by suspended particulate matter (Covelli et al., 2007). Several earlier studies suggest that in the river system suspended particles can play an important role in carrying metals (Giesy and Briese 1977; Reuter and Perdue 1977; Hoffmann et al.,1981; Salbu et al., 1985; Tanizaki et al.,1992; Dai and Martin 1995; Ross and Sherrell 1999, Hill et al 2001).

There are two ways of transported heavy metal in fluvial system by the suspended particulate matter in the dissolved form, and adsorbed to the surface coating (Gallo et al 2006). In addition, oxides coating and hydrous Fe and Mn oxides are play important as carrier particles for metal. Moreover, clays, alumino silicates and organic matter influences heavy metal partitioning onto suspended particle (Horowitz, et al 1991). In the water system is an important process to study the metals transport is the exchange of metal ions between water and sediment (Singh, et al 2005).

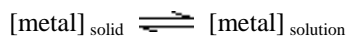
Metals absorption rate and the availability of dissolved metals are controlled by suspended materials. The chemical and physical property of the clay materials such as a high ion exchange capacity that may be made metal is linked easily to clay materials (Boenigk et al., 2005). The change in total surface area of the sediment in suspension is control the correlation between the concentrations of trace metal and sediment and its ability to adsorb sediment-associated contaminants (Bradley et al., 1982;Gibbs et al., 1977; Horowitz and Elrick 1987).

Kaolinite is a one silica sheet: one alumina sheet clay mineral. The kaolinite tetrahedral sheet carries a small permanent negative charge due to isomorphous substitution of Si+4 by Al+3, causing a single negative charge. The permanent charge is minor in kaolinite clay. (Bohn et al., 1985). There are two distinct processes that have been proposed for the adsorption of heavy metals by kaolinite. The first is adsorption onto permanent negatively charged sites by electrostatic interaction with positively charged ions, and the second occurs on variable-charge groups at the edges of kaolinite crystals and these sites are generally more important than the permanent negatively charged sites (Schinder et al, 1987). The layer edges are primarily responsible for interaction of kaolinite with contaminant metals (Farrah et al., 1980).

Iron oxide has high surface area between 30-100 m²/g (Ponthieu et al., 2006). Iron oxide (goethite) has a variable charge, which depends on the pH of the environment; the variable charge allows iron oxide (goethite) to interact with metals. The surface charge of the iron oxide (goethite) is positive under acidic conditions and negative under alkaline conditions. Iron oxide with net negative charge can bind or hold cations on their surface by ion exchange processes. Also iron oxide can bind or hold ions by ligand exchange process. In the current study the pH was unfortunately not measured and there is no explanation of how metals were associated with the solid phase.

This paper tries to evaluate the heavy metal uptake in a mixed system of clays. Experiments were carried out to measure the distribution of copper, lead and zinc between an aqueous phase and solid phase sediment material. The distribution coefficient, K_d , is the ratio of the concentrations of metal held on the solid phase to the concentration of the metal in solution:

$$K_d = \frac{[\text{metal}]_{\text{solid}}}{[\text{metal}]_{\text{solution}}}$$



It represents the equilibrium that is achieved when metal ions in solution interact with sorption sites on the solid phase. It does not however give any information about the mechanism of binding. K_d values have frequently been used to assess the relative concentration of metals in solution associated with suspended material (Yin et al, 2002). Use of K_d values has proven to be especially useful for assessing the ability of soil and sediments to immobilize contaminant heavy metals (Jalali and Moharrami, 2007; Pulford et al., 1998; Standring et al., 2002).

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II. METHODS

The experiment was performed by adding different weights of kaolinite and iron oxide (goethite). Approximately e.g. (0.2 g - 0.8 g, 0.5 g - 0.5 g and 0.8 g - 0.2 g) of dry material was weighed in a beaker. 1 ml of 1 g/l concentration of metal was added to the one litre of distilled water.

The mixed material was added to the 1 mg/l concentration solution. A stirrer bar was added and the beaker placed on a magnetic stirrer for mixing the sample. The sample was mixed for times ranging between 15 and 30 minutes. Sample material was filtered through the weighted 0.2 mm pore size filters and the filter paper was reweighed to determine the mass of material recovered. The filter paper was digested using aqua regia, and the metal associated with the test material was measured by FAAS; between each reading, the instrument was zeroed with a metal-free solution containing solvent.

III. RESULTS AND DISCUSSION

The recovery of materials and distributions of Zn, Cu, and Pb between solid and solution phases are shown in Table 1. The K_d values were low. This indicated that smaller quantities of the metals were associated with the suspended particles than the aqueous phase. The results show most of the adsorbent materials were recovered and most of the metal was accounted for. The K_d value of the mixture of kaolinite and iron oxide (goethite) was low. This may be due to iron oxide coating the kaolinite, and a decrease the adsorption sites on the kaolinite surface. That may be because of changes to the negative charges on the surface of kaolinite occurring when iron oxides accumulate on the surface. Xu and Axe, (2005) and Gallez et al. (1976) suggest that iron oxide coatings reduce the negative charges and increase the positive charges on clay particles. At near neutral pH or high ionic strength iron oxides tend to coagulate (Kumulainen et al., 2008).

Table 1: Recovery of mixed material weights and distribution of (Zn, Cu, and Pb) metals between solid and solution phase for Kaolinite and Iron oxide mixtures

Sample weight	Weight of materials recovered in filter paper	Recovery of materials	Concentration of metal recovered in water	concentration of metal recovered in solid materials	Concentration of metal in materials	Total Recovery of metals	Kd
(g)	(g)	(%)	(mg/l)	(mg/l)	(mg/g)	(mg/l)	
1mg/l Cu							
1K - 0IO	0.98	98	0.80	0.18	0.183	0.98	0.225
0.8K-0.2IO	0.98	98	0.93	0.02	0.020	0.95	0.022
0.5K-0.5IO	0.97	97	0.92	0.02	0.020	0.94	0.022
0.2K-0.8IO	0.974	97	0.92	0.05	0.047	0.96	0.054
0K- 1IO	0.97	97	0.99	0.03	0.028	1.04	0.03
1mg/l Pb							
1K - 0IO	0.99	99	0.65	0.22	0.22	0.86	0.33
0.8K-0.2IO	0.98	98	0.77	0.06	0.064	0.83	0.077
0.5K-0.5IO	0.97	97	0.76	0.13	0.128	0.89	0.17
0.2K-0.8IO	0.98	98	0.58	0.20	0.204	0.78	0.34
0K- 1IO	0.98	98	0.90	0.03	0.025	0.93	0.03

1mg/l Zn							
1K - 0IO	0.96	96	0.87	0.087	0.079	0.95	0.1
0.8K-0.2IO	0.97	97	0.90	0.058	0.059	0.96	0.06
0.5K-0.5IO	0.99	99	0.93	0.034	0.034	0.97	0.36
0.2K-0.8IO	0.97	97	0.98	0.020	0.020	1.01	0.02
0K- 1IO	0.97	97	0.99	0.009	0.009	1.05	0.009

K=Kaolinite, IO=Iron Oxide

Flocculation is the aggregation of fine particles in the aqueous solution system. Flocculation can be attained by different mechanisms, such as approach to the point of zero charge (PZC) and polymer bridging (Rattanakawin et al., 2005). Iron oxide helps to collect the clays particles in flocs (Maa and Pierre, 1992). Iron oxide coating kaolinite can cause aggregation (Sowder et al., 2003). Flocculation is brought about by a decrease in repulsion. The situation of kaolinite is complicated because the different charges between the edges and faces of the particles, depending on the circumstances (Swarten et al., 1974, Van Olphen, 1977; Worrall, 1986).

In the current study three types of aggregation behaviour were observed by visual examination of the mixed systems. A single sediment layer is separated by accumulation in the solution, which happened with 0.8 g kaolinite and 0.2 g iron oxides (goethite). This may be because the iron oxides coated the adsorption sites of kaolinite, decreasing the sorption capacity. The availability of free adsorption sites on the (0.8 g) kaolinite was coated by 0.2 g of iron oxides (goethite). On the other hand, little flocculation occurred with the mix of 0.8 g iron oxide and 0.2 g kaolinite, possible because of the limited of adsorption sites on the 0.2 g kaolinite. In addition, little flocculation was observed in the solution, from 0.5 g-0.5 g of the mixed materials.

The result shows that the affinity order of K_d for the metals for mixtures of kaolinite and iron oxide are (Pb > Cu > Zn). The order is the same as order was observed Pb > Cu > Zn for the mixture of 0.8 g of iron oxide and 0.2 kaolinite, the order was different to previous studies Covelo et al, (2007). Covelo et al, (2007) used different conditions such as a range of pH values and large weights to determine adsorption of metal on clay minerals.

Prediction model

A prediction model can used to calculate metal the distingustion of in the mixture of kaolinite and iron oxide (goethite). The equation below used to calculate the prediction model in the mixed materials. The prediction model was comparing with actual weight of metal was used in the mixed materials kaolinite and iron oxide (goethite).

$$Kd = \frac{[solid]}{[solution]} 1kg^{-1}$$

$$Kd = \frac{(weight\ of\ metal\ in\ solid\ material) \div (weight\ of\ solid\ material)}{(weight\ of\ metal\ in\ solution) \div (volume\ of\ solution)}$$

$$Kd = \frac{(weight\ of\ metal\ in\ solid\ material) \times (volume\ of\ solution)}{(weight\ of\ metal\ in\ solution) \times (weight\ of\ solid\ material)}$$

$$Kd = \frac{w \times 1}{(1 - w) \times mass\ of\ solid\ material}$$

$$Kd \times mass\ of\ solid\ material = \frac{w}{(1 - w)}$$

$$w = \frac{Kd \times mass\ of\ solid\ material}{1 + (Kd \times mass\ of\ solid\ material)}$$

Sample weight (g)	Prediction model (mg)	Actual measured (mg)
1mg/l Cu		
1K - 0IO	0.169	0.18
0.8K-0.2IO	0.149	0.02
0.5K-0.5IO	0.115	0.02
0.2K-0.8IO	0.092	0.046
0K- 1IO	0.043	0.028
1mg/l Pb		

1K - 0IO	0.32	0.22
0.8K-0.2IO	0.28	0.06
0.5K-0.5IO	0.21	0.13
0.2K-0.8IO	0.15	0.2
0K- 1IO	0.04	0.03
1mg/l Zn		
1K - 0IO	0.124	0.087
0.8K-0.2IO	0.106	0.0579
0.5K-0.5IO	0.075	0.0342
0.2K-0.8IO	0.055	0.02
0K- 1IO	0.018	0.009

Where w is the weight of metal in solid materials, and $(1-w)$ is the weight of metal in solution. Figure (1) to (3) shows the actual weight of metals measured in the mixed materials and the weight of metals was calculate by prediction model. The result shows the weight of metals were different in the actual weight and in the prediction model for Cu and Pb. While the same weight of the metals were observed in the prediction model and in actual system for Zn. That may be because the different between the concentrations of metal measured in the solution and the limit of detection. The different between the concentrations of metal measured in the solution and the limit of detection were high for Cu and Pb, which result different in the actual weight and in the prediction model. On the other hand, the same weight of the metals was observed in the prediction model and in actual system for Zn, because no different between the concentrations of metal measured in the solution and the limit of detection.

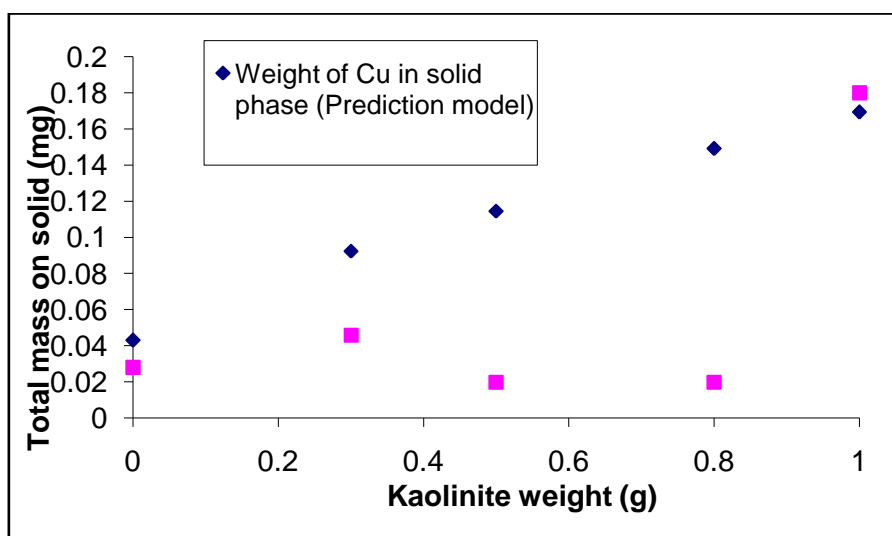


Figure 1 weight of Cu (mg) measured on solid phase and in the prediction model.

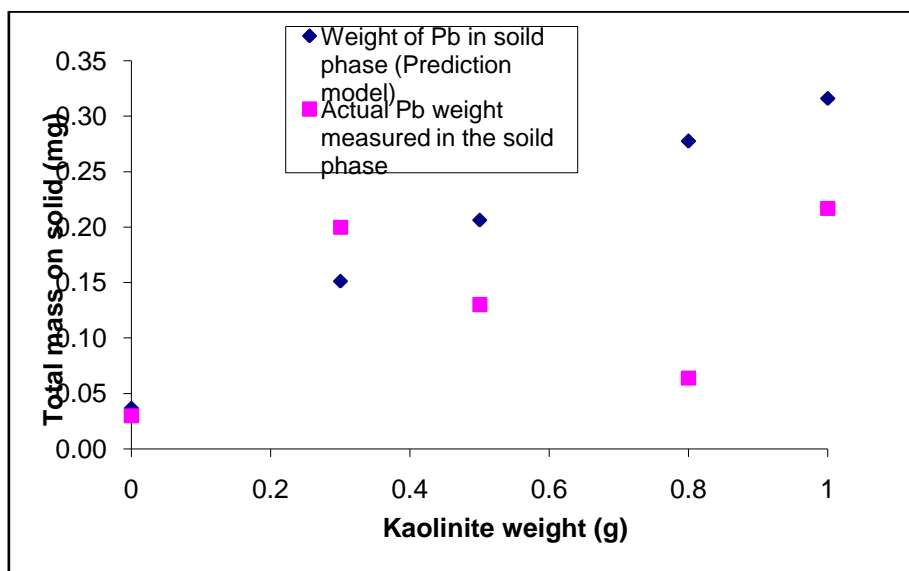


Figure -2 weight of Pb (mg) measured on solid phase and in the prediction model.

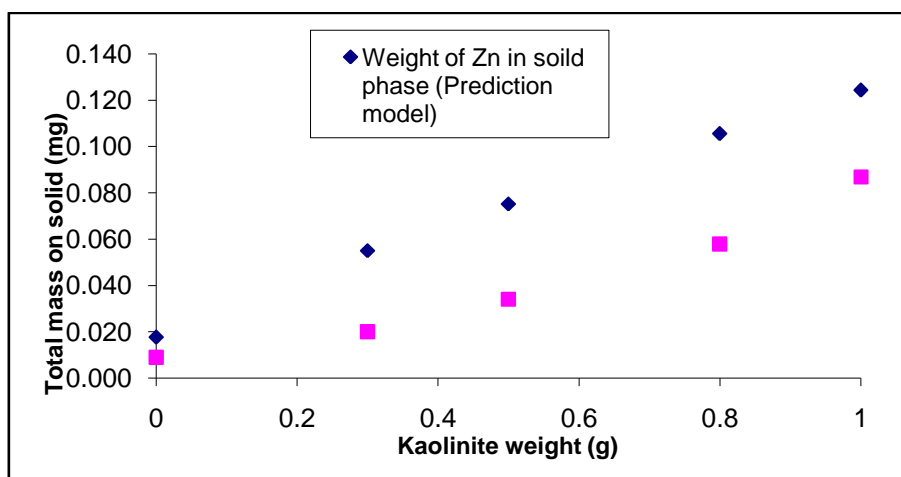


Figure -3 weight of Zn (mg) measured on solid phase and in the prediction model.

IV. CONCLUSION

The results show K_d values and distributions of Zn, Cu, and Pb between solid and solution phases. The K_d values were low. This may be due to iron oxide coating the kaolinite, and an increase the adsorption sites on the kaolinite surface. Xu and Axe, (2005) and Gallez et al. (1976) suggest that iron oxide coatings reduce the negative charges and increase the positive charges on clay particles. At near neutral pH or high ionic strength iron oxides tend to coagulate (Kumulainen et al., 2008).

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