Sorption of Copper, Lead and Zinc on Kaolinite sediment material

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Abstract: *The retention studies of Cu, Pb and Zn on kaolinite samples, in the laboratory to understanding metal adsorption between solution phase and solid phase of the suspended materials. The metals adsorption shows different adsorption responses between these different weight materials. In this study the most of heavy metal Cu, Pb and Zn concentration was measured in the solution phase, which consequence low K_d value.*

I. Introduction

In the water, system the suspended sediment is contains of sand, clay and other silicate minerals and hydrous metal oxides, as well as organic particle such as microorganisms, diatoms and plant detritus (Hart et al, 1982). A mixture of factors such as natural efficiency, soil, flora, water cycle, and element controls the availability of metals in the fluvial system (Jain and Sharma 2001; Zhang and Huang 1993; Aurada et al.,1983; Warren et al.,1981). The most of the metals load is held and distributed by suspended particulate matter in river system environments (Covelli et al., 2007). Several earlier studies suggest that suspended particles can play an important role in carrying metals in the river system (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).

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

Suspended materials nature can control metals absorption rate and the availability of dissolved metals. Metal is linked easily to clay materials that may be because the chemical and physical properties of the clay materials such as a high ion exchange capacity (Boenigk et al., 2005). The correlation between the concentrations of trace metal and sediment are important, which may be due to the change in total surface area of the sediment in suspension (Bradley et al., 1982). The surface area of a sediment particle controls the surface chemistry and its ability to adsorb sediment-associated contaminants (Gibbs et al., 1977, Horowitz and Elrick 1987). The fine particle size is increasing the surface area of the clay, which may be resulting increase the ability to absorption metal per unit mass (Lead et al., 1999).

Kaolinite is a one silica sheet: one alumina sheet clay mineral. Kaolinite is very inflexible because of the way the unit layers are held together. The unit layers are held by hydrogen bonds between oxygen atoms on the tetrahedral face and hydroxyls on the octahedral face, which results in a low cat ion exchange capacity (CEC) (10-100 mmol Kg^{-1}) and low surface area (10-20 10^3 m^2 Kg^{-1}) of the kaolinite (Bohn, 2001). Kaolinite structure allows a little atomic substitution. The metal adsorption is usually accompanied by the release of hydrogen (H^+) ions from the edge sites of the mineral. The results indicate that kaolinite suspended sediment has low metal carrying ability.

The distribution coefficient (K_d = [metal] $_{solid}$/ [metal] $_{solution}$) was determined for each system as a function of adsorbent concentration. K_d values have frequently been used to assess the relative concentration of metals in solution associated with suspended materials (Yin et al 2002). The higher the K_d value, the more metal is associated in the solid materials. Materials representative of components of suspended particles were: kaolinite, bentonite, humic acid and iron oxides. This study will evaluate the ability of different components of suspended material to take up heavy metals. Experiments were carried out to measure the distribution of copper, lead and zinc between an aqueous phase and solid phase sediment material. This study tries to simulate the natural system, exploring the effects of trace metals on important materials, which are commonly found in the soil.

II.   Methods

Four representatives of kaolinite sample were investigated. The samples were analysed by Atomic absorption Spectrometry a Perkin Elmer 400 B model. The experiment was performed by adding different masses (0.3 g, 0.5 g, 0.8 g and 1 g) of the kaolin to one litre of distilled water containing trace metal at a1mg/l concentration of metal in a clean, dry glass beaker.

Approximately e.g. 0.3 g of dry material was weighed in a beaker.1 ml of 1 mg/l concentration of metal was added to one litre of distilled water. The 0.3 g of the 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. The nylon membrane filter paper with 0.2 □ m pore size was weighed. The sample material was filtered through 0.2 □ m pore size filters and the filter paper was reweighed to determine the mass of material recovered. The filter paper was digested in 3:1 hydrochloric acid /nitric acid solution, an aqua regia digest.

III.   Results and discussion

The results in table (1) give the recovery of kaolinite and distribution of Cu, Pb, and Zn metals between metals adsorbed in solid phase and metal concentration in solution phase. The results show most of the kaolinite was recovered in the filter paper. The majority of the metal was measured in the aqueous phase, with only a small amount measured in the solid phase. That may be caused a decreased in K_d values. K_d values are < 1. 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, these sites are generally much higher reactions than the permanent negatively charged sites (Schinder et al, 1987).

The affinity order of metal K_d for kaolinite were, Pb > Cu > Zn with 0.3 g and 1 g masses of kaolinite as shown in table (2). This was similar to previously reported (Jiang et al 2010, Gu et al 2008, Spark et al 1995, Schinder et al, 1987, and Farrah et al 1976). On the other hand, a different   order was noticed with between 0.5 g and 0.8 g masses of kaolinite was Pb > Zn > Cu. In general, the K_d value of Pb was slightly higher than the other metals tested.   In this study the pH value was not measured, because of the fixed parameters of the solution phase, the concentration of metal and limited material masses of less than 1 g.

Table (1) Recovery of kaolinite and distribution of Cu, Pb, and Zn metals between solid and solution phase.

A	B Weight of kaolinite recovered in filter paper	*C Recovery of kaolinite	D Concentration of metal in digest of recovered kaolinite	E Weight of metal in recovered kaolinite	F Weight of metal in 1 L of filtered water	**G Total weight of metal recovered	***H Total weight of metal adjusted for recovery of kaolinite	#I
Sample weight (g)	(g)	(%)	(mg/l)	(mg)	(mg)	(mg)	(mg)	Kd
1 mg/l Cu								
0.3	0.2985	99.5	0.75	0.075	0.90	0.975	0.950	0.083
0.5	0.4723	94.4	0.61	0.061	0.94	1.004	1.004	0.064
0.8	0.7849	98.0	1.12	0.112	0.83	0.952	0.965	0.134
1.0	0.9806	98.0	1.80	0.180	0.80	0.980	0.985	0.225
1 mg/l Pb								
0.3	0.2943	98.0	1.09	0.109	0.85	0.965	0.967	0.120
0.5	0.4846	97.0	1.90	0.190	0.64	0.832	0.838	0.291
0.8	0.7746	97.0	2.18	0.218	0.60	0.821	0.828	0.360
1.0	0.9913	99.0	2.16	0.216	0.64	0.863	0.865	0.330
1 mg/l Zn								
0.3	0.2866	96.0	0.32	0.032	0.89	0.924	0.929	0.036
0.5	0.4704	94.0	0.70	0.070	0.84	0.915	0.919	0.083
0.8	0.7851	98.0	1.07	0.107	0.78	0.895	0.925	0.137
1.0	0.9644	96.0	0.77	0.077	0.87	0.94	0.950	0.088

*C= (B/A)*100, *G= (E+F), ***H= (E*100/C) +F, #I= (E/F)

*C= (B/A)*100, *G= (E+F), ***H= (E*100/C) +F, #I= (E/F)

Table (2): The order of metal K_d values in different weights of kaolinite

Weight	Kaolinite
0.3 g	Pb > Cu > Zn
0.5 g	Pb > Zn > Cu
0.8 g	Pb > Zn > Cu
1 g	Pb > Cu > Zn

IV. Conclusion

The results show most of the kaolinite was recovered in the filter paper. The majority of the metal was measured in the aqueous phase, with only a small amount measured in the solid phase. That may be due to a decrease in K_d values. The small adsorption capacities of the kaolinite can cause small changes in metal uptake (Farah, 1977). In the current study the small in metal K_d may be because of a variable-charge on clay edges with different masses of materials used, which attract the cations to the surface.

References

[1]. Aurada. K.D.1983.Physiographic and anthropogenic controls of global and regional ionic runoff, in webb, b.w Dissolved loads of rivers and surface Water Quantity Quality Relationship .Hamburg, IAHS publ.141,31-39.

[2]. Boenigk. J, Wiedlroither. A, Pfandl. K.2005.Heavy metal toxicity and bioavailability of dissolved nutrients to a bacterivorous flagellate are linked to suspended particle physical properties .Aquatic Toxicology71,249-259.

[3]. Bohan. H, McNeal .b, O'Connor. G, 2001.Soil Chemistry. John Wiley and Sons.

[4]. Bradley. S. B, Lewin.J.1982.Transport of heavy metals on suspended sediments under high flow conditions in a mineralized Region of Wales.

[5]. Covelo. E. F, Vega. F. A, Andrade. M. I, 2007.Competitive sorption and desorption of heavy metals by individual soil components. Journal of Hazardous Materials, 140,308-315.

[6]. Dai. M. H, J, M. Martin.1995.First data on trace metal level and behaviour in two major Arctic river –estuarine systems (Ob and Yennisey) and in the adjacent Kara Sea, Russia. Earth Plant.Sci.Lett.131, 127-141.

[7]. Droppo. I. G, Krishnappan. B. G, Rao. S. S, Ongley. E. 1992,.Investigation of a Sequential Filtration Technique for Particle Fractionation. Environmental Sciences &Technology. 29,2,1995.

[8]. Farrah. H, Hatton. D, Pickering.W.F.1980, The affinity of metal ions for clay surfaces. Chemical Geology, 28, 55-68.

[9]. Farrah. H, Pickering .W.F.1976. Influence of clay solute interactions on aqueous heavy metal ion levels. Water, Air and Soil Pollution, 8,189-197.

[10]. Farrah. H, Pickering. W.F, 1977, Extraction of heavy metals ions sorbed on clays. Water, Air and Soil Pollution,9,491-498.

[11]. Forbes. E .A, Posner. A. M, Quirk. 1976,. The specific adsorption of divalent, Cd, Co, Cu, Pb and Zn, 27,154-66.

[12]. Gallo. M, Trento.A,Alavrez.A,Beldomenico.H,Campagnoli.D.2006.Dissolved and particulate heavy metals in the Salado River(Santa Fe, Argentina).Water ,Air and Soil Pollution174,367-384.

[13]. Garcia. J. 1978. Sorption of trace quantities of cadmium by soil with different chemical and mineralogical composition. Water, Air, and Soil Pollution 9, 289-299.

[14]. Gibbs. J. R., 1977. Transport phases of transition metals in the Amazon and Yukon Rivers. Geol. Soc. Am. Bull., 88: 829-843.

[15]. Giesy. J. P, L. A. Briese. 1977. Metals associated with organic carbon extracted from Okefenokee swamp water.Chem.Geol.20,109-120.

[16]. Grimme. H.1968,.Adsorption of manganese cobalt copper and Zinc by goethite from dilute solutions,., Zeit fuer Pflan und Bodee,121,1, 58-65.

[17]. Gu. Xueyuan, Evans. Les J, Barabash. Sarah J.2010.Modeling the adsorption of Cd, Cu, Ni, Pb and Zn onto montmorillonite. Geochemical et Cosmochmical Acta 74, 5718-5728.

[18]. Gu. Xueyuan, Evans. Les J.2008.Surface complexation modeling of Cd, Cu, Ni, Pb and Zn adsorption onto kaolinite .Geochemical et Cosmochmical Acta 72,267-276.

[19]. Hart. B. T.1982. Uptake of trace metals by sediments and suspended particulates, a review. Hydrobiologia, 91,299-313.

[20]. Hill. M. D, Aplin.C.A.2001, Role of colloids and fine particles in the transport of metals in rivers draining carbonate and silicate terrains. Limnol. Oceanogr. 46(2), 2001, 331–344.

[21]. Hoffmann. M. R, E. C. Yost, S. J. Eisenreich, W.J. Maier. 1981. Characterisation of soluble and colloidal –phase metal complexes in river water by ultrafiltration.A mass-balance approach .Env.Sci.Technol.15,655-661.

[22]. Horowitz. A. J. & Elrick, K. A. 1987, "The relation of stream sediment surface area, grain size and composition to trace element chemistry", Applied Geochemistry, vol. 2, no. 4, pp. 437-451.

[23]. Horowitz. A. J. A Primer on Sediment-Trace Element Chemistry; Lewis Publishers Inc.: Chelsea, MI, 1991.

[24]. Jain. C. K, Sharma. M.K .2001.Distribution of trace metals in the Hindon River system, India. Journal of Hydrology 253,81-90.

[25]. Jiang. J, Xu. R, Li. S, 2010, Effect of Ionic Strength and Mechanism of Cu(II) Adsorption by Goethite and γ-Al$_2$O$_3$., J. Chem. Eng. 55, 12, 5547–5552.

[26]. Lead. J. R, Taylor. H, Davison. W, Harper.M.1999.Trace metal sorption by natural particles and coarse colloids. Geochimica ET Cosmochimica Acta.63.1661-1670.

[27]. Ponthieu. M, Juillot .F, Hiemstra. T ,Van Riemsdijk. W. H, Benedetti, M. F, 2006 Metal ion binding to iron oxides. Geo-chemical et Cosmochimical Acta,70,2679-2698.

[28]. Reuter. J .H. E.M.Perdue.1977.Importance of heavy metal –organic matter interactions in natural waters.Geochim.Acta.41:325-334.

[29]. Ross. J.M,, R.M.Sherrell.1999.The role of colloids in trace metal transport and adsorption behaviour in New Jersey Pinelands streams .Limnol.Oceanogr,44,1019-1034.

[30]. Salbu. B, H. E. Bjornstad, N.S. Lindstrom, E. Lydersen ,E. M. Brevik, J .P.Rambaek,P.E.Paus.1985.Size fractionation techniques in the determination of elements associated with particulate or colloidal material in natural fresh waters .Talanta 32.907-913.

[31]. Schinder. P. W, Liechtip, and Westall.J.C,. 1987., Adsorption of copper, cadmium and lead from aqueous solution to the Kaonilite/water interface, Neth, J, Aqu, 35,219-230.

[32]. Shukla L. M, 2000,. Sorption of zinc and cadmium on soil clays,. Agrochimica, 44,3-4, 101-106.

[33]. Singh. K. P, Mohan. D, Singh. V. K, Malik.A.2005.Studies on distribution and fractionation of heavy metals in Gomti river sediments- atributary of the Ganges, India. Journal of Hydrology 312,14-27.

[34]. Spark. K, M. Johnson, B.B, Wells, J.D.1995,. Characterizing heavy metal adsorption on oxide and oxy-hydroxides, Eur, J, Soil, 46,621-631.

[35]. Tanizaki. Y, T. Shimokawa, M.Nakmura.1992.Physicochemical speciation of trace elements in river water by size fractionation. Env.Sci.Technol.26, 1433-444.

[36]. Warren. L.J.,1981. Contamination of sediments by lead, zinc and cadmium- a review. Environ. Pollution, ser 2,401-436.

[37]. Yin. Y, Impellitteri. Christopher A, You. Sun-Jae, Allen. H. E., 2002. The importance of organic matter distribution and extract soil: solution ratio on the desorption of heavy metals from soils. The Science of the Total Environment 287.107,119.

[38]. Yun.I,Xing,S. iming.X,Haidong.C,Huixian.Z,Shixiang.G.,2006.,Adsorption of copper and lead in aqueous solution onto bentonite modified by 4-methylbenzo-15-crown-5.Journal of Hazardous MaterialsB,137,1149-1155.

[39]. Zhang. J., Huang, W.W., 1993.Dissolved trace metals in the Huanghe: the most turbid large river in the world .Wat. Res, 27, 1-8.