

Competitive Sorption of Cadmium, Copper and Lead in Soils around Nasarawa Industrial Waste Disposal Site in Kaduna Metropolis

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Abstract- Sorption of lead cadmium and copper was studied using mono, bi-and tri-metal batch test. Simple mathematical expressions were applied to establish relationship between concentration of the adsorbent in the liquid phase and the solid phase at equilibrium and at constant temperature. The studies revealed in general that the soil around the Nasarawa industrial waste dumpsite has a high capacity to sorb metal ions. Results from the kinetics batch tests have shown the applicability of a pseudo second order model to describe adsorption rates of each metal ion in the soil.

Index Terms- sorption, cadmium, copper, lead.

I. INTRODUCTION

Heavy metals ions in soils have been a very useful indicator of environmental quality worldwide. Heavy metal ions are the most toxic inorganic pollutants which occur in soils and can be of natural or of anthropogenic origin. Lead, Copper, and Cadmium belong to the group of serious hazardous heavy metals and are generally considered a threat to human health and ecosystems because of their potentially high toxicity. Their mobility in soils may be controlled by different chemical mechanisms such as surface complex formation, ionic exchange, precipitation, and adsorption processes. However, the most important chemical process that affects heavy metal availability is adsorption onto soil solid phases. Their solubility and bioavailability may also be controlled by soils characteristics, such as pH, redox potential, clay minerals, soil organic matter, Fe and Mn oxides, and calcium carbonate, therefore, metals adsorption and hence availability does not only depend on soil constituents (inorganic and organic), but also on the available metals, and their competition for soil sorption sites. Many authors have investigated metals adsorption on different soils materials and under different experimental conditions. Most trace element adsorption has been derived from studies conducted using single metal solutions. Usually, single metal solutions have limited practical applications. However, multi-metal solutions are extremely important for a better understanding of competitive sorption of metal ions. In addition, it is well-known that most heavy metal contamination in the surface environment is associated with a cocktail of contaminants rather than one metal. Previous research has shown an impact of groundwater quality related to the contribution of urban contaminants. In this study, we have investigated the potential capacity of Pb, Cu and Cd to

sorb on soils of around dump site. Knowledge about the mobility of these heavy metals in soils may play a key role in the designing of control strategies to achieve better groundwater protection. This study attempt to study the sorption of lead, copper and cadmium around Nasarawa industrial waste dump sites competitive sorption of lead, cadmium and copper in soils around Nasarawa industrial waste disposal site, in Kaduna metropolis.

II. MATERIALS AND METHODS

2.1 Soil Samples and Characterization

Three approximately 3-kg soil samples from 2m apart of the same site were collected and combined prior to the experiments from which is not subjected to human activities.

The ≤ 2 mm size soil fraction was used for laboratory experiments. This grain size is most reactive. In general, coarse-grained soil exhibit lower tendency for heavy metal adsorption than fine-grained areas. Clay minerals, iron and manganese oxyhydroxides, humic acids, and others minerals present have enhanced adsorption properties. All the samples were air dried at room temperature, passed through a 2mm sieve, homogenized, and stored pending measurement of physicochemical properties such as pH, organic carbon, clay, and CaCO₃ using standard analytical methods. Soil pH was measured using a pH meter at a soil to solution ratio in both deionizer water in 1:2.5 and 1 mol L⁻¹ KCL. Soil organic matter (OM) was determined by calcinations at 550°C for 2 h. the inorganic carbon was determined using the calcimeter method and carbonate concentrations were calculating using universal Gas law (3). The cation exchange capacity (CEC) of the soil was determined using the metson method (22) concentrations of available heavy metals in the soil sample were determined by atomic absorption spectrometry (AAS).

2.2 Experimental Set-up

Batch tests were carried out by equilibrating 5g soil with 50mL of solutions containing different metal concentrations in 0.01 M NaNO₃. All our experiments were performed at pH 6.0 (adjusted using dilute HNO₃ or NaOH) in order to have a stable solution and avoid metals precipitation on hydroxides forms which can introduce uncertainty into the interpretation of result. The metals cations were applied in the form Pb(NO₃)₂, Cu(NO₃)₂ · 3H₂O and Cd(NO₃)₂ · 4H₂O. Nitrates were used because these ions have no affinity for metal. After equilibrium,

the suspensions were filtered through a 0.45 μ m membrane, and samples were carefully dispensed to 50mL polyethylene sample cups, acidified to pH 1.5-2 using strong HNO₃ and stored at 4^oC until the heavy metal ion measurements by AAS.

2.2.1 Adsorption Kinetics

Metal adsorption depends on the reaction kinetics and the time of contact between metal ions and soil. In this study, Kinetics batch tests were carried out at room temperature and samples were taken after 1min, 3min, 8min, 15min, 30min, 60min, 120min, 360min, 720min, 1,440min, 2,880min and 4,320min. The metal concentrations equilibrated with the soil sample were 250, 80 and 123mg.L⁻¹ of Pb, Cu and Cd respectively. The metal suspensions were prepared and analyzed by AAS.

2.2.2 Monometal Adsorption

Monometal batch tests were performed over a 24 h period by shaking range concentrations of Pb (0-186mg L⁻¹), Cu (0-5777mg. L⁻¹) and Cd(0-101 mg L⁻¹) at room temperature. After equilibrium time, the suspensions were prepared for metal ions measurements by AAS. The amount of the metal ions sorbed by soil was calculated by:

$$q_e = \frac{(C_0 - C_e) \times V}{W} \quad (1)$$

Where q_e is amount of Pb²⁺, Cu²⁺ or Cd²⁺ adsorbed on the soil (mg. g⁻¹), C_e is the concentration of Pb²⁺, Cu²⁺ or Cd²⁺ at equilibrium (mg. L⁻¹), C_0 is the initial concentration of Pb²⁺, Cd²⁺ or Cu²⁺ in solution (mg. L⁻¹), V is the solution volume (mL), and W is the weight of air-dried soil (g).

2.2.3 Competitive Adsorption

Bi- and tri-metal batch tests were carried out by solubilizing a combination of either (Pb²⁺ - Cu²⁺), (Pb²⁺ - Cd²⁺), (Cu²⁺ - Cd²⁺) and (Pb²⁺ - Cu²⁺ - Cd²⁺). These experiments were conducted with the same operating conditions as for Monometal batch tests in terms of volume (50mL), soil sample weight (5 g), heavy metals concentrations ranges, pH (6.0) and agitation time (24h).

2.3 Theory

To study the adsorption process, simple mathematical expressions are usually applied to establish relationships between concentration of the adsorbent in the liquid phase and the solid phase at equilibrium and at constant temperature. During these experiments, adsorption processes not always have time to reach equilibrium, but it is limited instead by reaction kinetics.

2.3.1 Kinetics Models

Kinetics batch tests were performed in order to evaluate the reaction rates of Pb, Cu and Cd on the selected soil. Two simplified kinetics models including pseudo-first-order and pseudo-second-order were tested. The pseudo-first-order equation is linearly expressed as:

Where Q_e (mg.g⁻¹) is the adsorption capacity at equilibrium, Q_t (mg.g⁻¹) is the amount of the metal adsorbed at time t , and k_1

(min⁻¹) is the rate constant of the pseudo-first-order equation. The values of k_1 can be obtained from the slope of the linear plot of $\ln(Q_e - Q_t)$ vs. t at different metal concentration. The linearized form of pseudo-second-order equation is expressed as:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (3)$$

Where k_2 is the rate constant of pseudo-second-order kinetics. The values of k_2 (g.mg.min⁻¹) and Q_e can be determined from the slope and intercept of the plot obtained by plotting t/Q_t vs. t respectively.

2.3.2 Isotherms Adsorption models

Langmuir and Freundlich models were used to study Monometal isotherms of Pb²⁺, Cd²⁺ and Cu²⁺ on the soil. The above two models are given, respectively, as follows:

$$q_e = \frac{Q_{max} b C_e}{1 + b C_e} \quad (4)$$

$$q_e = k_F C_e^{1/n} \quad (5)$$

Where C_e (mg.L⁻¹) and q_e (mg. g⁻¹) are the equilibrium adsorbate concentrations in the aqueous and solid phases, respectively; Q_{max} is the maximum adsorption (mg.g⁻¹) and b (L. mg⁻¹) is the adsorption equilibrium constant; k_F (L. mg⁻¹) is the Freundlich distribution coefficient and n is an empirical constant (unit less).

Jain and Snoeyink (JS) have proposed a modified equation of the Langmuir model Equation for bi-solute adsorption systems. The extended Langmuir model takes into consideration that the presence of other metals in solution can affect the apparent affinity of the metal for the adsorption on an active site. The JS modified model equations is given by:

$$q_1 = \frac{(Q_{m1} - Q_{m2}) b_1 C_1}{1 + b_1 C_1} + \frac{Q_{m2} b_1 C_1}{1 + b_1 C_1 + b_2 C_2} \quad (6)$$

$$q_2 = \frac{Q_{m2} b_2 C_2}{1 + b_1 C_1 + b_2 C_2} \quad (7)$$

Where q_1 and q_2 are the amount of metals 1 and 2 adsorbed per unit weight of adsorbent at equilibrium concentrations C_1 and C_2 . The first term of the Equation is the Langmuir expression for the number of molecules of solute 1 that sorb without competition on the surface area and the term is proportional to $(Q_{m,1} - Q_{m,2})$. The second term of this equation represents the number of molecules of solute 1 sorbed on the surface area proportional to $Q_{m,2}$ in competition with solute 2, and is based on the Langmuir model for competition adsorption. The number of molecules of solute 2 sorbed on the adsorbent surface is proportional to $Q_{m,2}$ in competition with solute 1, can be calculated from Equation 7. The JS model was used in this study to assess the bi-metal competitive and adsorption of Pb, Cu and Cd on the studied soil.

Experimental data from tri-metal batch tests was modeled using Langmuir extended model, as follows:

III. RESULT AND DISCUSSION

3.1. Soil Characteristics

Table 1 shows the physicochemical characteristics of the studied soil. The result confirmed that the soil have alkaline pH value due the presence of the free CaCO₃(343 g.kg⁻¹). The CaCO₃ value is consistent with a watershed rich in carbonate formations. Data indicate abundant organic matter(OM) (58 g.kg⁻¹) and Cation Exchange Capacity (CEC) of soil sample. The CEC can be estimated by the clay content and organic matter. Therefore, soils with very little OM have a low CEC, but heavy clay soils with high levels of OM would have a much greater capacity to sorb cations. Soil samples had Pb and Cd concentrations below detection limits. These values have justified the choice of soil sample area. Cu concentrations (61.4 mg.kg⁻¹) are probably related to natural concentrations.

$$\ln(Q_e - Q_t) = \ln Q_e - k_f t \tag{2}$$

$$q_{e,i} = q_{m,i}^0 \left[\frac{b_i^0 C_{e,i}}{1 + \sum_{j=1}^n b_j^0 C_{e,j}} \right] \tag{8}$$

Where $q_{m,i}^0$, b_i^0 and b_j^0 are Langmuir extended parameters obtained form Equation 4 in Monometal batch tests and $C_{e,i}$ and $C_{e,j}$ are respectively the concentrations of metals i and j from tri-metal batch tests after equilibrium.

Table 1. Physicochemical characteristics of soil from Nasarawa dumpsites

Parameters	Concentration
pH-H ₂ O	8.26
pH-KCl	7.46
CaCO ₃ (g.kg ⁻¹)	343.00
Organic carbon (g.kg ⁻¹)	100.00
Organic matter (g.kg ⁻¹)	57.85
Clay (g.kg ⁻¹)	17.00
CEC (meq. Kg ⁻¹)	134.00
Surface area (m ² . g ⁻¹)	9.48
Total Ca (g. kg ⁻¹)	9.67
Total Mg (g. kg ⁻¹)	0.45
Total K (g. kg ⁻¹)	0.051
Total Cu (mg.kg ⁻¹)	61.40
Total Zn (mg.kg ⁻¹)	28.10
Total Cd (mg. kg ⁻¹)	Ud*
Total Pb (mg.kg ⁻¹)	Ud

* Undetected

3.2. Kinetics

The adsorption rates of the three metals have been evaluated using Equation. The obtained parameters for pseudo-first-order

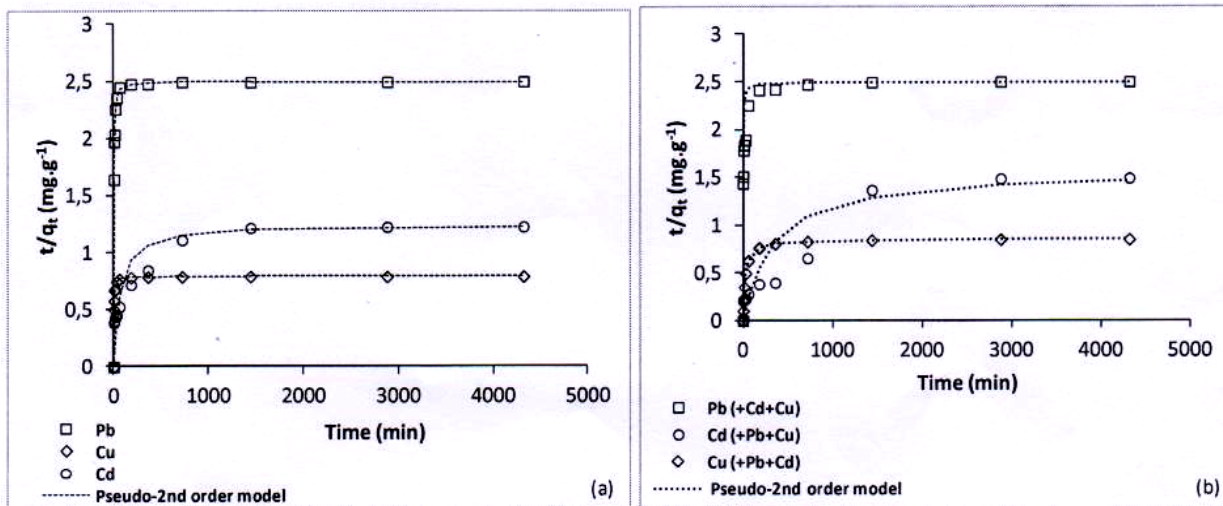
are given in Table 2.The low values of correlation coefficient indicate that the pseudo-first-order model is inappropriate to describe the adsorption rates process.

Table 2. Constants and correlation coefficients obtained by pseudo-first-order and pseudo-second-order kinetics models.

Metal ions	Pseudo-first order		Pseudo-second order		
	K_1 (min ⁻¹)	R_1^2	Q_e (mg.g ⁻¹)	K_2 (g.mg ⁻¹ .min)	R_2^2
Pb ²⁺	0.00139	0.66	2.50	0.25	1.00
Cu ²⁺	0.00147	0.68	0.79	0.77	1.00
Cd ²⁺	0.00010	0.83	1.24	0.01	0.99
Pb ²⁺ (Pb ²⁺ -Cu ²⁺ -Cd ²⁺)	0.00047	0.48	2.61	0.075	1.00
Cu ²⁺ (Cu ²⁺ -Pb ²⁺ -Cd ²⁺)	0.0012	0.71	0.86	0.055	0.99
Cd ²⁺ (Cd ²⁺ -Pb ²⁺ -Cu ²⁺)	0.00073	0.91	1.58	0.002	0.94

The pseudo-second order kinetic plots (t/q_t vs. t) appeared to give a better understand of the interactions. However, the good fitting ($R^2 = 1.0$) of the experimental data for Pb^{2+} and Cu^{2+} ions with pseudo-second-order model indicates the applicability of this model to predict adsorption rates for each metal on the soil. It was donated that a pseudo-second-order approach can sometimes provide a better description of the adsorption kinetics.

Figure 2. Pseudo-second order kinetics plots of Pb^{2+} , Cu^{2+} and Cd^{2+} in the soil: (a) Monometal batch tests; (b) Tri-metal batch tests.



Result from Monometal batch tests have showed that Pb displayed the fastest adsorption rates comparatively to Cu and Cd. Therefore, at about 180min, the maximum adsorption capacity of Pb and Cu were obtained as Cd had continued to sorb over 4,320 min. result from tri-metal batch tests have proved that a decrease of adsorption rates for the three metal. These results have showed that the maximum adsorption capacity for Pb, Cu and Cd was obtained respectively at 2,880, 4,320 and over 4,320 min. These results showed that when two or more metal ions are together in soils, their adsorption rates is decreased each other. Therefore, their mobility in soils can be limited by competition for the adsorption sites and they don't represent a potential risk at short-term for ground water of Nasarawa dumpsite.

3.3 Monometal Adsorption

The adsorption isotherms of Langmuir and Freundlich for Pb, Cu and Cd ions at pH 6.0 are illustrated in Figures 3 and 4, respectively. These isotherms represent the adsorption behavior of these metals on the soil as a function of increasing aqueous metal ion concentration after equilibrium. The results indicated

that the adsorption data of the three metals were well correlated with Langmuir and Freundlich models. The Freundlich equation habitually provides a good description of adsorption onto heterogeneous solid surfaces. However, the adsorption of Pb^{2+} data gave a good satisfactory fit with both Langmuir ($R_L^2 = 0.91$) and Freundlich ($R_F^2 = 0.91$). The q_{max} , b , R_L^2 (correlation coefficient for Langmuir isotherm); K_F , n and R_F^2 (correlation coefficient for Freundlich isotherm) are given in Table 3. Freundlich parameters (K_F and n) indicate whether the nature of adsorption is either favorable or unfavorable. The values of n are less than 1 indicate a favorable adsorption mechanisms and formation of relatively stronger bonds between the adsorbents. In table 3, the low values of n ($n < 1$) for Pb^{2+} and Cd^{2+} indicate that adsorption intensity is favourable at high range of concentrations studied, while for Cu^{2+} ($n > 1$) means that adsorption intensity is unfavorable at high concentrations but much less at lower concentrations. Some studies on other sites area have supported this conclusion.

Figure 3. Freundlich adsorption isotherm for Pb^{2+} , Cu^{2+} and Cd^{2+} on the studied soil at pH 6.

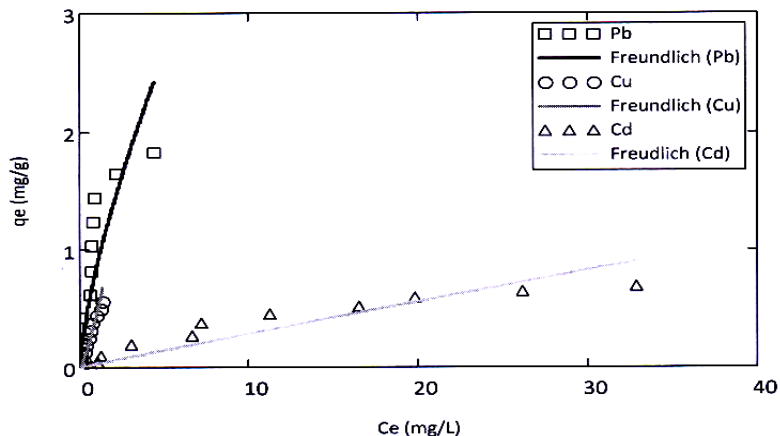
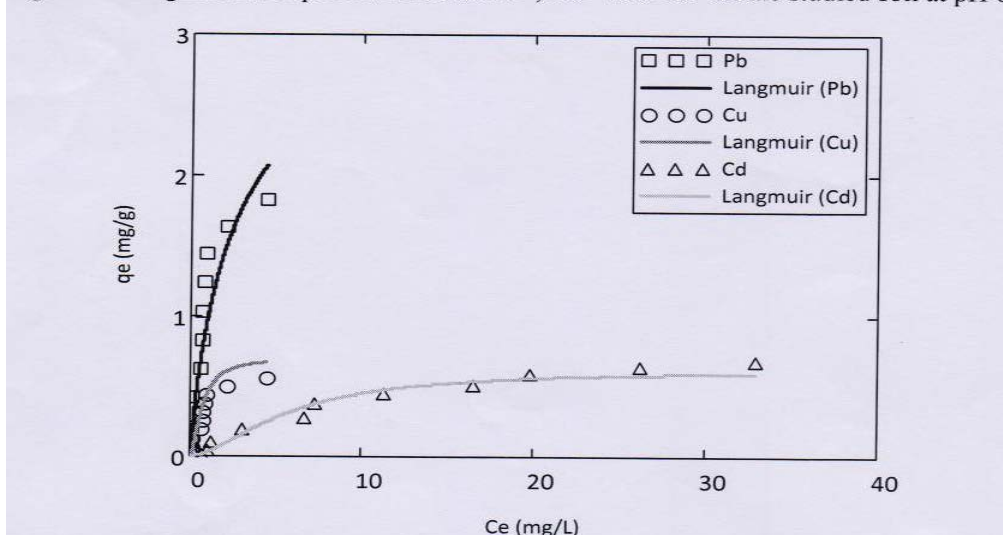


Figure 4. Langmuir adsorption model for Pb^{2+} , Cu^{2+} and Cd^{2+} on the studied soil at pH 6.



The q_{max} , from the Langmuir equation, may be a useful parameter for comparing the potential capacity of the soil among all the three metals, Pb showed the highest value of adsorption maximum (q_{max}). On the basis on the q_{max} value, the order selectivity of these metals for the soil is $Pb^{2+} > Cu^{2+} > Cd^{2+}$. The selectivity order can be influenced by the valency and the ionic size of the heavy metals one hydrated. Then, smaller ions with the same valency, such as Cd compared with Pb, have higher charge densities and attract more water molecules, resulting in a larger hydrated radius. Metals with higher hydrated radius exert weaker columbic forces of attraction. Therefore, Cd (0.23 nm radius) is expected to be mobile that Pb (0.187 nm radius) because of its larger hydrated radius. In order case, the higher affinity of the soil for Pb may probably due to the existence of a greater number of active sites (mostly organic matter) with high specificity for Pb, so when it is present these sites would not be occupied by others cations. According to these results, Cd may pose more threat to soils and groundwater around the dump sites. These results strongly suggest why Berti and Jacobs found that soil loading of Cd, Ni, and Zn appeared to be of greater environmental concern than Cr, Cu, and Pb and that the first

group could accumulate in the tissue of plants grown on sludge-treated plots.

3.4 Competitive Adsorption

Competitive adsorption studies were useful to assess the degree of interference posed common metal ions in the soil. The parameters of the JS and Langmuir extended models used in this study are summarized in table 3. It was observed that Pb was always favorably sorbed on the soil over Cu and Cd in all the experiments. The experimental data from Pb and Cu bi-metal batch tests were better fitted than Cd with the JS model. The geochemical behavior of the three metals was evaluated following to their maximum adsorption capacity in the soil. These results indicated that competitive between the three metals have been reduced the adsorption capacity in the soil. Qin *et al.* suggested that when two or more metal ions are present together, they may increase, decrease or not change the metal-ion adsorption capacity of the adsorbment. The competitive of Cd and Pb in acid soils was studied by Serrano *et al.*, and they noted that the co-existence of Pb and Cd reduces their tendency to be sorbed on the soil solid phases, thereby affecting the adsorption capacity of Cd to a greater extent than Pb. The same

phenomenon was observed by Morera *et al.* using competitive adsorption isotherms to evaluate the mobility of Cd, Cu, Ni, Pb and Zn in four soils differing in their physicochemical properties.

Table 3. Isotherm adsorption parameters for Pb, Cu and Cd in monometal and bi-solutes systems on the soil ($q_{max}L$; $q_{max}JS$: $mg \cdot g^{-1}$; b_L , b_{JS} , K_F : $L \cdot mg^{-1}$).

Metals	Adsorption batch tests		Langmuir parameters			Freundlich parameters		
	Monometal		$q_{max}L$	b_L	R_L^2	1/n	K_F	R_F^2
Pb	Cd ²⁺		3.64	0.37	0.91	1.41	0.85	0.91
Cu	Cu ²⁺		0.70	1.81	0.91	0.78	0.45	0.92
Cd	Cd ²⁺		0.63	0.05	0.90	1.01	0.03	0.89
Jain and Snoeyink parameters								
	Bi-metal		$q_{max}JS$	b_{JS}	R_{JS}^2	Δq_{JS} (%)	r_{JS}	
Pb	(Pb ²⁺ -Cd ²⁺)		3.09	0.36	0.99	15.11	0.85	
	(Pb ²⁺ -Cu ²⁺)		2.95	1.40	0.97	18.95	0.81	
Cu	(Cu ²⁺ -Cd ²⁺)		0.59	2.07	0.98	15.71	0.84	
	(Cu ²⁺ -Pb ²⁺)		0.45	1.63	0.94	35.71	0.64	
Cd	(Cd ²⁺ -Pb ²⁺)		0.46	0.09	0.87	26.98	0.73	
	(Cd ²⁺ -Cu ²⁺)		0.10	0.44	0.75	84.13	0.16	
Extended Langmuir parameters								
	Tri-metal		$q_{max}LE$	b_{LE}	R_{LE}^2	Δq_{LE} (%)	r_{LE}	
Pb	(Pb ²⁺ -Cu ²⁺ -Cd ²⁺)		0.77	1.56	0.95	78.86	0.21	
Cu	(Cu ²⁺ -Pb ²⁺ -Cd ²⁺)		0.43	1.79	0.98	38.57	0.61	
Cd	(Cd ²⁺ -Pb ²⁺ -Cu ²⁺)		0.10	0.85	0.91	84.13	0.16	

Mohan and Singh have investigated the mutual effects of metals ions on their adsorption in multi-solute system by measuring the adsorption capacity ratio of one metal in multi-solute, q_i^{mix} and the single-solute system, q_i^0 , following this equation:

$$r = \frac{q_i^{mix}}{q_i^0} \tag{9}$$

Where q_i^0 and q_i^{mix} are the maximum amount sorbed according to Monometal or multi-metal batch tests, respectively and r is the adsorption capacity ration. If $r > 1$, metal I completed for with other metals for the adsorption sites of adsorbents. As showed in table 3, all the values of r are lower than 1 which indicates the mutual competitive effect of each metal in all the experiments. The r values obtained from tri-metal batch tests are lower than those from bi-metal adsorption systems. These results indicated that the competitive adsorption processes depend on the quantity of metals ions from solid and liquid phases.

The rate of adsorption reduction (Δq) can be calculated following the equation (10). This rate is the ratio of the difference between non-competitive and competitive adsorption observed at equilibrium:

$$\Delta q(\%) = \left((q_i^0 - q_i^{mix}) / q_i^0 \right) \times 100$$

According the Δq , Pb, Cu and Cd ions had different competitive effect. For Pb, adsorption capacity was reduced by 15.11%, 18.95% and 48.86% respectively (Pb²⁺ - Cd²⁺), (Pb²⁺ - Cu²⁺) and (Pb²⁺ - Cu²⁺ - Cd²⁺) systems. Similarly, the rate of adsorption equilibrium reduction of Cu, comparing to its adsorption in Monometal, decreased respectively by 15.71%, 35.71% and 38.57% in (Cu²⁺ - Cd²⁺), (Cu²⁺ - Pb²⁺) and (Pb²⁺ - Cu²⁺ - Cd²⁺) systems. Finally, for Cd, its adsorption capacity was reduced by 26.98% in (Cu²⁺ - Pb²⁺), by 84.13% in both (Cd²⁺

- Cu²⁺) and (Pb²⁺ - Cu²⁺ - Cd²⁺) systems. Therefore, the similarity between the Δq of Cd in (Cd²⁺ - Cu²⁺) and (Pb²⁺ - Cu²⁺ - Cd²⁺) systems may indicate that Cu can suppress Cd adsorption greater than Pb. According to the different rates of adsorption equilibrium reduction effect, the affinity sequence of the three metals for the soil in tri-metal adsorption systems is Cu²⁺ > Pb²⁺ > Cd²⁺. That means, when the three metals are in competition for the same sorption sites, Cu could displace Pb and Pb could displace Cd. Indeed, the affinity order found from Monometal adsorption batch tests, Pb²⁺ > Cu²⁺ > Cd²⁺, remained the same in competitive batch tests. In spite of the maximum capacity of Pb decreased related to competitive adsorption, it was mostly adsorbed on the soils over Cu and Cd.

IV. CONCLUSIONS

This study has shown in general that the soil of Nasarawa dumpsite has a high capacity to sorb metal ions. Results from kinetics batch tests have shown the applicability of a pseudo-second order model to describe the adsorption rates of each metal on the soil. The ranked affinity of the selected metals for the soil was Pb²⁺ > Cu²⁺ > Cd²⁺ according to maximum adsorption capacity obtained by the Langmuir model. Results from multi-metal batch tests indicated that competition between heavy metals for sorption sites can reduce their maximum adsorption capacity on the soil. On the basis of results from this study, Cd

may pose more threat to soils and groundwater of Nasarawa dumpsite than Pb and Cu. In short, regular groundwater samples and analysis may be carried out to assess changes in groundwater quality.

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