Adsorption-Desorption Characteristics of Zinc and Copper in Oxisol and Ultisol Amended With Sewage Sludge

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(Received on 21st April 2017, accepted in revised form 1st February 2018)

Summary: The process of adsorption-desorption of zinc and copper in highly weathered soils may affect their mobility and toxicity. In this study, we evaluated the effect of sewage sludge application on the adsorption-desorption behavior of Zn and Cu in highly weathered soils. Laboratory batch experiments were carried out to investigate the adsorption and desorption of Zn and Cu in an Oxisol and Ultisol amended with three rates of sewage sludge (T1=0% (control), T2=5% and T3 =10% sludge). The findings showed that sewage sludge application had significantly affected the processes of adsorption-desorption of the tested soils. This is shown by the systematic change of the distribution coefficients (Kd). Comparison between Kd values for both soils indicated the following selectivity of metals: Cu > Zn. It is clear that Zn adsorption was lower than that of the Cu. Generally, metals adsorption-desorption was higher in the Ultisol compared to that of the Oxisol which was due to Ultisol having higher CEC and OM content in comparison to those of the Oxisol. The adsorption isotherms of Zn and Cu of both soils were well fitted to linear Freundlich and Langmuir equations (with minimum R^2 = 0.96 and maximum R^2 = 0.99, respectively). The adsorption-desorption of metals was strongly correlated ($p<0.05$) with sewage sludge rates, CEC and OM.

Keywords: Adsorption-Desorption, Zinc, Copper, Sewage sludge, Oxisol, Ultisol.

Introduction

The presence of heavy metals in the sewage sludge has received great attention due to their potential toxicity to the environment. Addition of sewage sludge to soil has demanded great effort in the attempt to assess the dynamics of potentially heavy metals pollution [1].Presently, heavy metals in soils have been found in elevated concentrations, mostly due to anthropogenic inputs such as industrial waste deposits and sewage sludge application [2].Polluted soils often contain more than one heavy metal. Currently, there is a dearth of information on the maximum amount of heavy metals adsorbed from soil solution and the potential of these heavy metals migrating through soils [3].

Huang *et al.,* [4] define processes of adsorption-desorption as the most important mechanism which controlled bioavailability of metal ions in soils, transport as well as transformation. On the other hand, desorption mechanism is defined as the release of metal ions from different process of retention. Adsorption is the main contributors to the steady state of heavy metals such as Cu, Zn, and Cd in the soil [5]. The processes of adsorption-desorption is the most important mechanism which controlled bioavailability of heavy metals ions in soils. On the other hand, desorption mechanism is the release of heavy metal ions from different process of retention. Adsorption is the main contributors to the steady state of heavy metals such as Cu, Zn, and Cd in the soil [6, 7].

Adsorption–desorption process of heavy metals in soils affects their behavior in the environment. In most soil environment**,** adsorption is the dominating speciation process and thus the largest fraction of heavy metals in a soil is associated with the solid phase of that soil**.** Zinc and Cu gain more attention because of their high concentrations in sewage sludge (7012 and 732 mg kg^{-1} for Zn and Cu respectively). Consequently, we chose to study Zn and Cu, which are needed by plants even though at low concentration; but are toxic when they are present at high concentration. Yet zinc and copper have a contrasting behavior in soils, with Cu typically found less mobile than Zn [8].

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Zinc and copper toxicity depends on pH, which controls thier concentrations of soils.According to the World Health Organization-WHO and the Food and Agriculture Organization FAO [9], the concentrations of heavy metals in soils must not exceed permissible limits as a result of sewage sludge application. The maximum permissible concentration of Zn in acidity soil (pH 5-6) is 250 mg kg^{-1} and 135 mg kg^{-1} for Cu. According to the United States Environmental Protection Agency - USEPA [10] and Page *et al.,* [11], the limits for land application of sewage sludge shall not exceed the Maximum Acceptable Concentrations (MAC) Zn< 1850 mg kg^{-1} and Cu <760 mg kg^{-1} Zn and Cu respectively.

Compared to adsorption processes of heavy metals studies, very little information is available on desorption processes of heavy metals of soil, many studies have been undertaken in an attempt to clarify the factors that contribute to metal adsorption[12]. On other hand, relatively few studies have specifically examined the heavy metals desorption by a sewage sludge amended soils.

Thus, we aimed at studying Zn and Cu adsorption-desorption behavior in weathered Malaysian soils amended with sewage sludge to identify clearly their effects on the behavior of Zn and Cu. To make sound decision regarding Zn and Cu contamination in soils, it is necessary to have a thorough understanding of the mechanisms of Zn and Cu adsorption-desorption. Keeping this in view, the present study was conducted to investigate zinc and copper adsorption-desorption behavior in an Oxisol and Ultisol in Malaysia amended with sewage sludge.

Experimental

Materials

Two soil types, an Oxisol (Munchong Series) and Ultisol (Bungor Series), were used in this study. Soil samples were taken from the topsoil (0-20 cm depth) from two sampling sites located in Universiti Putra Malaysia, Serdang, and Peninsular Malaysia. The sewage sludge used was obtained from Indah Water Konsortium (IWK) Plant at Bandar Tun Razak Sewage Treatment, located in Kuala Lumpur. Soil samples and sewage sludge were dried, homogenized and then sieved (<2 mm). In this study, three rates of sewage sludge were applied (0, 5 and 10 % sludge w/w) in three replicates.

Methods

Soil pH was determined by a pH meter (soil: water ratio at 1:2.5) [13]. Texture was determined by the pipette method [14]. Soil mineralogy was determined by X-ray diffraction analysis using Philips x'pert[1] X-Ray diffractometer [15]. Cation exchange capacity was determined using autoanalyzer (8000series, Lachat Quick Chem FIA+, USA) according to the method of Ariyakanon and Winaipanich [16]. Organic matter content (OM %) in sewage sludge and soils was determined using loss on ignition mothed [17], where one gram of sample was placed in a crucible and put into a furnace at 350 °C for an h. The temperature was then raised to 550 °C and left for 24 hs. Then, the samples were cooled and weighed. Organic matter content (OM %) was calculated as the difference between the initial and final sample weights divided by the initial weight times 100%. Total concentrations of Zn and Cu in the solution were determined using inductively coupled plasma-optical emission spectrometry (ICP-OES) (Optima 8300, PerkinElmer, USA).

Batch adsorption study

In order to study the adsorption of Zn and Cu, a set of 5.00 g (< 2 mm fraction) was weighed into each of three 50 mL polyethylene centrifuge tubes and equilibrated with 35 mL of six concentration levels of metals at 0, 50, 100, 150, 200 and 250 mg L^{-1}. The tubes were shaken at room temperature for 24 hs until the adsorption reach the equilibration between soil and adsorption solution then centrifuged at 7000 rpm for 20 minutes using benchtop Centrifuge 4-16 BBI-8570060. The supernatant was collected, filtered (Whatman No.42) then analyzed for Zn and Cu (ICP-OES) (Optima 8300, PerkinElmer, USA). The adsorption was described empirically by the Freundlich and Langmuir equation [18]. All analyses were carried out in triplicate.

Desorption Study

Desorption of Zn and Cu was carried out following 24 hs adsorption step using sequential or successive dilutions of the slurries to induce Zn and Cu release. Washings of the two treated soils by the previous concentrations (50-250 ppm) were carried out by washings with 5 mL of water. A total of 7 washings (35 mL) were carried out for each sample. Filtration and determination of the released amounts were carried out as previously mentioned in the adsorption study used to describe the desorption phenomenon.

Data analysis

The amount of Zn and Cu adsorbed onto the solid phase was calculated as the difference between the concentration added and the concentration in solution at equilibrium:

$$q = C_0 - C_e \quad (1)$$

C_0 is initial concentration of sorbate
C_e is equilibrium liquid-phase concentration of sorbate

Distribution Coefficient

The simplest isotherm is the linear distribution coefficient (Kd), also called linear partition coefficient, is widely used to describe adsorption in soil [19]. Distribution coefficient (L kg^{-1}) was calculated as:

$$\mathbf{Kd} = \frac{\textbf{amount adsorbed (mg kg}^{-1}\textbf{ solid)}}{\textbf{adsorbed in the solution (mgL}^{-1}\textbf{)}} \quad (2)$$

The distribution coefficient is commonly used with the hypothesis that adsorption and desorption reactions are reversible. Using Kd for different soils is of potential importance to evaluate their adsorption capacity and the distribution between solid and soil solution phase [20].

However, distribution coefficients is a useful parameter for comparing the adsorption capacities of different soils under the same conditions, it can be obtained easily from batch adsorption experiments as a ratio of the heavy metal concentration in the solid phase (mg kg^{-1}) to that in solution (mg L^{-1}). A high value of Kd indicates a high adsorption [21]

The experimental data were fitted into the two most widely used isotherm models (Freundlich and Langmuir); these two models were linearized appropriately [18].

Freundlich Adsorption Isotherm

Freundlich equation is shown as:

$$Q_e = K_f \; C_e^{\frac{1}{n}} \quad (3)$$

where K_f= Freundlich isotherm constant (mg kg^{-1})

n= adsorption intensity
C_e =the equilibrium concentration of adsorbate (mg L^{-1})
Q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg kg^{-1})

Linearizing the equation we have

$$\log Q_e = \log K_f + {}^{1}\!/_{n} \; \log C_e \quad (4)$$

The constant K_f is an approximate indicator of adsorption capacity, while ${}^{1}\!/_{n}$ is function of the strength of adsorption in the adsorption process

Langmuir Isotherms

This equation described quantitatively the formation of a monolayer adsorbate

$$q_e = \frac{Q_0 \, K_L \, C_e}{1 + K_L C_e} \quad (5)$$

Langmuir adsorption parameters were determined by transforming the Langmuir equation into linear form:

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{Q_0 \, K_L \quad C_e} \quad (6)$$

where:

C_e= the equilibrium concentration of adsorbate (mg L^{-1})
q_e = the amount of metal adsorbed per gram of adsorbent at equilibrium (mg kg^{-1})
Q_0= maximum monolayer coverage capacity (mg kg^{-1})
K_L= Langmuir isotherm constant (L kg^{-1})

The values of q_{max} and K_L were computed from the slop and intercept of the Langmuir plot of ${}^{1}\!/_{q_e}$ versus ${}^{1}\!/_{C_e}$.

The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L, which is a dimensionless constant referred to as separation factor or equilibrium parameter

$$R_L = \frac{1}{1 + (1 + K_L \; C_0)} \quad (7)$$

where:

C_0 = initial concentration
K_L= the constant related to the energy of adsorption (Langmuir isotherm constant Lkg^{-1})

This monolayer model is obtained under the perfect supposition of a totally homogenous adsorption surface. It is then expected that once an adsorbate particle possesses a site, no further adsorption can occur at that site [22].

Desorption

Desorption stage was calculated as the difference between the initial adsorbed amount and the final desorbed amount [19]**:**

$$R_b = \frac{C_d}{C_a} 100 \quad (8)$$

where:

R_b is percent metal desorbed (%)
C_d is concentration of sorbate onto the solution (mg L^{-1})
C_a is initial concentration of sorbate (mg L^{-1})

Statistical analysis

Data collected from this study were analyzed by analysis of correlations, variances and Tukey for mean comparison using SAS version 9.4 (SAS Institute, Inc., Cary, N.C., USA). Pearson correlation coefficient analysis was used to find the correlation between adsorbed and desorbed of studied metals and selected soil properties. By this correlation we measured the strength of a linear relationship between two variables at $p < 0.05$ and were represented by r.

Results and Discussion

Soils and sewage sludge characterization

As seen in Table-1, both of the Oxisol (Munchong Series) and Ultisol (Bungor Series) were acidic (pH 4.77 - 5.84). The Ultisol showed a higher organic matter content (OM) and cation exchange capacity (CEC) than the Oxisol; their topsoil was sandy clay loam in texture. The pH of the sewage sludge was 6.04 with high OM content of 30.10%, while its CEC was 26.28 $cmol_c$ kg^{-1}. Based on the results of this study, the application of sewage sludge to highly weathered soils, such as Oxisol and Ultisol, was justified because of the improvement of soil fertility, shown by the increase in their pH, OM and CEC. Cation exchange capacity is a measure of the soil's ability to hold positively charged ions, It is a useful indicator of soil fertility because it shows the soil's ability to supply the important plant nutrients such as Ca, Mg and K [23]. Soil pH has an effect on CEC of soil. It is important for CEC because as pH increases, the number of negative charges on the colloids increase, thereby increasing CEC. The chemical properties of the soils were much affected by sewage sludge addition. This was especially shown by the increase in soil pH Due to its application, the CEC of the Oxisol was increased from 8.00 to 9.39 $cmol_c$ kg^{-1}, while that of the Ultisol, it was from 10.33 to 11.22 $cmol_c$ kg^{-1}. The best treatment was when 10% sewage sludge was applied. The CEC of the soils is expected to increase with increasing soil pH because of the presence of variable change minerals in both soils.

The Oxisol and Ultisol used in this study were dominated by kaolinite and sesquioxides, which are known to have variable charge surfaces. The XRD peaks of 7.21 and 3.58 Å proved the presence of kaolinite (Fig. 1), while that of gibbsite and hematite were shown by the respective peaks of 4.18 and 2.51 Å. The result of the XRD analysis was consistent with that of Shamshuddin and Anda [24].

Adsorption isotherm and distribution coefficients

Distribution coefficient represents the adsorption affinity of metals for the solid phase. The adsorption of Zn and Cu in the Oxisol and Ultisol was studied through batch equilibration. The amount of metal adsorbed by soil was calculated from the difference between the amount added and that recovered after 24 hs of equilibration. The distribution coefficient for each metal was calculated. This approach is the ratio of the concentration of metal adsorbed on a solid to the metal concentration in a liquid phase at equilibrium Kd (L kg^{-1}). It is also the simplest adsorption model available. The impact of sewage sludge rates has been explained based on the computed Kd values. Adsorption isotherms for Zn and Cu were determined by plotting the concentration of Zn and Cu adsorbed in soil q= x/m (where x/m is the maximum adsorbed metal concentration) versus their concentrations in the solution phase at equilibrium (Ce) (Fig. 2 and 3).

The results (Fig. 2 and 3) showed that the distribution coefficients increased as the sewage sludge rates increased in the following sequence: T3 (10% sewage sludge) ≥ T2 (5% sewage sludge) > T1 (control soil-0% sewage sludge). For the Oxisol, the Kd of Zn was 2.81 L kg^{-1} in T3 > 2.72 L kg^{-1} in T2 > 2.18 L kg^{-1} in T1 (control soil - 0% sewage sludge). On the other hand, for Cu, Kd was 3.35 L kg^{-1} in T3 > 3.24 L kg^{-1} in T2 > 3.18 L kg^{-1} in T1. A similar trend was observed in the Ultisol where the Kd for Zn was 2.82 L kg^{-1} in both T2 and T3 > 2.68 L kg^{-1} in T1, while for Cu Kd was 3.42 L kg^{-1} in T3 > 3.41 L kg^{-1} in T2 > 3.23 L kg^{-1} in T1. It is worthy to note that Cu reported the highest distribution coefficients values, followed by Zn. A high value of Kd means high metal retention by the solid phase through chemical reactions [25].

The increased adsorption of the studied metals by the treated soils is expected due to the increase in CEC and OM content. The increase in soil organic matter would increase the CEC which, in turn, increased Zn and Cu adsorption. Soil organic matter is the main factor affecting adsorption of Zn and Cu in soil.The presence of organic matter is important due to its properties as a complexing agent, OM has a strong affinity for Cu, especially under acidic conditions. However, the result of this study showed that the adsorption of Cu was higher in contrast to that of Zn. This phenomenon was already confirmed by the study of Shaheen *et al.* [26] who found that more Cu was adsorbed into soils than Zn.

Table-1: Chemical, physical and mineralogical properties of the Oxisol and Ultisol.

Properties	Sewage Sludge	Oxisol			Ultisol		
		Treatments			Treatments		
		0%	5%	10%	0%	5%	10%
pH	6.04	5.36c	5.66b	5.84a	4.77 c	5.01 b	5.37a
CEC (cmol$_c$ kg^{-1})	26.28	8.00c	9.11b	9.39a	10.33c	10.67b	11.22a
OM (%)	30.10	1.23b	2.20ab	2.4a	2.20c	4.48b	5.52a
Sand (%)	-		66.48			62.69	
Clay (%)	-		28.01			28.37	
Silt (%)	-		5.44			8.89	
Mineralogy	-		kn, gb,ht			kn, gb,gt	
Texture	-		Sandy clay loam			Sandy clay loam	

OM = organic matter, *Kn= kaolinite; gb= gibbsite; gt=goethite; ht=hematite*

Means in same column for same soil with the same letter are not significantly different at p≥0.05 according to Tukey test.

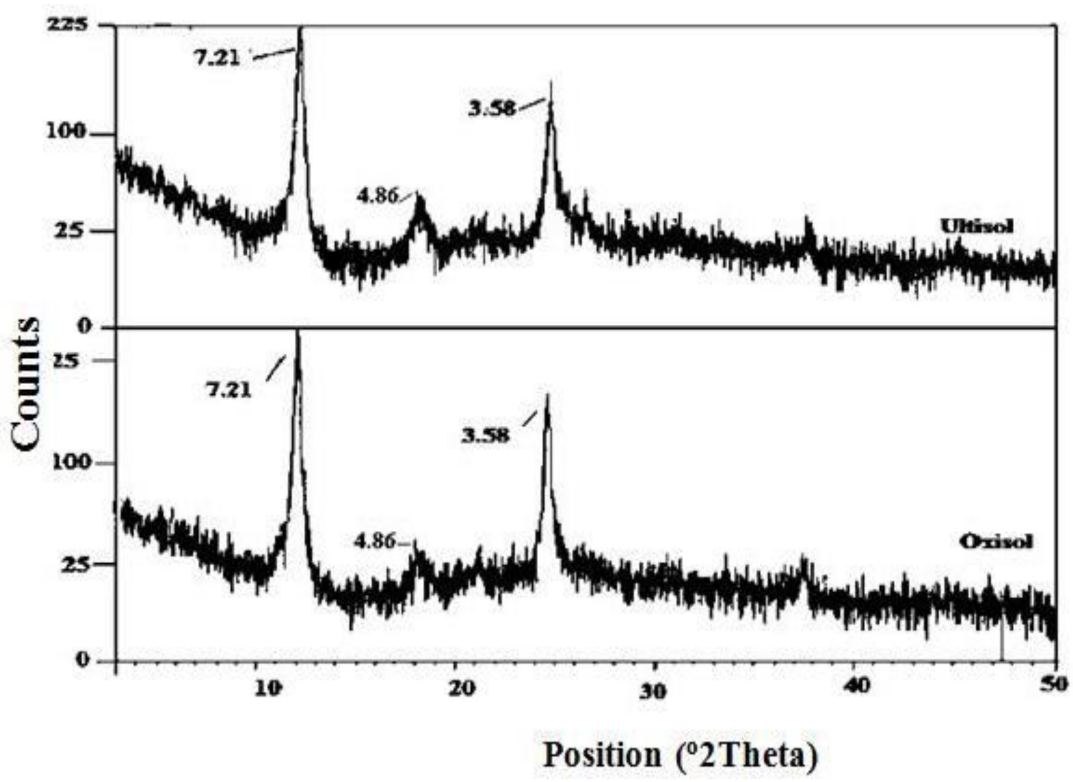

Fig. 1: X-ray diffractograms of clay fraction of the soils.

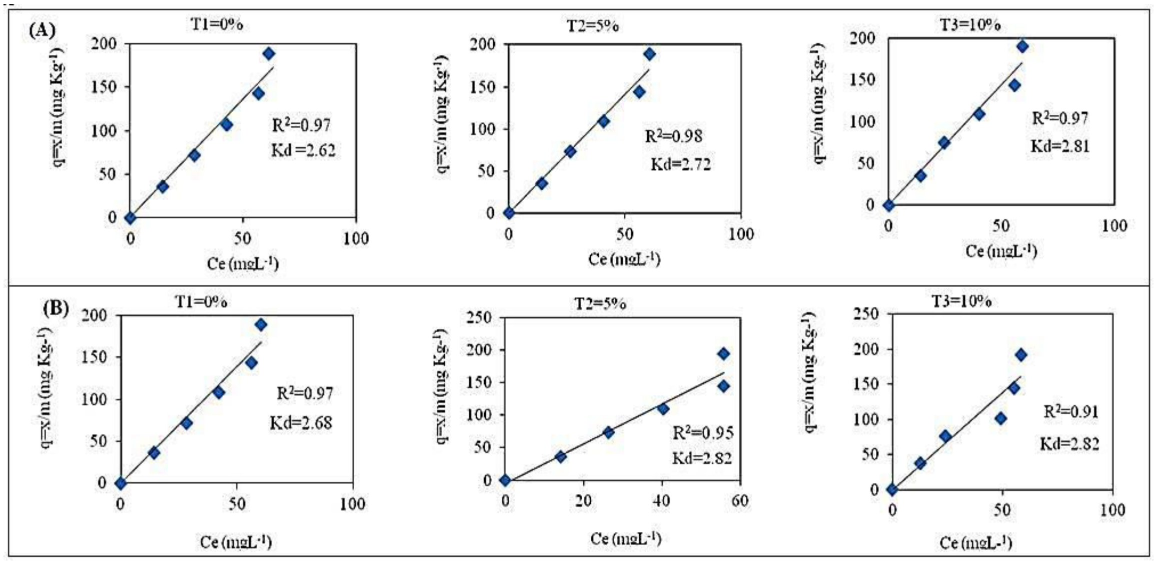

Fig. 2: Distribution coefficients of zinc for Oxisol amended with sewage sludge (A) and Ultisol (B).

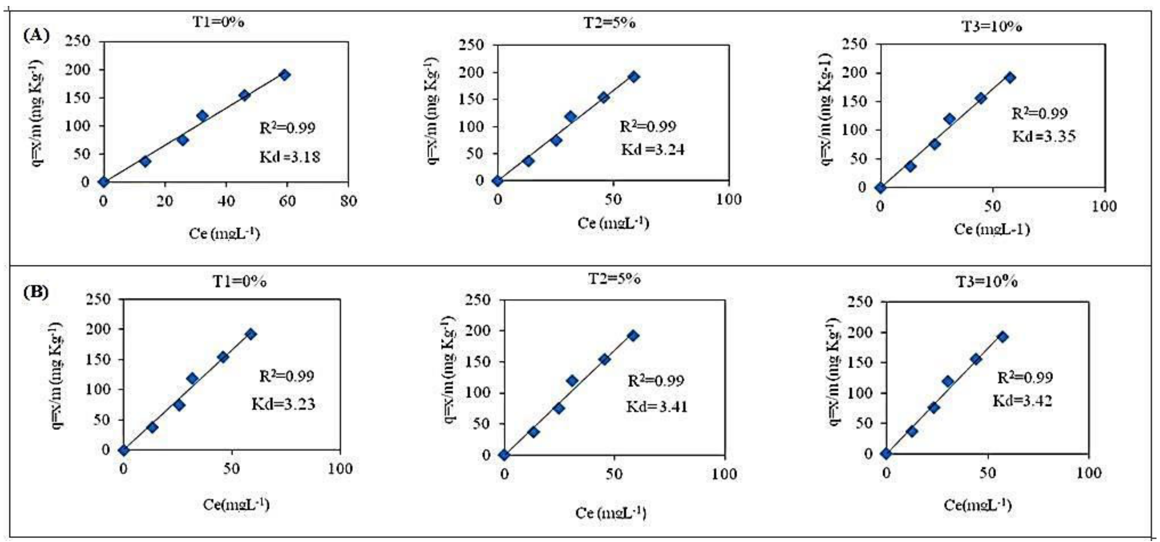

Fig. 3: Distribution coefficients of copper for Oxisol amended with sewage sludge (A) and Ultisol (B).

This study indicated that the adsorption and desorption data were of major importance in understanding the overall fate of Zn and Cu in the soils. The impact of sewage sludge application was explained based on the computed Kd values (Fig. 2 and 3). The distribution coefficient (Kd) was used to compare the behavior of the heavy metals in the two soils. It was found that Kd was positively correlated with metal adsorption capacity of the soils, which was in line with the finding of Cerqueira *et al* [27].

As indicated by the results, treatment T2 (5% sewage sludge) and T3 (10% sewage sludge) showed higher Kd values than that of the control (T1) for all soil types. The higher Kd values for treated soils means that the application of sewage sludge provided additional adsorption sites for Zn and Cu, with the following sequence: T3 > T2 > T1. This order of adsorption was consistent with the increase in OM and CEC due to treatment. Thus, the adsorption process was dependent on numerous factors, such as sewage sludge rates and soil properties. Based on Kd values, Cu was adsorbed more compared to that of Zn. Copper affinity for organic matter (OM) complex formation is recognized as one of the most effective mechanism of Cu retention in soils.

Freundlich and Langmuir isotherms

Adsorption Freundlich and Langmuir isotherms were employed to describe the adsorption of Zn and Cu on Oxisol (Munchong Series*)* and Ultisol (Bungor Series) amended with sewage sludge. Langmuir isotherm is mainly applied to monolayer adsorption. The obtained data were well fitted to linear Freundlich and Langmuir models with high R^2 values (Fig. 4, 5).

For the Freundlich isotherm model, R^2 values ranged between 0.97 and 0.99 for Zn and Cu, respectively in the case of Oxisol, while for the Ultisol, the R^2 values ranged between 0.96 and 0.97 for Zn and Cu, respectively (Fig. 4). In the case of the Langmuir isotherm model**,** the R^2 values ranged between 0.96 and 0.99 for Zn of the Oxisol. For the Ultisol, the R^2 value for Zn was 0.99. The R^2 values ranged between 0.97 and 0.99 for Cu in the Oxisol and Ultisol, respectively (Fig. 5). Copper have strong affinity for fulvic and humic acids and form stable complexes with humic substances

The linear plots were obtained for both cases, pointing to the ability of these isotherms to describe the adsorption phenomenon [28]. A comparison of coefficient of determination for two isotherms has been made and listed in Table-2. The Freundlich and the Langmuir isotherms were fitted for the adsorption of Zn nd Cu. Linear forms of the isotherms models are also widely adopted to determine the isotherm parameters or the most fitted model for the adsorption system due to the mathematical simplicity [29]. The Freundlich isotherm parameter 1/n measures the adsorption intensity of Zn and Cu ions on the tested soils. The high 1/n value of Cu (0.68) in compare to Zn (0.59) indicates the preferential sorption of Cu than Zn, and shows the ability of the amended soils to adsorb these two metal ions. The maximum K_f value of Cu (2.29 L kg^{-1}) is greater than that of Zn (1.28 L kg^{-1}) suggesting and confirming that Cu has greater adsorption tendency than Zn.

For Langmuir isotherm model, the maximum K_L value of Cu (1.65 L kg^{-1}) is greater than that of Zn (0.39 L kg^{-1}). The data in Table-2 further indicated that, the effectiveness of amended soils in the sorption of Zn and Cu was Cu >Zn. The results indicated that the adsorption data of Cu and Zn were generally well correlated with Langmuir and Freundlich models.

Kinetics of zinc and copper desorption

Desorption process resulted in the mobilization of the previously adsorbed zinc and copper. As the results in Table-3 showed, the quantity of desorption of the metals was related to their initial concentration in the soils, with the amount increasing with the increase in their concentration. This is probably due to an already high enough Zn and Cu concentration in the soils to cause an appreciable increase in desorption of these metals.

The percentage of desorption of Zn and Cu from the Oxisol and Ultisol varied and it increased with the increase in the added sewage sludge for both soils. As shown in Fig. 5, high percentage of desorbed Zn and Cu were found in the treated soils (51.7 and 41.74% of Zn in the Oxisol and Ultisol, respectively) and (39.74 and 38.34% of Cu in the Oxisol and Ultisol, respectively). Zinc is much more easily desorbed owing to its weak attraction with soil components [30]. It is thus important to assess desorption phenomenon in soil as it reflects some of the interactions involving its chemical properties and heavy metals [31].

Desorption is the inverse of adsorption phenomenon and is a key process affecting heavy metals behaviors in soils. It was found that sewage sludge treatments had major influence on Zn and Cu desorption, with its values increased with increasing rate of sewage sludge application. The highest value was found for the 10% sewage sludge application. The results showed that 41.74 - 51.70% of Zn and 38.34 - 39.74 % of Cu were desorbed from the treated Oxisol and Ultisol.

Zinc desorption was higher in comparison to that of Cu due to its lower adsorption affinity [32]. The high percentage of Zn desorption from the soils receiving sewage sludge was indicative of its potential pollution risk in the soils. Zinc and copper are heavy metals of much of interest in recent years because of their toxic effects on crops if present at high concentration [33].

Adsorption-desorption phenomena of Zn and Cu in soil

A correlation study was conducted to investigate the relationship between soil properties and Zn or Cu adsorption-desorption behavior. Factors governing the adsorption-desorption depend not only on Zn and Cu concentration in the tested soils, but also on soil chemical properties (Table-4).

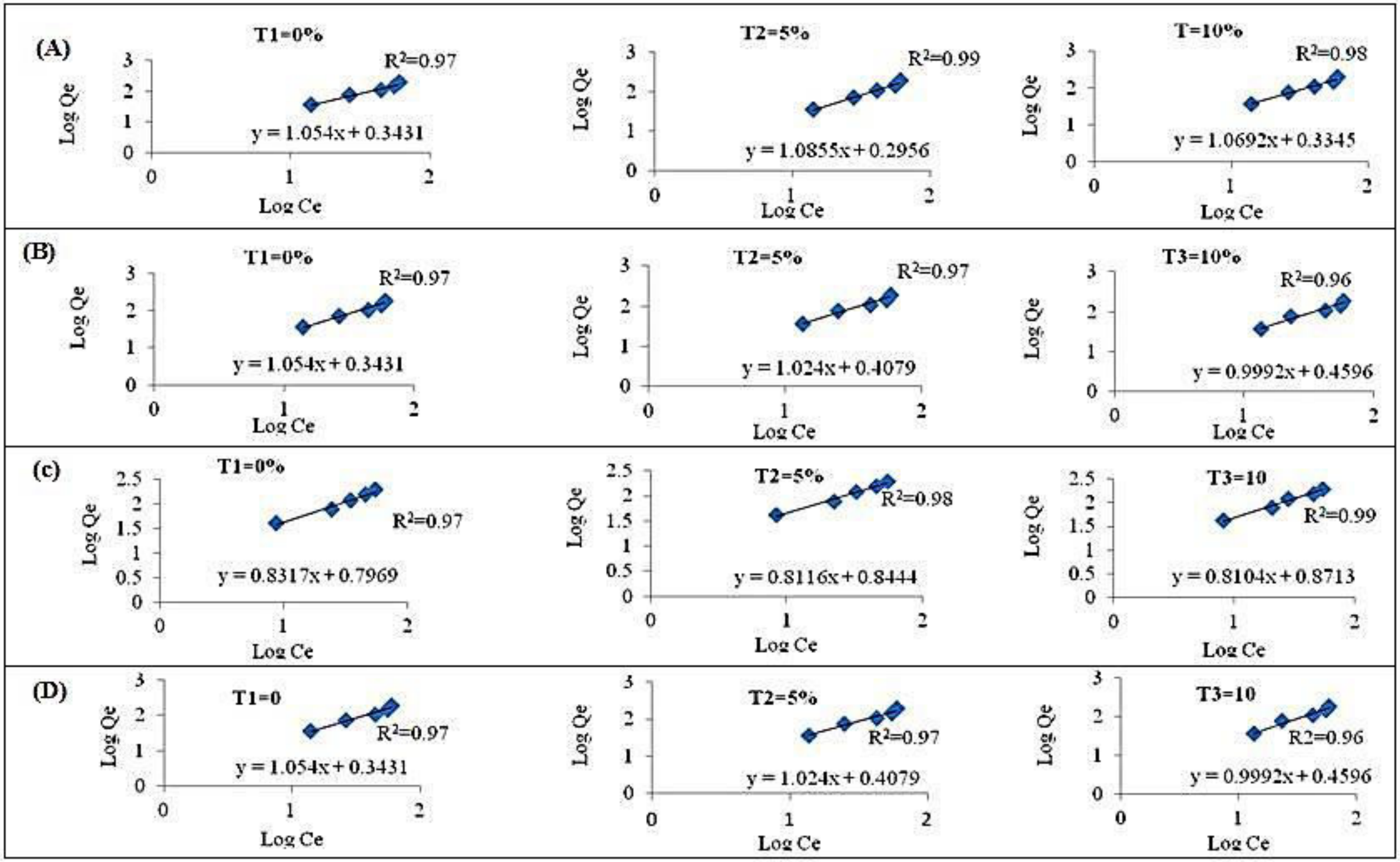

Fig. 4: Freundlich adsorption isotherm of Zn for the Oxisol (A), Freundlich adsorption isotherm of Zn for the Ultisol (B), Freundlich adsorption isotherm of Cu for the Oxisol (C) and Freundlich adsorption isotherm of Cu for the Ultisol (C).

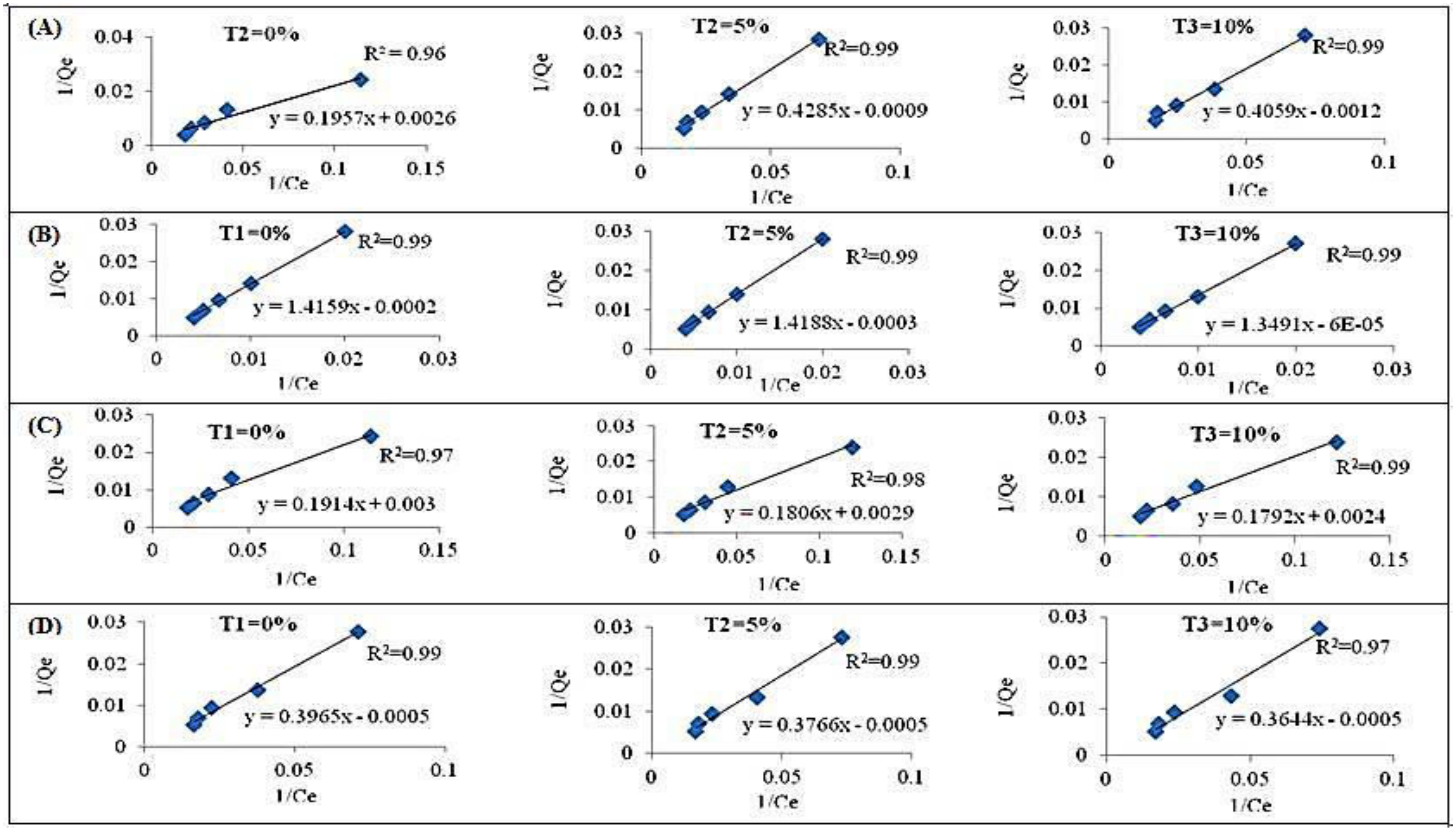

Fig. 5: Langmuir adsorption isotherm of Zn for the Oxisol Figure (A), Langmuir adsorption isotherm of Zn for the Ultisol (B), Langmuir adsorption isotherm of Cu for the Oxisol (C) and Langmuir adsorption isotherm of Cu for the Ultisol (D).

Table-2: Parameters of the Freundlich and Langmuir equations for adsoroption of Zn and Cu in Oxisol and Ultisol treated with sewage sludge.

Element	Soil	Sewage sludge(%)	Freundlich model			Langmuir model	
			K_f ((L kg^{-1})	$1/n$	R^2	K_L (L kg^{-1})	R^2
Zn	Oxisol	0	1.23	0. 13	0.97	0.21	1.00
		5	1.24	0. 16	0.97	0.20	1.00
		10	1.28	0.15	0.98	0.22	0.99
	Ultisol	0	1.23	0. 53	0.97	0.34	1.00
		5	1.22	0. 36	0.97	0.38	1.00
		10	1.24	0.59	0.96	0.39	1.00
Cu	Oxisol	0	1.31	0.21	0.97	0.42	0.97
		5	1.32	0.41	0.98	0.41	0.98
		10	1.32	0.61	0.99	0.49	0.99
	Ultisol	0	1.24	0.25	0.97	1.40	0.99
		5	1.24	0.41	0.97	1.40	0.99
		10	2.29	0.68	0.96	1.65	0.97

Table 3. Desorption of Zn and Cu from the Oxisol and Ultisol

Soil	Sewage sludge (%)	Initial concentrations of metals (mgL^{-1})									
		50		100		150		200		250	
		Zn	Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn	Cu
Oxisol	0	17.46±1.02e	16.46±0.98e	21.70±0.56d	21.52±0.84d	29.23±0.82c	26.92±0.40c	42.06±0.22b	38.61±0.44b	70.81±0.19a	60.83±0.49a
	5	19.91±1.01e	17.95±0.97e	22.14±0.60d	22.05±0.85d	30.11±0.84c	27.11±0.43c	42.53±0.28b	35.53±0.49b	71.13±0.18a	61.85±0.42a
	10	20.87±1.01e	19.87±0.87e	24.46±0.63d	24.07±0.89d	30.61±0.86c	27.68±0.47c	43.03±0.21b	40.61±0.48b	71.50±0.15a	62.53±0.44a
Ultisol	0	17.46±1.01e	16.15±0.88e	21.20±0.78d	21.05±0.84d	28.58±0.48c	26.39±0.35c	38.61±0.69b	38.16±0.87b	70.14±0.10a	60.18±0.19a
	5	19.91±1.05e	17.25±0.87e	21.50±0.77d	21.60±0.89d	29.61±0.49c	26.72±0.39c	39.53±0.62b	39.23±0.85b	70.38±0.15a	61.65±0.15a
	10	20.87±1.02e	19.17±0.85e	23.70±0.44d	23.66±0.84d	30.26±0.42c	27.58±0.31c	40.99±0.67b	40.31±0.88b	70.50±0.18a	62.13±0.19a

Values shown are the means ± Standard deviations of three replicates

Mean values with the same letter within a row for each soil are not significantly different at $p<0.05$.

Table-4: Pearson correlation coefficient between Zn and Cu Adsorption-desorption and soil properties.

Soil		T	pH	CEC	OM
Oxisol	Adsorbed-Zn	0.98*	0.98*	0.93*	0.93*
	Adsorbed-Cu	0.60*	0.76*	0.63*	0.75*
	Desorbed-Zn	0.99*	0.94*	0.90*	0.88*
	Desorbed-Cu	0.99*	0.97*	0.97*	0.95*
Ultisol	Adsorbed-Zn	0.79*	0.72*	0.66*	0.90*
	Adsorbed-Cu	0.98*	0.97*	0.93*	0.95*
	Desorbed-Zn	0.94*	0.91*	0.92*	0.95*
	Desorbed-Cu	0.96*	0.92*	0.88*	0.99*

* Significant at $p<0.05$

T = Treatments of sewage sludge

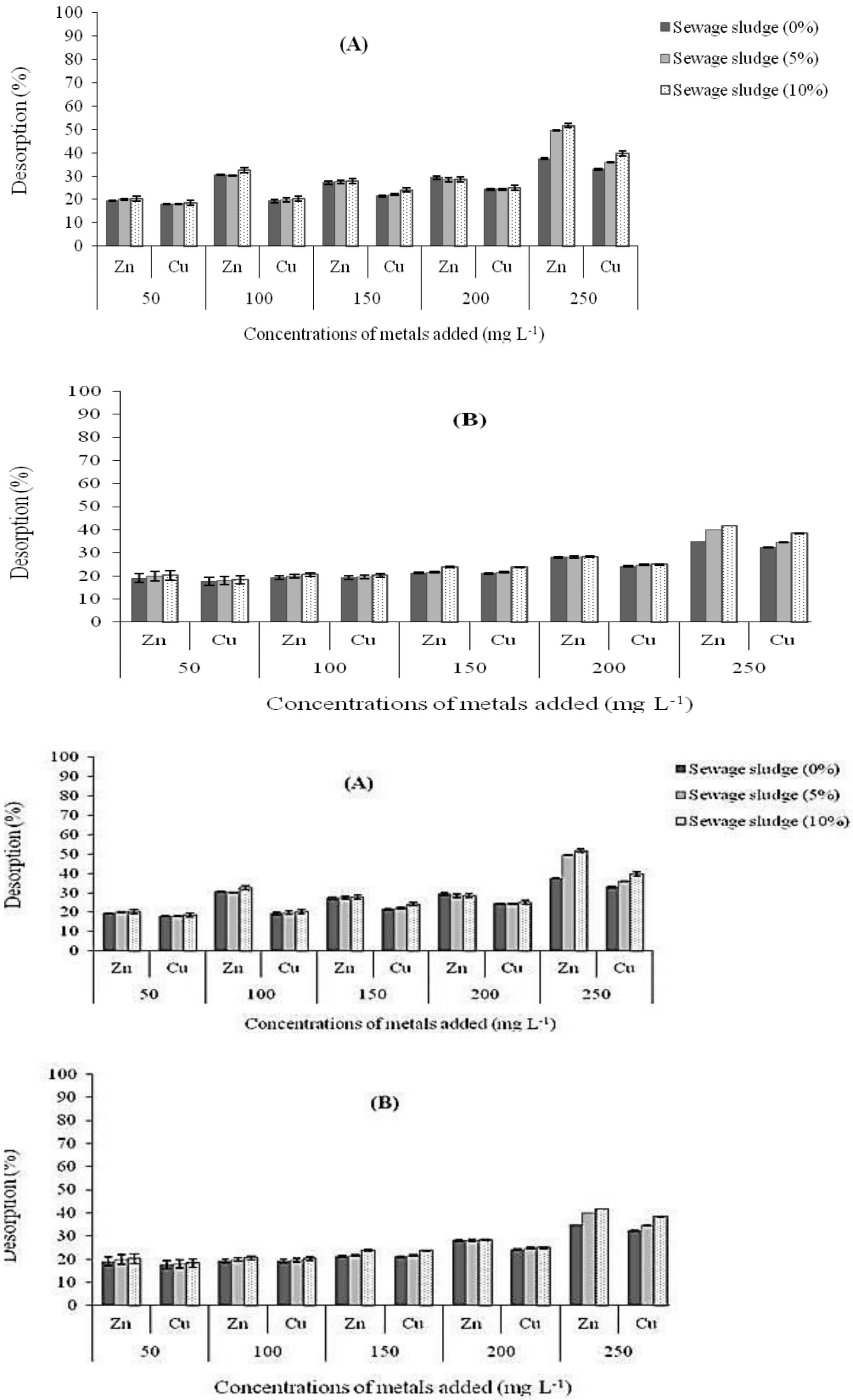

Fig. 6: Desorption of Zn and Cu from the Oxisol (A) and Utisol (B).

Significant correlations were clearly appeared according to Pearson correlation between adsorption-desorption processes of Zn and Cu and sewage sludge treatments, pH, CEC and OM. As the results had shown, the amounts of adsorbed–desorbed Zn and Cu present significant correlation with those parameters (minimum r= 0.60 and maximum r = 0.99) in all treatments (N=18). The variances in these properties can be expected to affect Zn and Cu adsorption-desorption characteristics in the tested soils.

Significant correlations at $p<0.05$ were found between sewage sludge treatments and adsorption-desorption of Zn and Cu, with r ranging between 0.60 and 0.99 for the Oxisol and between 0.79 and 0.98 for the Ultisol. Additionally, the results indicated that pH played a significant role on controlling the adsorption-desorption of Zn and Cu, with r of 0.76-0.98 and 0.72-0.97 for the Oxisol and Ultisol, respectively.

Data from current study clearly indicated high correlations existed between the studied metals and CEC. The significant correlation of Zn and Cu adsorption with CEC showed that the higher the value of CEC was, the more sites of exchange on soil minerals were available for Zn and Cu retention, since these heavy metals are cations that can be adsorbed on the soil exchange complex . This is consistent with the explanation given by Shaheen *et al.* [34].

The results of the present study clearly indicated the role of organic matter on adsorption-desorption of Zn and Cu. The interaction between adsorption-desorption of the studied metals and OM was significant at $p < 0.05$ in all treatments. The OM has a great impact on desorption of the studied metals, where high correlations were observed between the OM and desorption of Cu, with r of 0.95 and 0.99 in the Oxisol and Ultisol, respectively. For Zn, the r was slightly lower, with the value of 0.88 and 0.95 in Oxisol and Ultisol, respectively. From these results, it is clear that Cu was highly bound to the organic matter.

The adsorption of Cu and Zn on the soils was greater in the treated compared to that of the untreated soils (Table-4). Thus, it was clear that the adsorption of both metals were related with sewage sludge application which, in turn, affecting OM content, soil pH and CEC. Copper has been found to be adsorbed strongly by the OM contained in the sewage sludge (with r=0.95), which was in line with the findings of Karam *et al.* [33].

The CEC of the soils is their capacity to adsorb metals, meaning that increase in CEC would create extra exchange sites on mineral surfaces in the soils [35]. This study found that the two soils had exhibited different capacities to adsorb Zn and Cu at different rates of sewage sludge application. Therefore, it can be assumed that sewage sludge application not only had the ability to change soil properties, but also had positive impact on the Zn and Cu adsorption in the Oxisol and Ultisol. Due to their adsorption, Cu and Zn would finally become part of the soil solid phase. In acid soils, it is known that Cu is mainly adsorbed on the specific sites, Copper ions forms strong coordination complexes with organic matter. While Zn is retained on nonspecific sites of the soils. Zinc prefers sorption to the mineral fraction of soils and bonding is often expected as exchangeable [36]. Zn readily forms complexes with organic matter it does not compete for these sites as well as Cu. The increased affinity for organic matter of Cu relative to Zn has been reported by several workers [37]

According to the results given in Tabe4, desorption of the studied metals was significantly correlated with the rate of sewage sludge application (T), pH, CEC and OM at $p < 0.05$ for all treatments. Further, it was found that treatments and soil properties have major influence on Zn and Cu desorption. Highly significant correlations were found between desorption of Zn and Cu and OM. However, sewage sludge application is a useful way of disposal compared to other methods, but can lead to the increase of heavy metals concentrations in soils. The environmental risk associated with heavy metals accumulation in soils that received sewage sludge applications depends primarily on the pH of soil and sewage sludge treatments [38].

Sewage sludge organic matter may increase CEC soil values, and strongly bind heavy metals to the soil. The behavior of soils treated with sewage sludge might be expected to differ from untreated soils, because of the increase of both organic matter and heavy metal levels

Conclusion

The present study illustrated the sewage sludge application effect on the behavior of zinc and copper adsorption-desorption isotherm on Oxisol and Ultisol. The absorptive capacities of zinc and copper ions were observed to be higher in the sewage sludge treated soils than untreated soils. The adsorption selectivity were found to follow the following trend Cu > Zn in both soils. Copper was much controlled by organic matter content, while Zn is found to be much more easily desorbed due to its chemical characteristics and weak binding to the soil. It could be concluded that adsorption-desorption isotherm is influenced by soil properties, such as pH, CEC and OM

Acknowledgements

We wish to acknowledge Universiti Putra Malaysia for financial and technical supports.

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