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## Research Article

# Adsorption of Cadmium, Copper, Lead and Zinc on Organically Amended Soil Fractions Using the Freundlich, Langmuir and Dubinin-Raduskevich Models

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## Abstract

**Background and Objective:** High concentration of heavy metals has been discovered in the vegetables in growing area of Kano posing a risk to the soil and its productivity. The feasibility of organic residues such as maize cob and rice husk as adsorbent were evaluated in heavy metal-contaminated soils. The objective of this study was to assess efficacy of using maize cob and rice husk obtained as bio-sorbents in reducing soil solution concentration of heavy metals as well as the influence of contact and residence time on the adsorption of heavy metals: Cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn) by different soil fractions (silt-clay and very fine sand).

**Materials and Methods:** Soil samples were collected from five vegetable gardens in Kano and fractionated into silt-clay and very fine sand fractions. Cu, Pb, Zn in the varying concentration 0, 50, 200 and 400 mg kg<sup>-1</sup> and 0, 5, 10 and 50 mg kg<sup>-1</sup> Cd were added to the soil along with organic residue. This was incubated for a period of 1 and 7 days. Concentration of the heavy metal after the incubation periods was determined at time intervals of 1, 2, 4 and 8 h in a batch experiment. Data were analyzed using two-way ANOVA. **Results:** Results obtained showed that sorption increased with time, dosage of the organic residue and incubation. Amongst all the residues, maize cob had better sorption efficiency. The adsorption data obtained were perfectly fitted to the Freundlich adsorption model with an R<sup>2</sup> value of 0.99 for Cu, Pb and Zn and the sorption process was found to be a cooperative process between Cu, Pb and Zn. For Cd, the R<sup>2</sup> was >0.80 with a favorable and normal adsorption process. **Conclusion:** Heavy metal sorption by the organic residues at all concentrations was very high. A positive relationship between the rate of adsorption and dosage was obtained indicating that the adsorption process was influenced by increasing the dosage of the residue as well as the shaking period. These amendments which are mostly byproducts of agricultural processing can be used as an excellent source of reducing heavy metal availability in contaminated soils.

**Key words:** Heavy metals, incubation, shaking period, adsorption model, sorption efficiency, organic residues, contact time, residence period

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**Data Availability:** All relevant data are within the paper and its supporting information files.

## INTRODUCTION

Heavy metal is a loose term for a group of elements that exhibit metallic properties including the transition elements, some metalloids, actinides and lanthanides<sup>1</sup>. Agricultural activities such as wastewater irrigation and use of agrochemicals<sup>2-7</sup> have led to the excessive release of heavy metals such as Cd, Zn, Cu and Pb into the environment, thus, creating a major global concern related to environmental and human health problems. Very worrisome concentration of Pb, Cd, Cu and Zn has been reported in Kano<sup>8-10</sup>. These high concentrations affect the soil productivity as well as physiological process in plant such as inhibition of photosynthesis as in the case of Pb uptake. Heavy metals pose a great danger to human health in areas where vegetable is cultivated due to its direct inclusion in food chain<sup>11,12</sup>.

Various treatment techniques and processes have been used to remove heavy metals from contaminated water and soils<sup>13</sup>. Among all the approaches proposed, sorption has been considered as one of the most popular methods for economic and efficient purification of heavy metal contaminated soils and water<sup>14</sup>. Adsorption is one of the physicochemical treatment process effective in removing heavy metals from aqueous solutions and according to Bailey *et al.*<sup>15</sup>, an adsorbent can be considered as cheap if it is abundant in nature and requires little processing and is a by-product or waste material from industry. The major advantages of using organic residue as adsorbent in sorption processes as compared to conventional treatment methods are: Low cost, minimization of chemical and/or biological sludge, regeneration of bio-sorbent and no additional nutrient requirement and possibility of metal recovery. Plant wastes are inexpensive as they have very low economic value. Several studies have been conducted on the use of organic residues such as papaya wood<sup>16</sup>, maize leaf<sup>17</sup>, teak leaf powder<sup>18</sup>, lalang (*Imperata cylindrica*) leaf powder<sup>19</sup> and rubber (*Hevea brasiliensis*) leaf powder<sup>20,21</sup> as adsorbent for heavy metal removal in contaminated soil. There is a growing trend to evaluate the feasibility and suitability of natural, viable, renewable and low-cost materials as adsorbent to ameliorate heavy metal pollution. The objectives of the current study were:

- To determine the efficacy of using maize cob and rice husk obtained as bio-sorbents in reducing soil solution concentration of heavy metals in polluted soils
- To determine the influence of contact and residence time on the adsorption of heavy metals such as Cd, Zn, Cu and Pb in soils

## MATERIALS AND METHODS

**Sampling and sample preparation:** Soil samples were collected to a depth of 20 cm from five different vegetable gardens in Gadon-Kaya area of Kano city at a co-ordinate of 11°58'25.040" N and 8°29'46.056" E. Five sub-samples were taken from each vegetable gardens and mixed thoroughly together to obtain a single representative sample. The soil samples were air dried, crushed gently and passed through 2 mm sieve and further separated by sieving into silt- clay and very fine sand fraction.

Two different types of organic residues were used: Rice husk, maize cob and a mixture of the rice husk and maize cob. The rice husk was used in its original form while the maize cob was crushed into fine particles.

**Laboratory analysis:** Particle size distribution was determined using the principles of Bouyoucous-hydrometer method following chemical dispersion of the soil with calgon solution<sup>22</sup>. Cation exchange capacity (CEC) was determined by replacing the cations on the exchange sites with 1 M ammonium acetate (NH<sub>4</sub>OAC) buffered at pH 7 as described by Rhoades<sup>23</sup> while exchangeable bases was determined as according to Anderson and Ingram<sup>24</sup>. Soil pH was measured in both water and CaCl<sub>2</sub> at a soil: Water and soil CaCl<sub>2</sub> ratio of 1:2.5 using a glass electrode pH meter. Organic carbon (OC) content of the soil was determined by dichromate oxidation method<sup>25</sup>. Total N was determined using the micro- Kjeldahl digestion method of Bremner and Mulvaney<sup>26</sup> while available P was extracted using the Bray 1 method<sup>27</sup>.

**Adsorption experiment:** The soil samples from each fraction i.e. silt- clay and very fine sand were thoroughly mixed with the organic residue in the ratio 1:2, 1:3 and 1:4 (i.e. 1 g of soil: 2 g of organic residue, 1 g of soil: 3 g of organic residue and 1 g of soil: 4 g of organic residue). The soil sample plus organic residue were then transferred into the incubation vessels and 20 mL each of the varying concentrations of heavy metal (0, 50, 200 and 400 mg of Cu, Pb and Zn per gram of soil while 0, 5, 10 and 50 mg of Cd per gram of soil) were added. The samples were subjected to two different incubation period (1 and 7 days). All samples were replicated 3 times.

After the incubation period, the samples were placed on a mechanical shaker and shaken for a period of 1, 2, 4 and 8 h. Fifteen milliliter of the suspension was taken and filtered into a bottle after each shaking period and the amounts of Cd, Cu, Pb and Zn in the supernatant were determined using the AAS (Buck Scientific VGP 210). The amount of heavy metal sorbed

by the soil organic residue mixture was calculated from the difference of the initial and equilibrium heavy metal concentration.

**Sorption isotherms:** Sorption isotherms were used to partition added heavy metals between soil and solution phase. The adsorption isotherms used are Langmuir, Freundlich and Dubinin-Radushkevich (D-R) models.

**Freundlich adsorption isotherm:** The Freundlich isotherm<sup>28</sup> can be applied for non-ideal sorption on heterogeneous surfaces and multilayer sorption. The Freundlich Eq. is expressed as:

$$q_e = K_f C_e^{1/n}$$

Where:

- $q_e$  = Amount of metal adsorbed (mg g<sup>-1</sup>)
- $C_e$  = Concentration of the metal at equilibrium (mg L<sup>-1</sup>)
- $K_f$  = Intercept at zero equilibrium concentration
- $n$  = Adsorption intensity

The linear form of the above Eq. is given as:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

**Langmuir adsorption isotherm:** The Langmuir adsorption model<sup>29,30</sup> is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with no lateral interaction between the adsorbed molecules. Langmuir model is represented by the following Eq.:

$$q_e = \frac{q_0 K_L C_e}{1 + K_L C_e}$$

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

Where:

- $q_e$  = Amount of metal adsorbed (mg g<sup>-1</sup>)
- $C_e$  = Concentration of the metal at equilibrium (mg L<sup>-1</sup>)
- $q_0$  = Maximum adsorption capacity (mg g<sup>-1</sup> or mol g<sup>-1</sup>)
- $K_L$  = Langmuir constant related to the energy of adsorption (L mg<sup>-1</sup> or L mol<sup>-1</sup>)
- $R_L$  = Separation factor

The adsorption parameters can be determined when the above equation is converted into a linear form as:

$$\frac{1}{q_e} = \frac{1}{q_0} + \frac{1}{q_0 K_L C_e}$$

The main characteristic of the Langmuir equation is that it is based on the assumption that all sites have equal adsorption energies. The value of  $K_L$  indicates the shape of the isotherm to be either unfavorable ( $K_L > 1$ ), linear ( $K_L = 1$ ), favorable ( $0 < K_L < 1$ ), or irreversible ( $K_L = 0$ ). The RL values between 0 and 1 indicate favorable adsorption<sup>31-34</sup>.

**Dubinin-radushkevich adsorption isotherm:** The Dubinin-Radushkevich adsorption isotherm<sup>35</sup> is usually used to distinguish physical or chemical adsorption processes<sup>33,34,36,37</sup>. It is expressed mathematically as:

$$q_e = q_{max} \cdot \exp(-K_{DR} \cdot \varepsilon^2)$$

The linear form given as:

$$\ln q_e = \ln q_{max} - (K_{DR} \cdot \varepsilon^2)$$

With:

$$\varepsilon = RT \cdot \ln \left( 1 + \frac{1}{C_e} \right)$$

Fitting experimental data to the Dubinin-Radushkevich model<sup>34,35,36</sup> provides a value of an absolute mean free energy of adsorption |E| in J mol<sup>-1</sup>:

$$|E| = \frac{1}{\sqrt{2 \cdot k_{DR}}}$$

Where:

- $q_e$  = Amount of metal adsorbed (mg g<sup>-1</sup>)
- $C_e$  = Concentration of the metal at equilibrium (mg L<sup>-1</sup>)
- $q_{max}$  = Maximum adsorption capacity (mg g<sup>-1</sup> or mol g<sup>-1</sup>)
- $K_{DR}$  = Dubinin-Radushkevich constant (mol<sup>2</sup> J<sup>-2</sup>)
- $\varepsilon$  = Polanyi potential related to the equilibrium concentration
- $R$  = Universal gas constant
- $T$  = Absolute temperature
- $|E|$  = Absolute mean free energy of adsorption

The value of mean sorption energy gives information about chemical and physical sorption. The |E| values ranging from 1-8 kJ mol<sup>-1</sup> indicates physical sorption mechanism (van der Waals interactions) and values ranging from 9-16 kJ mol<sup>-1</sup> indicates chemical sorption (ionic or covalent bonding). Values between 8 and 9 kJ mol<sup>-1</sup> show a possibility of both physical and chemical adsorption processes<sup>33,34,36,38,39</sup>.

**Data analysis:** Data were analyzed using two-way ANOVA for complete randomized design (CRD)<sup>40</sup> to determine the difference in removal efficiency of the heavy metals by the adsorbents and for comparison of the different treatments mean. The analysis was done using SAS version 9.0<sup>40</sup>. The goodness of fit of each graph was used as model confirmation for data. Significant means were separated using SNK at 5% probability level.

## RESULTS AND DISCUSSION

**Physicochemical properties of soil and organic residue:** The physicochemical properties of the soil and the organic residues are shown in Table 1 and 2. The soil is a sandy loam soil and has slightly acidic pH in water and moderately acidic in CaCl<sub>2</sub>. It is low in organic matter and cation exchange capacity (CEC) with average values of exchangeable bases and available P. Amongst the organic residues, maize cob had the highest electrical conductivity (EC) of 1.74 dS m<sup>-1</sup>. Of all the metals, Zn had the highest total content and the highest availability in both soil fraction and organic residue. Generally, maize cob had the lowest availability of all the metals.

**Sorption efficiency of metal ions on soils amended with organic residue:** The adsorption efficiency of the heavy metals with the different organic residue for the clay-silt fraction is presented in Table 3. A significant difference (p ≤ 0.05) was observed in the sorption of Cu, Cd and Pb with sorption increasing with concentration. However, adsorption of Zn was observed to decrease at high concentration. Interaction between concentration and type of residue was significant (p ≤ 0.01) for all the metals except Zn. Significant differences (p ≤ 0.05) were observed in the effects of organic residues for adsorption of Zn and Pb.

Incubation had a positive influence on sorption as fewer metal ions were available in solution after 7 days as compared to incubating for a day. Shaking period was significantly (p ≤ 0.05) different in all the metals with the exception of Zn which had no significant difference in adsorption of heavy metals between shaking for 2 and 4 h. The interaction

Table 1: Characterization of the soil of used for the experiment

Properties	Minimum	Maximum	Mean	
<b>Soil textural class</b>				
Sandy loam				
Sand (%)	80.00	80.00	80.00	
Silt (%)	9.00	9.00	9.00	
Clay (%)	11.00	11.00	11.00	
Available P (mg kg <sup>-1</sup> )	17.00	21.00	17.40	
Organic matter	0.79	0.88	0.80	
<b>pH</b>				
Water	6.42	6.77	6.64	
CaCl <sub>2</sub>	6.37	6.50	6.45	
EC (dS m <sup>-1</sup> ) (1:2.5)	1.60	1.90	1.70	
<b>Exchangeable bases</b>				
Ca (cmol kg <sup>-1</sup> )	2.50	2.62	2.56	
Mg (cmol kg <sup>-1</sup> )	1.28	1.34	1.30	
Na (cmol kg <sup>-1</sup> )	0.38	0.40	0.39	
K (cmol kg <sup>-1</sup> )	0.28	0.28	0.28	
CEC (cmol kg <sup>-1</sup> )	4.10	5.00	4.63	
Total nitrogen (g kg <sup>-1</sup> )	0.85	0.88	0.86	
	Cd	Cu	Pb	Zn
	----- mg kg <sup>-1</sup> -----			
<b>Available heavy metal (m kg<sup>-1</sup>)</b>				
S-C	0.26	0.27	0.24	2.19
FS	0.18	0.45	0.18	1.63
<b>Total heavy metal (mg kg<sup>-1</sup>)</b>				
S-C	0.88	0.53	0.90	2.73
FS	0.49	0.67	0.63	2.01

S-C: Silt clay fraction, VFS: Very fine sand

Table 2: Characterization of the organic residue used for the experiment

Organic residue	Properties	Minimum	Maximum	Mean
Maize cob	pH water	5.43	5.47	5.45
	CaCl <sub>2</sub>	5.12	5.12	5.12
	EC (dS m <sup>-1</sup> )	1.67	1.80	1.74
Rice husk	pH water	5.67	5.68	5.68
	CaCl <sub>2</sub>	5.28	5.48	5.38
	EC (dS m <sup>-1</sup> )	1.29	1.32	1.30
Maize plus rice husk	pH water	5.44	5.54	5.49
	CaCl <sub>2</sub>	5.05	5.07	5.06
	EC (dS m <sup>-1</sup> )	1.13	1.16	1.40
	Cd	Cu	Pb	Zn
	----- mg kg <sup>-1</sup> -----			
<b>Available heavy metal (m kg<sup>-1</sup>)</b>				
MC	0.17	0.18	0.12	0.40
RH	0.17	0.23	0.25	0.68
MR	0.17	0.23	0.19	0.95
<b>Total heavy metal (mg kg<sup>-1</sup>)</b>				
MC	0.55	0.45	0.61	1.36
RH	0.55	0.45	0.61	1.36
MR	0.55	0.45	0.61	1.36

MC: Maize cob, RH: Rice husk and MR: Maize cob plus rice husk

between the different concentrations of heavy metals with the different types of organic residue used for Cd, Cu and Pb were highly significant (p ≤ 0.01).

An overview of the adsorption capacity of Cd, Cu, Pb and Zn by the very fine sand fraction is presented in Table 4. A significant difference (p < 0.05) between all the concentration and amount adsorbed was observed. Significant interactions

Table 3: Sorption efficiency of Cd, Cu, Pb and Zn by organic residues in a silt-clay soil fractions

Treatments	Cd	Cu	Pb	Zn
	mg kg <sup>-1</sup>			
<b>Concentration (mg L<sup>-1</sup>)</b>				
0	0.00	0.00	0.00	0.00
50 (5)	2.05 <sup>c</sup>	4.47 <sup>b</sup>	5.79 <sup>b</sup>	19.79 <sup>a</sup>
200 (10)	3.62 <sup>b</sup>	4.89 <sup>b</sup>	5.87 <sup>b</sup>	17.08 <sup>ab</sup>
400 (50)	10.24 <sup>a</sup>	5.70 <sup>a</sup>	6.85 <sup>a</sup>	14.99 <sup>b</sup>
±SE	0.23	0.18	0.16	1.38
<b>Residues (R)</b>				
Maize cob	5.28	4.86	6.35 <sup>a</sup>	14.83 <sup>b</sup>
Rice husk	5.73	4.85	6.35 <sup>a</sup>	21.14 <sup>a</sup>
Maize+rice	5.51	5.35	5.80 <sup>b</sup>	15.89 <sup>b</sup>
±SE	0.23	0.18	0.16	1.38
<b>Incubation period (IP) (days)</b>				
1	6.19 <sup>a</sup>	5.51 <sup>a</sup>	6.84 <sup>a</sup>	19.06 <sup>a</sup>
7	4.82 <sup>b</sup>	4.52 <sup>b</sup>	5.50 <sup>b</sup>	15.51 <sup>b</sup>
±SE	0.19	0.15	0.13	1.13
<b>Shaking period (SP) (h)</b>				
1	7.59 <sup>a</sup>	7.20 <sup>a</sup>	8.65 <sup>a</sup>	25.45 <sup>a</sup>
2	6.04 <sup>b</sup>	5.51 <sup>b</sup>	6.85 <sup>b</sup>	17.34 <sup>b</sup>
4	4.60 <sup>c</sup>	4.32 <sup>c</sup>	5.39 <sup>c</sup>	16.86 <sup>b</sup>
8	3.73 <sup>d</sup>	3.05 <sup>d</sup>	3.79 <sup>d</sup>	9.49 <sup>c</sup>
±SE	0.26	0.21	0.17	1.59
<b>Interactions</b>				
HM × R	**	**	**	NS
HM × levels of R (R)	**	NS	NS	NS
HM × IP	**	NS	NS	NS
R × IP	NS	NS	*	NS
Levels of R × IP (R)	NS	NS	*	NS
HM × SP	**	NS	NS	NS
HM × SP × R	NS	NS	NS	*

HM: Heavy metal concentration, R: Residue, IP: Incubation period, SP: Shaking period. Means followed by different letter(s) are significantly different at 5% level of probability, \*,\*\*Significant at 5 and 1% level of probability, respectively, NS: Not significant

( $p < 0.01$ ) effect were observed between concentration and residues, concentration and dosage of residue, concentration and shaking and also concentration and incubation period for all the metals except Cu (Table 3). There was a significant difference ( $p < 0.05$ ) among the entire residue for the sorption of Cd and Zn. Incubation periods showed significant difference ( $p < 0.05$ ) amongst all the heavy metals with the exception of Cu. Shaking period of all the metals was also significantly different (Table 4).

**Sorption isotherms:** The results of fitting the experimental data to Freundlich adsorption model are presented in Table 5. The model had a good fit for the sorption for Cu, Pb and Zn. Adsorption intensity ( $1/n$ ) was  $< 1$  in Cd and  $> 1$  in Cu, Pb and Zn. The Freundlich constant ( $K_f$ ) value observed in Cd ranged between 0.26-0.29, while the value observed in the rest of the metals was less than 0.1. From Table 5, the Langmuir model was a good fit for Cu, Pb and Zn, however, Cd adsorption did not fit the adsorption model with  $R^2 < 0.115$ .

Table 4: Sorption efficiency of Cd, Cu, Pb and Zn by organic residues in a very fine sand fraction

Treatments	Cd	Cu	Pb	Zn
	mg kg <sup>-1</sup>			
<b>Concentration (mg L<sup>-1</sup>)</b>				
0	0.00	0.00	0.00	0.00
50 (5)	2.66 <sup>c</sup>	14.19 <sup>c</sup>	15.07 <sup>c</sup>	21.34 <sup>c</sup>
200 (10)	4.79 <sup>b</sup>	26.02 <sup>b</sup>	23.81 <sup>b</sup>	43.18 <sup>b</sup>
400 (50)	5.76 <sup>a</sup>	34.18 <sup>a</sup>	27.12 <sup>a</sup>	49.68 <sup>a</sup>
±SE	0.063	1.39	0.27	0.53
<b>Residues (R)</b>				
Maize cob	4.65 <sup>a</sup>	26.21	21.83 <sup>ab</sup>	32.29 <sup>c</sup>
Rice husk	4.46 <sup>b</sup>	24.83	22.57 <sup>a</sup>	41.72 <sup>a</sup>
Maize+rice	4.10 <sup>c</sup>	23.35	21.60 <sup>b</sup>	40.13 <sup>b</sup>
±SE	0.063	1.39	0.27	0.53
<b>Incubation period (IP) (days)</b>				
1	4.92 <sup>a</sup>	27.55	23.62 <sup>a</sup>	41.31 <sup>a</sup>
7	3.89 <sup>b</sup>	22.04	20.38 <sup>b</sup>	34.82 <sup>b</sup>
±SE	0.054	1.13	0.22	0.13
<b>Shaking period (SP) (h)</b>				
1	6.47 <sup>a</sup>	36.32 <sup>a</sup>	29.87 <sup>a</sup>	51.68 <sup>a</sup>
2	5.12 <sup>b</sup>	27.20 <sup>b</sup>	24.54 <sup>b</sup>	42.55 <sup>b</sup>
4	3.69 <sup>c</sup>	20.94 <sup>c</sup>	19.52 <sup>c</sup>	33.31 <sup>c</sup>
8	2.29 <sup>d</sup>	14.73 <sup>d</sup>	14.07 <sup>d</sup>	24.71 <sup>d</sup>
±SE	0.022	1.60	0.31	0.61
<b>Interactions</b>				
HM × R	**	NS	**	**
HM × levels of R(R)	**	NS	**	**
HM × IP	**	NS	*	**
HM × SP	**	NS	**	**
R × SP	NS	NS	NS	**

HM: Heavy metal concentration, R: Residue, IP: Incubation period, SP: Shaking period. Means followed by the different letter(s) are significantly different at 5% level of probability. \*,\*\*Significant at 5 and 1% level of probability, respectively. NS: Not significant

In the very fine sand fraction the model had a good fit for the sorption of Cu, Pb and Zn. The  $R^2$  value observed for Cd was also high between 0.797-0.830. The value of the adsorption intensity ( $1/n$ ) was  $< 1$  in Cd. For the rest of the metals,  $1/n > 1$ . The Freundlich constant ( $K_f$ ) value in Cd ranged from 0.30-0.31 and less than 0.1 for the rest of the metals.

Use of the Langmuir model for sorption of Pb, Cu and Zn gave a good fit and it was observed that Cd adsorption did not fit the adsorption model well ( $R^2 < 0.115$ ). Langmuir constant ( $k_1$ ) was high for the adsorption of Cd (0.071-0.072) when compared to that of the other metals (0.000-0.004). Amount of metal sorbed per min ( $q_e$ ) was high for Cu, Pb and Zn while the  $q_e$  value obtained for Cd was  $< 0.01$ .

An overview of the separation factor ( $R_L$ ) of all the heavy metals is presented in Table 6. The  $R_L$  value in Cd was observed to decrease with increase in the concentration used and the same trend was observed in Zn. In the sorption of Cu by rice husk and maize plus rice husk, concentration had no influenced on the  $R_L$  value, has the value remained the same regardless of the change in concentration. The same behavior was observed in the sorption of Pb by rice husk. The Dubinin-Raduskevich model was a poor fit as shown (Table 7).

Table 5: Freundlich and langmuir adsorption isotherm constants for adsorption of metal ions on different organic residues

Metal ions	Maize cob					Maize plus rice husk					Rice husk				
	1/n	N	k <sub>f</sub>	R <sup>2</sup>	SE	1/n	N	k <sub>f</sub>	R <sup>2</sup>	SE	1/n	N	k <sub>f</sub>	R <sup>2</sup>	SE
<b>Freundlich adsorption constants</b>															
<b>Cd</b>															
Clay and silt fraction	0.849	1.18	0.285	0.821	0.067	0.889	1.12	0.262	0.852	0.067	0.860	1.16	0.276	0.836	0.065
Very fine sand fraction	0.853	1.17	0.303	0.830	0.068	0.823	1.22	0.319	0.813	0.068	0.820	1.22	0.311	0.797	0.068
<b>Cu</b>															
Clay and silt fraction	1.003	0.997	0.007	0.999	0.102	1.002	0.998	0.014	0.998	0.103	1.003	0.997	0.007	0.999	0.103
Very fine sand fraction	1.013	0.987	0.053	0.991	0.101	1.017	0.983	0.031	0.995	0.101	1.016	0.984	0.030	0.996	0.101
<b>Pb</b>															
Clay and silt fraction	1.003	0.997	0.016	0.99	0.102	1.003	0.997	0.015	0.999	0.103	1.003	0.997	0.014	0.999	0.103
Very fine sand fraction	1.011	0.989	0.053	0.993	0.100	1.011	0.989	0.048	0.993	0.103	1.014	0.986	0.035	0.995	0.102
<b>Zn</b>															
Clay and silt fraction	1.003	0.99	0.021	0.998	0.103	1.006	0.994	0.043	0.994	0.102	1.005	0.995	0.053	0.991	0.102
Very fine sand fraction	1.010	0.990	0.083	0.982	0.101	1.028	0.973	0.059	0.988	0.101	1.012	0.988	0.053	0.991	0.102
<b>Langmuir adsorption constants</b>															
<b>Cd</b>															
	q <sub>e</sub>	k <sub>i</sub>	R <sup>2</sup>	SE		q <sub>e</sub>	k <sub>i</sub>	R <sup>2</sup>	SE		q <sub>e</sub>	k <sub>i</sub>	R <sup>2</sup>	SE	
Clay and silt fraction	0.019	0.073	0.115	0.145		0.026	0.072	0.116	0.105		0.027	0.071	0.071	0.113	
Very fine sand fraction	0.0270	0.071	0.124	0.105		0.024	0.072	0.119	0.115		0.021	0.072	0.096	0.115	
<b>Cu</b>															
Clay and silt fraction	0.914	0.000	0.997	0.001		0.814	0.000	0.947	0.001		0.915	0.000	0.997	0.001	
Very fine sand fraction	0.503	0.001	0.843	0.001		0.675	0.000	0.953	0.001		0.690	0.000	0.959	0.001	
<b>Pb</b>															
Clay and silt fraction	0.835	0.000	0.989	0.001		0.843	0.000	0.990	0.001		0.848	0.000	0.993	0.001	
Very fine sand fraction	0.588	0.001	0.908	0.001		0.577	0.001	0.923	0.001		0.649	0.000	0.935	0.001	
<b>Zn</b>															
Clay and silt fraction	0.787	0.000	0.980	0.001		0.623	0.001	0.942	0.001		0.562	0.001	0.911	0.001	
Very fine sand fraction	0.360	0.002	0.752	0.002		0.423	0.002	0.766	0.002		0.194	0.004	0.482	0.003	

Table 6: Langmuir R<sub>L</sub> value for the different concentration of heavy metals amended with organic residue

Heavy metal	Soil fraction	Concentration (mg)	Maize cob	Maize and rice husk	Rice husk	
Cd	Clay and silt soil fraction	5	0.42	0.42	0.42	
		10	0.37	0.37	0.37	
		50	0.18	0.18	0.18	
	Very fine sand soil fraction	5	0.42	0.42	0.42	
		10	0.37	0.37	0.37	
		50	0.18	0.18	0.18	
	Cu	Clay and silt soil fraction	50	0.50	0.50	0.50
			200	0.50	0.50	0.50
			400	0.50	0.50	0.50
Very fine sand soil fraction		50	0.49	0.50	0.50	
		200	0.45	0.50	0.50	
		400	0.42	0.50	0.50	
Pb		Clay and silt soil fraction	50	0.50	0.50	0.50
			200	0.50	0.50	0.50
			400	0.50	0.50	0.50
	Very fine sand soil fraction	50	0.49	0.49	0.50	
		200	0.45	0.45	0.50	
		400	0.42	0.42	0.50	
	Zn	Clay and silt soil fraction	50	0.50	0.49	0.49
			200	0.50	0.45	0.45
			400	0.50	0.42	0.42
Very fine sand soil fraction		50	0.48	0.48	0.45	
		200	0.42	0.42	0.36	
		400	0.36	0.36	0.28	

**Effect of concentration of heavy metal on metal sorption:**

The increasing rate of adsorption of all the metals with rate of concentration is related to the retention of the metals ions

occurring through an initial rapid sorption onto the external surface of the soil and organic residue, which was then followed by slow diffusion into the soil and organic residue

Table 7: Dubinin-Radushkevich adsorption isotherm constants for adsorption of metal ions on different organic residue

Metal ions	Maize plus rice husk				Rice husk					
	Q <sub>max</sub> (mg g <sup>-1</sup> )	K <sub>DR</sub> (mol <sup>2</sup> KJ <sup>-2</sup> )	E (KJ mol <sup>-1</sup> )	R <sup>2</sup>	SE	Q <sub>max</sub> (mg g <sup>-1</sup> )	K <sub>DR</sub> (mol <sup>2</sup> KJ <sup>-2</sup> )	E (KJ mol <sup>-1</sup> )	R <sup>2</sup>	SE
<b>Cd</b>										
Clay and silt fraction	206.2	-24.41	-0.143	0.050	0.153	208.8	-26.00	-0.139	0.056	0.149
Very fine sand fraction	208.0	-26.58	-0.137	0.059	0.154	202.8	-22.49	-0.149	0.044	0.158
<b>Cu</b>										
Clay and silt fraction	9.794	1.571	0.575	0.039	0.237	9.792	1.511	0.575	0.039	0.237
Very fine sand fraction	11.50	1.097	0.675	0.020	0.234	10.72	1.298	0.621	0.028	0.233
<b>Pb</b>										
Clay and silt fraction	10.19	1.411	0.595	0.034	0.237	10.14	1.426	0.592	0.035	0.237
Very fine sand fraction	11.24	1.161	0.656	0.023	0.234	10.91	1.247	0.633	0.026	0.234
<b>Zn</b>										
Clay and silt fraction	10.43	1.352	0.608	0.031	0.237	11.58	1.068	0.684	0.019	0.236
Very fine sand fraction	12.39	0.867	0.759	0.012	0.233	12.70	0.790	0.796	0.010	0.229

pores. Similar observations were also made by Roth *et al.*<sup>39</sup>, Selim *et al.*<sup>41</sup>, Bruemmer *et al.*<sup>42</sup> and Kyzas<sup>43</sup> and Kyzas *et al.*<sup>44</sup> although an opposing result was obtained by Abdel Salam *et al.*<sup>45</sup> and Attia *et al.*<sup>46</sup> in which sorption was observed to decrease with increasing concentration. Liu<sup>47</sup> also proposed that adsorption process may be dependent on the availability of adsorption sites on the surface of adsorbent rather than adsorbate concentration in the bulk solution. However, Zaragoza *et al.*<sup>48</sup> was of the opinion that the chemical and physical properties of the residue as well as its decomposition rate might have an influence on the process.

In the silt-clay fraction, the rate of Cu sorption was higher than all other heavy metals even at a low initial concentration indicating that metal adsorption was influenced by ion characteristic as well as presence of clay minerals<sup>39,47</sup>. Since all the ions are divalent cations at the same original solution levels, a correlation between ionic size and adsorption selectivity may be expected. The sequence for the rate of sorption was observed as follows: Cu>Pb>Zn>Cd. Higher selectivity for Cu was reported by Hegazi<sup>49</sup>, Kyzas<sup>43</sup> and Wu *et al.*<sup>50</sup> While contrasting results were observed in the study of Elliott *et al.*<sup>51</sup> and Pagnanelli *et al.*<sup>52</sup> where Pb adsorption was highest while Abdel Salam *et al.*<sup>45</sup> and Oh and Tshabalala<sup>53</sup> reported an increased affinity for Zn. For the ion exchange process, the strength with which cations of equal charge are held is inversely proportional to the unhydrated radii<sup>51,52</sup>. Thus, the predicted order of selectivity based on unhydrated radii is Pb<sup>2+</sup> (0.120 nm)>Cd<sup>2+</sup> (0.097 nm)>Zn<sup>2+</sup> (0.074 nm)>Cu<sup>2+</sup> (0.072 nm)<sup>42,51,52</sup>. Although the unhydrated radii of Cu<sup>2+</sup> and Zn<sup>2+</sup> are similar, the complexation of Cu<sup>2+</sup> with soil is more stable than Zn<sup>2+</sup>. Therefore, Cu<sup>2+</sup> is more readily adsorbed onto soil surface and occupies more adsorption sites than the other ions.

However, in the very fine sand fraction, it was discovered that there is a correlation between ionic size and adsorption selectivity as the rate of Pb sorption was the highest. Brummer *et al.*<sup>42</sup>, Pagnanelli *et al.*<sup>52</sup> and Yang *et al.*<sup>54</sup> predicted an order of selectivity for divalent unhydrated radii as Pb<sup>2+</sup> (0.120 nm)>Cd<sup>2+</sup> (0.097 nm)>Zn<sup>2+</sup> (0.074 nm)>Cu<sup>2+</sup> (0.072 nm) though the selectivity sequences observed in this soil fraction was Pb>Cu>Zn>Cd. This result was supported by previous findings of Elliott *et al.*<sup>51</sup>, Appel and Ma<sup>55</sup> and Pagnanelli *et al.*<sup>52</sup> thus indicating that the unhydrated radius may serve as a predictive index of metal adsorption.

**Effect of dosage of organic residue on sorption of Cd, Cu, Pb and Zn:** The increased adsorption of Cd, Cu, Pb and Zn observed irrespective of metal concentration can be attributed to the availability of larger surface area for



adsorption with increase in the amount of adsorbate. This is in consonant with the study of Al-Anber and Al-Anber<sup>56</sup>, who observed that using 5 g of olive cake had better efficiency of 77% over 1 g which has an efficiency of only 42%. Vieira *et al.*<sup>57</sup> also observed an increase in heavy metal removal percentage by clay as the amount of clay used increases. Similar results were observed by Hegazi<sup>49</sup>.

**Effect of time on sorption of Cd, Cu, Pb and Zn:** The rate of sorption of Cd, Cu, Pb and Zn ions onto different organic residue was observed to be very fast in the 1st h with a gradual increase in sorption till after the 8 h. This may be abundance of adsorption sites on the surface of the different residues which allowed easy interaction of heavy metal ions with the adsorption sites. Afterwards, the adsorption sites were almost saturated and the concentrations of heavy metal ions had become low which resulted in the decreased adsorption rate. Similar observation was also made by Salam *et al.*<sup>45</sup>, Kyzas<sup>43</sup>, El-Kamash<sup>58</sup> and Wu *et al.*<sup>50</sup>. Of importance is the fact that equilibrium was attained much later in this work when compared with Kyzas *et al.*<sup>44</sup>, Kyzas<sup>43</sup>, Hegazi<sup>49</sup> and Wu *et al.*<sup>50</sup> where the contact time was less than 4 h. However, the rate of Cd sorption increased with increasing shaking time and the reduced rate of sorption may be as a result of competition between the different metals as Cd, Cu and Zn are divalent elements hence correlation between ionic size and adsorption selectivity may be expected as suggested by Yang *et al.*<sup>54</sup>.

**Effect of soil fraction on adsorption of Cd, Cu, Pb and Zn:** The adsorption of metals was expected to be high in clay and silt fraction due to the presence of clay minerals. This observation is accorded with the fact that these materials have numerous adsorption sites due to their high specific surface areas. The clay and silt fraction sorbed more Cu, Pb and Zn than the very fine sand soil fraction. Spark and Swift<sup>59</sup>, Zachara and Smith<sup>60</sup> and Spark *et al.*<sup>61</sup> reported that adsorption capacity is linked to the surface site density and that the presence of clay minerals enhances the adsorption capacity. A general tendency of adsorption capacities can therefore be concluded that the adsorption capacity of the very fine sand fraction is not as high as compared to the clay and silt fraction due to the absence of clay minerals. The study of Roth *et al.*<sup>39</sup> and Kim and Fergusson<sup>62</sup> is in agreement with these results. However, the present study is not in agreement with both Kim and Fergusson<sup>62</sup> and Roth *et al.*<sup>39</sup> on the adsorption of Cd, because a reversal of the trend was observed in Cd as more Cd ions were sorbed by the very fine sand fraction as compared to the clay and silt soil size fraction which may be based on the

argument of Yang *et al.*<sup>54</sup> on the occurring competition between the various ions on the adsorptive sites of the adsorbate.

#### **Effect of organic residue on sorption of Cd, Cu, Pb and Zn:**

Organic residue had a great impact on sorption in very fine sand soil fraction as the rate of adsorption which is usually generally low was high due to the presence of the residues. Thus, organic residue favors sorption due to the release of humic substances, which enhance the sorption of positive ions by making the surface more negative. This collaborates the findings of Masset *et al.*<sup>63</sup> who observed that humic acid had an influence on sorption of Co (II), Sr (II) and Se (IV), Wu *et al.*<sup>50</sup> and Zaragoza *et al.*<sup>48</sup> The percentage of sorption for Pb and Cu were high when rice husk and maize cob were used as an adsorbent, whereas only maize cob gave good sorption efficiency for Zn and Cd.

The adsorption capacity of rice on the sorption of Pb and Cu were 11.14 and 10.77 mg g<sup>-1</sup> respectively which is low as compared to adsorption capacity obtained by Wong *et al.*<sup>64</sup> which was 108 and 29 mg g<sup>-1</sup> for both metals respectively. However the rice husk used in their study was modified with esterified tartaric acid. Tarley *et al.*<sup>65</sup>, obtained an adsorption capacity of 4 mg g<sup>-1</sup> for Cd, which is lower than 211 mg g<sup>-1</sup> obtained in the present. The sorption efficiency for all the organic residues obtained was found to be similar to that of Suemitsu *et al.*<sup>66</sup>, Hegazi<sup>49</sup> and Zaragoza *et al.*<sup>48</sup> where efficiency of over 80% was recorded. Removal efficiency of Cu by maize cobs was not affected by the presence of Pb and Zn as observed by Khan and Wahab<sup>67</sup>.

#### **Describing heavy metal sorption with Freundlich and Langmuir adsorption isotherms:**

The sorption data obtained was fitted into Langmuir, Freundlich and Dubunin-Radushkevich isotherms out of which Freundlich adsorption model was found to have the best fit for all the heavy metals.

Freundlich adsorption model was found to be favorable for the sorption of Cd as the value of 1/n was <1 in both fractions of the soil irrespective of the type of organic residue used. This value according to Mohan and Karthikeyan<sup>68</sup> indicates that the sorption process was normal and sorption process is favorable since the value of n is >1<sup>69</sup>. The value of 1/n observed for Cu, Pb and Zn was greater than 1. Hameed *et al.*<sup>70</sup> and Dada *et al.*<sup>71</sup> reported that adsorption process with 1/n > is a cooperative adsorption process. Similar fit with the Freundlich data were obtained by Wu *et al.*<sup>50</sup> and Roth *et al.*<sup>39</sup> however Kyzas<sup>43</sup> and Salam *et al.*<sup>45</sup> had better results with Langmuir model.

From the results obtained, it was observed that the Langmuir isotherm fits quite well with the experimental data of Cu and Pb with a high  $R^2$  value which is in agreement with the results of the Freundlich isotherm. This may be due to the presence and homogenous distribution of active sites on the organic residues which also agrees with the study of Dada *et al.*<sup>71</sup> on equilibrium studies using adsorption isotherms. The value of the  $K_L$  obtained indicates that the isotherm is irreversible<sup>32</sup> and since the  $R_L$  lies between 0 and 1, the sorption is said to be favorable and is in accordance with Eastoe and Dalton<sup>30</sup>, Zheng *et al.*<sup>34,72</sup>, Saltah *et al.*<sup>33</sup>. However, the sorption of Zn in the very fine sand fraction is in consonant with these authors. The isotherm was observed to show a very poor fit for Cd ions.

### CONCLUSION

The suitability of each residue as a potential adsorbent was observed, however, the sorption efficiency of maize cob was higher than that of rice husk or a mixture of maize cob and rice husk with a positive relationship between the rate of adsorption and dosage obtained. A perfect fit was observed for the Freundlich adsorption model with the sorption process of Cu, Pb and Zn found to be a cooperative process ( $1/n > 1$ ) while Cd was found to be favorable and normal adsorption process. These residues can be used as excellent source of heavy metal removal in contaminated soils.

### SIGNIFICANCE STATEMENT

Organic residues such as maize cobs, rice husk and mixture of both as adsorbents are capable of reducing heavy metal contamination. The adsorption of Cu, Pb and Zn is competitive on the adsorbent while Cd followed normal adsorption process. The possibility of improving adsorption by incubation and shaking was also explored.

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### REFERENCES

1. Duffus, J.H., 2002. Heavy metals: A meaningless term? *Pure Applied Chem.*, 74: 793-807.

2. Williams, C.J., D. Aderhold and R.G.J. Edyvean, 1998. Comparison between biosorbents for the removal of metal ions from aqueous solutions. *Water, Res.*, 32: 216-224.

3. Kadirvelu, K., K. Thamaraiselvi and C. Namasivayam, 2001. Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste. *Bioresour. Technol.*, 76: 63-65.

4. Sun, T.H., Q.X. Zhou and P.J. Li, 2001. *Pollution Ecology*. Science Press, Beijing, China, pp: 160-194.

5. Zhou, Q.X. and Y.F. Song, 2004. *Principles and Method of Treating Contaminated Soils*. Science Press, Beijing, China, pp: 367-377.

6. Zhou, Q., F. Sun and R. Liu, 2005. Joint chemical flushing of soils contaminated with petroleum hydrocarbons. *Environ. Int.*, 31: 835-839.

7. Abdu, N., J.O. Agbenin and A. Buerkert, 2012. Fractionation and mobility of cadmium and zinc in urban vegetable gardens of Kano, Northern Nigeria. *Environ. Monitor. Assess.*, 184: 2057-2066.

8. Awode, U.A., A. Uzairu, M.L. Balarabe, G.F.S. Harrison and O.J. Okunola, 2008. Assessment of peppers and soils for some heavy metals from irrigated farmlands on the bank of river challawa, Northern Nigeria. *Pak. J. Nutr.*, 7: 244-248.

9. Okunola, O.J., A. Uzairu, C.E. Gimba and J.A. Kagbu, 2011. Metal inter-relationship and its mobility in samples collected along roadside corridors of Kano Metropolis, Nigeria. *Res. J. Environ. Toxicol.*, 5: 336-347.

10. Abdu, N., A. Abdulkadir, J.O. Agbenin and A. Buerkert, 2011. Vertical distribution of heavy metals in wastewater-irrigated vegetable garden soils of three West African cities. *Nutr. Cycling Agroecosyst.*, 89: 387-397.

11. Argun, M.E., S. Dursun, C. Ozdemir and M. Karataş, 2007. Heavy metal adsorption by modified oak sawdust: thermodynamics and kinetics. *J. Hazard. Mater.*, 141: 77-85.

12. Bhattacharya, A.K., S.N. Mandal and S.K. Das, 2006. Adsorption of Zn(II) from aqueous solution by using different adsorbents. *Chem. Eng. J.*, 123: 43-51.

13. Qu, J., 2008. Research progress of novel adsorption processes in water purification: A review. *J. Environ. Sci.*, 20: 1-13.

14. Zhao, G., X. Wu, X. Tan and X. Wang, 2010. Sorption of heavy metal ions from aqueous solutions: A review. *Open Colloid Sci. J.*, 4: 19-31.

15. Bailey, S.E., T.J. Olin, R.M. Bricka and D.D. Adrian, 1999. A review of potentially low-cost sorbents for heavy metals. *Water Res.*, 33: 2469-2479.

16. Saeed, A., M.W. Akhter and M. Iqbal, 2005. Removal and recovery of heavy metals from aqueous solution using papaya wood as a new biosorbent. *Sep. Purif. Technol.*, 45: 25-31.

17. Babarinde, N.A.A., J.O. Babalola and R.A. Sanni, 2006. Biosorption of lead ions from aqueous solution by maize leaf. *Int. J. Phys. Sci.*, 1: 23-26.

18. King, P., P. Srivinas, Y.P. Kumar and V.S.R.K. Prasad, 2006. Sorption of copper(II) ion from aqueous solution by *Tectona grandis* L. f. (teak leaves powder). J. Hazard. Mater., 136: 560-566.
19. Hanafiah, M.A.K.H., W.S.W. Ngah, H. Zakria and S.C. Ibrahim, 2007. Batch study of liquid-phase adsorption of lead ions usingalang (*Imperata cylindrica*) leaf powder. J. Biol. Sci., 2: 222-230.
20. Hanafiah, M.A.K.M., S. Shafiei, M.K. Harun and M.Z.A. Yahya, 2006. Kinetic and thermodynamic study of Cd<sup>2+</sup> adsorption onto rubber tree (*Hevea brasiliensis*) leaf powder. Mater. Sci. Forum, 517: 217-221.
21. Hanafiah, M.A.K.M., W.S.W. Ngah, S.C. Ibrahim, H. Zakaria and W.A.H.W. Ilias, 2006. Kinetics and thermodynamic study of lead adsorption from aqueous solution onto rubber (*Hevea brasiliensis*) leaf powder. J. Applied Sci., 6: 2762-2767.
22. Bouyoucos, G.J., 1962. Hydrometer method improved for making particle size analyses of soils. Agron. J., 54: 464-465.
23. Rhoades, J.D., 1982. Soluble Salts. In: Methods of Soil Analysis, Part 2: Chemical and Microbiological Properties, Page, A.L., R.H. Miller and D. Keeney (Eds.). 2nd Edn., American Society of Agronomy Inc., Madison, Wisconsin, pp: 167-179.
24. Anderson, J.M. and J.S.I. Ingram, 1993. Tropical Soil Biology and Fertility a Handbook of Methods. 2nd Edn., CAB International, Wallingford, UK., Pages: 221.
25. Nelson, D.W. and L.E. Sommers, 1982. Total Carbon, Organic Carbon and Organic Matter. In: Methods of Soil Analysis, Part 2: Chemical and Microbiological Properties, Page, A.L., R.H. Miller and D.R. Keeney (Eds.). 2nd Edn., ASA and SSSA, Madison, WI., USA., pp: 539-579.
26. Bremner, J.M. and C.S. Mulvaney, 1982. Nitrogen-Total. In: Methods of Soil Analysis. Part 2. Chemical and Microbial Properties, Page, A.L., R.H. Miller and D.R. Keeney (Eds.). American Society of Agronomy, Madison, Wisconsin, pp: 595-624.
27. Bray, R.H. and L.T. Kurtz, 1945. Determination of total, organic and available forms of phosphorus in soils. Soil Sci., 59: 39-45.
28. Freundlich, H.M.F., 1906. Over the adsorption in solution. J. Phys. Chem., 57: 385-470.
29. Langmuir, I., 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. J. Am. Chem. Soc., 40: 1361-1403.
30. Eastoe, J. and J.S. Dalton, 2000. Dynamic surface tension and adsorption mechanisms of surfactants at the air-water interface. Adv. Colloid Interface Sci., 85: 103-144.
31. Hall, K.R., L.C. Eagleton, A. Acrivos and T. Vermeulen, 1966. Pore- and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions. Ind. Eng. Chem. Fundam., 5: 212-223.
32. Ho, Y.S., C.T. Huang and H.W. Huang, 2002. Equilibrium sorption isotherm for metal ions on tree fern. Process Biochem., 37: 1421-1430.
33. Saltah, K., A. Sari and M. Aydin, 2007. Removal of ammonium ion from aqueous solution by natural Turkish (Yildizeli) zeolite for environmental quality. J. Hazard. Mater., 141: 258-263.
34. Zheng, H., Y. Peng and Z. Luan, 2003. Sorption of aniline on Cr<sup>3+</sup> bentonite. Environ. Chem., 22: 369-372.
35. Dubinin, M.M., 1975. Physical Adsorption of Gases and Vapors in Micropores. In: Progress in Surface Membrane Science, Cadenhead, D.A. (Ed.), Academic Press, New York, pp: 1-70.
36. Dubinin, M.M., E.D. Zaverina and L.V. Radushkevich, 1947. Sorption and structure of active carbons. I. Adsorption of organic vapors. Zh. Fiz. Khim., 21: 1351-1362.
37. Saltali, K. and A. Sari, 2006. Sorption capacity and thermodynamic properties of natural Turkish (Resadiye) bentonite for the removal of ammonium ions from aqueous solution. Adsorp. Sci. Technol., 24: 749-760.
38. Donat, R., A. Akdogan, E. Erdem and H. Cetisli, 2005. Thermodynamics of Pb<sup>2+</sup> and Ni<sup>2+</sup> adsorption onto natural bentonite from aqueous solutions. J. Colloid Interf. Sci., 286: 43-52.
39. Roth, E., V. Mancier and B. Fabre, 2012. Adsorption of cadmium on different granulometric soil fractions: Influence of organic matter and temperature. Geoderma, 189-190: 133-143.
40. SAS., 2001. SAS User's Guide: Statistics. 9th Edn., SAS Institute Inc., Cary, NC. USA.
41. Selim, H.M., B. Buchter, C. Hinz and L. Ma, 1992. Modeling the transport and retention of cadmium in soils: Multireaction and multicomponent approaches. Soil Sci. Soc. Am. J., 56: 1004-1015.
42. Brummer, G.W., J. Gerth and K.G. Tiller, 1988. Reaction kinetics of the adsorption and desorption of nickel, zinc and cadmium by goethite. I. Adsorption and diffusion of metals. Eur. J. Soil Sci., 39: 37-52.
43. Kyzas, G.Z., 2012. Commercial coffee wastes as materials for adsorption of heavy metals from aqueous solutions. Materials, 5: 1826-1840.
44. Kyzas, G.Z., D.N. Bikiaris, M. Kostoglou and N.K. Lazaridis, 2013. Copper removal from aqueous systems with coffee wastes as low-cost materials. Proceedings of the 16th International Conference on Heavy Metals in the Environment, Volume 1, (HME'13), EDP Sciences.
45. Salam, O.E.A., N.A. Reiad and M.M. ElShafei, 2011. A study of the removal characteristics of heavy metals from wastewater by low-cost adsorbents. J. Adv. Res., 2: 297-303.
46. Attia, A.A., S.A. Khedr and S.A. Elkholy, 2010. Adsorption of chromium ion (VI) by acid activated carbon. Braz. J. Chem. Eng., 27: 183-193.
47. Liu, Y., 2008. New insights into pseudo-second-order kinetic equation for adsorption. Colloids Surfaces A: Physicochem. Eng. Aspects, 320: 275-278.

48. Zaragoza, V.M.D., R. Carrillo and C.M.G. Castorena, 2011. Lead sorption-desorption from organic residues. *Environ. Technol.*, 32: 353-361.
49. Hegazi, H.A., 2013. Removal of heavy metals from wastewater using agricultural and industrial wastes as adsorbents. *HBRC. J.*, 9: 276-282.
50. Wu, P., Q. Zhang, Y. Dai, N. Zhu and Z. Dang *et al.*, 2011. Adsorption of Cu (II), Cd (II) and Cr (III) ions from aqueous solutions on humic acid modified Ca-montmorillonite. *Geoderma*, 164: 215-219.
51. Elliott, H.A., M.R. Liberati and C.P. Huang, 1986. Competitive adsorption of heavy metals by soils. *J. Environ. Qual.*, 15: 214-219.
52. Pagnanelli, F., S. Mainelli, F. Veglio and L. Toro, 2003. Heavy metal removal by olive pomace: Biosorbent characterisation and equilibrium modelling. *Chem. Eng. Sci.*, 58: 4709-4717.
53. Oh, M. and M. Tshabalala, 2007. Pelletized ponderosa pine bark for adsorption of toxic heavy metals from water. *BioResources*, 2: 66-81.
54. Yang, J.Y., X.E. Yang, Z.L. He, T.Q. Li, J.L. Shentu and P.J. Stoffella, 2006. Effects of pH, organic acids and inorganic ions on lead desorption from soils. *Environ. Pollut.*, 143: 9-15.
55. Appel, C. and L. Ma, 2002. Concentration, pH and surface charge effects on cadmium and lead sorption in three tropical soils. *J. Environ. Qual.*, 31: 581-589.
56. Al-Anber, Z.A. and M.A. Al-Anber, 2008. Thermodynamics and kinetic studies of iron (III) adsorption by olive cake in a batch system. *J. Mexican Chem. Soc.*, 52: 105-115.
57. Vieira, M.G.A., A.F.A. Neto, M.L. Gimenes and M.G.C. da Silva, 2010. Sorption kinetics and equilibrium for the removal of nickel ions from aqueous phase on calcined *Bofe bentonite* clay. *J. Hazard. Mater.*, 177: 362-371.
58. El-Kamash, A.M., A.A. Zaki and M.A. El Geleel, 2005. Modeling batch kinetics and thermodynamics of zinc and cadmium ions removal from waste solutions using synthetic zeolite A. *J. Hazard. Mater.*, 127: 211-220.
59. Spark, K.M. and R.S. Swift, 1994. Investigation of the interaction between pesticides and humic substances using fluorescence spectroscopy. *Sci. Total Environ.*, 152: 9-17.
60. Zachara, J.M. and S.C. Smith, 1994. Edge complexation reactions of cadmium on specimen and soil-derived smectite. *Soil Sci. Soc. Am. J.*, 58: 762-769.
61. Spark, K.M., J.D. Wells and B.B. Johnson, 1995. Characterizing trace metal adsorption on kaolinite. *Eur. J. Soil Sci.*, 46: 633-640.
62. Kim, N.D. and J.E. Fergusson, 1992. Adsorption of cadmium by an aquent New Zealand soil and its components. *Aust. J. Soil Res.*, 30: 159-167.
63. Masset, S., F. Monteil-Rivera, L. Dupont, J. Dumonceau and M. Aplincourt, 2000. Influence of humic acid on sorption of Co(II), Sr(II) and Se(IV) on goethite. *Agronomie*, 20: 525-535.
64. Wong, K.K., C.K. Lee, K.S. Low and M.J. Haron, 2003. Removal of Cu and Pb by tartaric acid modified rice husk from aqueous solutions. *Chemosphere*, 50: 23-28.
65. Tarley, C.R.T., S.L.C. Ferreira and M.A.Z. Arruda, 2004. Use of modified rice husks as a natural solid adsorbent of trace metals: Characterisation and development of an on-line preconcentration system for cadmium and lead determination by FAAS. *Microchem. J.*, 77: 163-175.
66. Suemitsu, R., R. Uenishi, I. Akashi and M. Nakano, 1986. The use of dyestuff-treated rice hulls for removal of heavy metals from waste water. *J. Applied Polym. Sci.*, 31: 75-83.
67. Khan, M.N. and M.F. Wahab, 2007. Characterization of chemically modified corncobs and its application in the removal of metal ions from aqueous solution. *J. Hazard. Mater.*, 141: 237-244.
68. Mohan, S.V. and J. Karthikeyan, 1997. Removal of lignin and tannin colour from aqueous solution by adsorption onto activated charcoal. *Environ. Pollut.*, 97: 183-187.
69. Goldberg, S., 2005. Equations and Models Describing Adsorption Processes in Soils. In: *Chemical Processes in Soils*, (SSSA Book Series, No. 8). Tabatabai, M.A. and D.L. Sparks (Eds.), Soil Science Society of America, Madison, Wisconsin, USA., pp: 489-517.
70. Hameed, B.H., D.K. Mahmoud and A.L. Ahmad, 2008. Equilibrium modeling and kinetic studies on the adsorption of basic dye by a low-cost adsorbent: Coconut (*Cocos nucifera*) bunch waste. *J. Hazard. Mater.*, 158: 65-72.
71. Dada, A.O., A.P. Olalekan, A.M. Olatunya and O. Dada, 2012. Langmuir, freundlich, temkin and dubinin-radushkevich isotherms studies of equilibrium sorption of Zn<sup>2+</sup> unto phosphoric acid modified rice husk. *IOSR J. Applied Chem.*, 3: 38-45.
72. Zheng, H., Y. Wang, Y. Zheng, H. Zhang, S. Liang and M. Long, 2008. Equilibrium, kinetic and thermodynamic studies on the sorption of 4-Hydroxyphenol on Cr-bentonite. *Chem. Eng. J.*, 143: 117-123.