

## Removal of Some Heavy Metals from Aqueous Solution by Low-cost Sorbents

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**ABSTRACT:** This study compares the abilities of different low-cost sorbents ; rock phosphate, sawdust, sugar beet pulp and zeolite, to remove Cd, Ni, Cr, Cu, Zn and Pb from synthetic single ion aqueous solutions. Effect of initial concentration of metal ion was studied. This study was carried out in Alexandria Water Purification Company Lab. It is clear that when the initial concentration of the tested metal ion is increased, the amount of metal sorbed per unit weight of the sorbent (mg/g) is increase, as where the removal percentage is decrease . The experimental data of the sorption equilibrium were correlated by the Langmuir and Freundlich equations. The results proved that Freundlich model gave a better and acceptable fitting to the experimental data of most of the tested metals than Langmuir equation within the used concentrations range of metal ions. However Langmuir equation imposed a better fitting to the experimental data of Cu using rock phosphate, Pb using sawdust, sugar beet pulp, zeolite and rock phosphate sorbents than Freundlich equation. The data also indicated that sugar beet pulp, zeolite and rock phosphate was more effective to remove Cd, Ni, Cr and Pb ions with a highest sorption capacity. The tested sorbents, as low cost materials, were able to reduce the tested ion concentrations in aqueous solutions, suggesting that sugar beet pulp, zeolite and rock phosphate could be used as a low cost- practical option to remediate heavy metals contaminated waters.

**Key words:** heavy metals-low cost sorbent-sorption equations- zeolite- sugar beet pulp

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## INTRODUCTION

The use of low-cost adsorbents has been investigated for heavy metals removal from wastewaters as a replacement for costly current methods. In general, an adsorbent can be assumed as “low cost” if it requires little processing, is abundant in nature, or is a by-product or waste material from industry (*Bailey et al., 1999*). Heavy metals are often discharged by a number of industries, such as metal plating facilities, mining operations and tanneries. This can lead to the contamination of freshwater and marine environment (*Low and Lee, 2000*). It is well known that some metals such as antimony, chromium, copper, lead, manganese mercury, cadmium, etc., are significantly toxic to human beings and ecological environments (*Doris et al., 2000*). Generally, the techniques employed for heavy metal removal include precipitation, ion exchange, adsorption, filtration, electrode position, reverse osmosis (*Rao et al., 2000*). However, most of these techniques do not lead to a satisfactory depollution of metal ion considering the operational costs (*Marchetti et al., 2000*). Adsorption on solid-solution interface is an important means for controlling the extent of pollution due to heavy metal ions. Interest has recently arisen in the investigation of some unconventional methods and low cost materials for scavenging heavy metal ions from waste waters (*Gloaguen and*

Morvan, 1997). In recent years, many materials as coconut shells (*Crisafully et al., 2008*), rice husk (*Kishore et al., 2008*), zeolite (*Mamba et al., 2009*), phosphate rock (*Ma and Rao, 1999*), tea and coffee waste (*Amarasinghe and Williams, 2007*), peanut shells (*Qin et al., 2007*), saw dust (*AjayKumar et al., 2008*), activated carbon (*Gulnaziya et al., 2008*), dry tree leaves and barks (*Benhima et al., 2008*) and orange peel (*Ferda and Selen, 2012*); have been investigated for the elimination of heavy metals from waste water. The objective of this study is to contribute in the search for less expensive adsorbents and their utilization possibilities for the removal of heavy metals (Cd, Cu, Ni, Zn, Cr and Pb) from aqueous solutions.

## MATERIALS AND METHODS

### Sorbent materials:

Sorption studies have been focused on the use of low- cost sorbent materials. The first one is sugar beet pulp which is the by- product of sugar industry and it has been supplied from El Nile Sugar Factory, Egypt. It was milled and dried at 100 °C throughout 24 h, then screened, washed with distilled water and dried at 65 °C for 1 h and passed through 0.4 mm sieved and kept for experimental study. The organic matter content in this material was 94% as determined by the method described by Allison (1965). The second sorbent is sawdust which was collected from a workshop in Alexandria city and sieved through a set of laboratory sieves and the fraction < 0.4 mm was used in the sorption experiments. The sawdust organic carbon was 46 % as determined by the method of Allison (1965). The third one is a low grade rock phosphate which was obtained from a sedimentary phosphate rock deposit supplied in a fine powder (passed through 38 mm standard sieve) from Al Ahram Mining and Natural Fertilizer Company, Egypt. Chemical composition of the rock phosphate is presented in Table 1. The fourth sorbent was the (Zeolite) which purchased from Alex. for Import and Export with particle size of less than 0.6 mm. The chemical composition of zeolite is presented in Table 2.

**Table (1). The chemical composition of rock phosphate**

Constituents	Concentration ,%
P	10.863
Ca	28.123
Si	6.071
Cd	1.053
Pb	4.021
Na	0.668
Fe	0.871
K	0.108
Mn	0.036
Cl	0.570
L.O.I.	16.560

L.O.I.=Loss on ignition

sours: Al Ahram Mining and Natural Fertilizer Company, Egypt.

**Table (2). The chemical composition of zeolite**

composition	Weight, %
SiO <sub>2</sub>	68.03
TiO <sub>2</sub>	0.21
Al <sub>2</sub> O <sub>3</sub>	11.92
Fe <sub>2</sub> O <sub>3</sub>	1.77
MnO	0.01
MgO	0.83
CaO	2.65
Na <sub>2</sub> O	1.96
K <sub>2</sub> O	2.26
H <sub>2</sub> O	10.25
P <sub>2</sub> O <sub>5</sub>	0.06
AO <sub>3</sub>	0.05

Sours: from Alex for Import and Export.

### Single metal sorption experiments:

A fixed amount of dry sorbent material (2 g) with 40 ml of metal solution were placed in a 100 ml volumetric flask and shaken at 200 rpm using a temperature controlled incubator shaker at 25±2°C. The used metal ion concentrations were in the range of 5-400 mg/l (Cd<sup>2+</sup> and Ni<sup>2+</sup>), 25-400 mg/l (Cu<sup>2+</sup>, Zn<sup>2+</sup>, and Cr<sup>2+</sup>) and 50-700 mg/l (Pb<sup>2+</sup>). Stock solutions (1000 mg/L) of cadmium, lead, zinc, chromium, Nickel and copper were prepared by metal nitrate salts in CaCl<sub>2</sub> (0.01F) and the required concentrations were obtained by diluting the stock solutions (*Shaheen et al., 2013*). The contact time for batch tests was 2 h. Then, the aqueous /sorbent systems were filtered using Filter paper NO. (1) to remove any fine particles and the concentration of metal ions was determined using atomic absorption spectrophotometer (Schimadzu 6800). Each experiment was carried out in duplicate and the average results are presented. The initial and final metal concentrations in the solutions were determined by AAS. The sorption capacities of the sorbents were calculated after equilibrium was attained. The metal uptake capacity for each sample was calculated according to a mass balance of the metal ion using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m}$$

Where; **m** is the mass of adsorbent (g), **V** is the volume of the solution (L), **C<sub>0</sub>** is the initial concentration of metal (mg L<sup>-1</sup>), **C<sub>e</sub>** is the equilibrium metal concentration (mg L<sup>-1</sup>) and **q<sub>e</sub>** is the quantity of metal adsorbed at equilibrium (mg/g). The percent removal of metals from the solution was calculated by the following equation:

$$\%removal = \frac{C_0 - C_e}{C_0} \times 100$$

The Langmuir and Freundlich adsorption isotherms were used to investigate the adsorption process of Cd, Ni, Cu, Cr, Zn and Pb on sawdust, sugar beet pulp, zeolite and phosphate rock adsorbents. The Langmuir adsorption isotherm model is given by *Demiral et al. (2008)* as follows:

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

The linearization of it gives the following form:

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

Where  $C_e$ , equilibrium metal concentration,  $q_m$  and  $K_L$  are the Langmuir constants related to maximum adsorption capacity ( $\text{mg g}^{-1}$ ), and the relative energy of adsorption ( $1/\text{mg}$ ), respectively. Freundlich isotherm model is one of the most widely used mathematical models which fit the experimental data over a wide range of concentration. The Freundlich equation is given by *Singh et al. (2011)* as follows:

$$q_e = K_F C_e^{\frac{1}{n}}$$

The logarithmic form of the equation is:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

Where;  $q_e$  is the amount of metal ion adsorbed per specific amount of adsorbent ( $\text{mg g}^{-1}$ ),  $C_e$  is equilibrium concentration ( $\text{mgL}^{-1}$ ),  $K_F$  and  $n$  are Freundlich equilibrium constants.

## RESULTS AND DISCUSSION

### Sorption capacity of sorbents

Tables 3 and 4 show the effect of varying initial concentration of Cd, Ni, Cu, Cr, Zn and Pb on the sorption capacity of the sorbent and the removal percentage for each single solution. It is clear that when the initial concentration of Cd and Ni ions is increased from 5 to 400 mg/L, the amount of sorbed metal per unit weight of the sorbent (mg/g) is increase, where as the removal percentage is decrease with the tested sorbents. The range of Cd sorption increased from 0.03 to 0.63 mg/g on sawdust, 0.02 to 1.57 mg/g on sugar beet pulp, 0.06 to 1.79 mg/g on zeolite and 0.04 to 1.35 mg/g on rock phosphate. The corresponding values on Ni were 0.05 to 0.50 mg/g on sawdust, 0.04 to 1.34 mg/g on sugar beet pulp, 0.04 to 1.26 mg/g on zeolite and 0.02 to 0.64 mg/g for rock phosphate.

To evaluate the effect of initial metal ion concentration on adsorption/sorption behavior of Cu, Zn and Cr ions, studies were conducted with initial concentrations of 25, 50, 75, 100, 125, 200, 300, and 400 mg/L. Tables 5, 6 and 7 show the effect of varying concentration of Cu, Zn and Cr on sorption capacity and removal percentage of each metal ion. It is clear that when the initial concentrations of metal ions is increased from 25 to 400 mg/L, the amount of sorbed metal per unit weight of the adsorbent (mg/g) is increased, as where the percentage removal is decreased with the tested sorbents. The range of Cu sorption increased from 0.31 to 3.49 mg/g on sawdust, 0.45 to 5.95 mg/g on sugar beet pulp, 0.42 to 5.09 mg/g on zeolite and 0.47 to 5.75 mg/g on rock phosphate. The corresponding values for Cr sorption increased were from 0.23 to 2.40 mg/g on sawdust, 0.32 to 3.99 mg/g on sugar beet pulp, 0.40 to 4.39 mg/g on zeolite and 0.46 to 5.56 mg/g on rock phosphate. Also, the corresponding values for Zn adsorption were from 0.18 to 2.41 mg/g on sawdust, 0.24 to 3.05 mg/g on sugar beet pulp, 0.24 to 3.50 mg/g on zeolite and 0.33 to 3.32 mg/g on rock phosphate.

With respect to Pb ion adsorption/sorption, the studies were conducted with initial concentration of 50, 100, 200, 300, 400, 500, 600 and 700 mg/L. Table 8 show that as the initial concentration of Pb ion is increased from 50 to 700 mg/L, the amount of sorbed metal per unit weight of the adsorbent (mg/g) is also increased, where as the percentage removal has been decreased with the tested sorbents. The range of Pb ion increased from 0.03 to 0.06 mg/g on sawdust, 0.74 to 1.80 mg/g on sugar beet pulp, 0.88 to 2.40 mg/g on zeolite and 0.81 to 6.14 mg/g on rock phosphate. Tables (3-8) indicated that the higher sorptive capacities of adsorbents were found to take place at higher concentrations. This may be due to the interaction of all metal ions present in the solution with binding sites (*Azouaou et al., 2010*). The number of ions adsorbed from a solution of higher concentrations is more than that removed from the low concentrated solutions. It is observed also that the percentages of

removal decreased with increasing the initial metal concentrations. The low sorption, at higher metal concentration, is due to the increased ratio of initial number of moles of Cd, Ni, Cu, Cr, Zn and Pb to the vacant sites available. For a given adsorbent Cu, Cr, Zn the total number of the available adsorbent sites was fixed thus adsorbing almost equals amount of adsorbate resulted in a decrease in the removal of adsorbate, consequent to an increase in initial concentrations of Cd, Ni, Cu, Cr, Zn and Pb concentrations. Therefore it is evident from the obtained results that each Cd, Ni, Cu, Cr, Zn and Pb metal ion adsorption is dependent on the initial metal concentration.

Tables (3 and 4) show how the removal percentage of Cd and Ni ions varied as the initial metal concentration varied. Variation of the initial concentration from 5 to 400 mg/L decreased the removal percentage of Cd or Ni by all the tested adsorbent materials. The results showed that zeolite performed better at higher and lower concentration of Cd ion than the adsorbents used in this study. This is probably due to the presence of large number of binding sites on the surface of zeolite than the other adsorbents, used in this study. On other hand, the results showed that sugar beet pulp performed better at higher concentration of Ni ion than is the other adsorbents while zeolite was better at low concentrations and this is probably due to the large number of binding sites in zeolite.

Tables (5, 6 and 7) showed that the removal percentage of Cu, Cr and Zn ions varied as the initial metal concentration varied. Variation of the initial concentration from 25 to 400 mg/L decreased the percentage removal of Cu, Cr or Zn by the tested adsorbents. The results also showed that rock phosphate performed better at higher and lower concentration of Cu and Cr ions than the other adsorbents used in this study. On other hand, the results showed that zeolite performed better at the higher concentration of Zn ion than the other adsorbents while rock phosphate was better at all the concentrations except at the higher concentration of Zn (400 mg/L). Table 8 shows that the removal percentage of Pb ions varied as the initial metal concentration varied. Variation of the initial concentration from 50 to 700 mg/L decreased the percentage removal of Pb by all the tested materials. The results also showed that rock phosphate performed better at higher concentrations of Pb ion than the other adsorbents. On other hand, the results showed that zeolite performed better at lower concentrations of Pb ion.

**Table (3). Effect of initial concentration of cadmium on its adsorption by sawdust, sugar beet pulp, zeolite and rock phosphate adsorbents**

Sorbent material	Initial conc. (mg Cd/L)	Final conc. (mg Cd/L)	Sorption capacity (mg Cd/g of sorbent)	Removal (%)
<b>Sawdust</b>	5	3.50	0.03	30.00
	10	8.02	0.03	19.80
	20	15.42	0.09	22.90
	40	29.64	0.20	25.90
	80	62.60	0.34	21.70
	100	82.44	0.35	17.56
	200	165.40	0.69	17.30
	300	268.50	0.63	10.50
	400	368.50	0.63	7.87
<b>Sugar beet pulp</b>	5	3.49	0.03	30.10
	10	7.10	0.05	29.00
	20	14.40	0.11	28.00
	40	28.96	0.22	27.60
	80	58.70	0.42	26.60
	200	150.24	0.99	24.88
	300	237.50	1.25	20.83
	400	321.17	1.57	20.20
	<b>Zeolite</b>	5	1.55	0.06
10		3.19	0.13	68.10
20		8.45	0.23	57.75
40		18.40	0.43	54.00
80		40.60	0.78	49.25
200		138.60	1.22	30.70
300		208.14	1.83	30.00
400		310.16	1.79	22.50
<b>Rock Phosphate</b>		5	2.55	0.04
	10	5.18	0.09	48.20
	20	10.70	0.18	46.50
	40	21.15	0.37	47.12
	80	45.42	0.69	43.21
	200	159.14	0.81	20.43
	300	237.40	1.25	20.00
	400	332.50	1.35	16.87

**Table (4). Effect of initial concentration of nickel on its adsorption by sawdust, sugar beet pulp, zeolite and rock phosphate adsorbents**

<b>Sorbent material</b>	<b>Initial conc. (mg Ni/L)</b>	<b>Final conc. (mg Ni/L)</b>	<b>Sorption capacity (mg Ni /g of sorbent)</b>	<b>Removal (%)</b>
<b>Sawdust</b>	5	3.75	0.03	25.00
	10	7.60	0.05	24.00
	20	15.20	0.10	24.00
	40	30.60	0.19	23.50
	80	63.50	0.33	20.62
	100	78.32	0.43	21.60
	200	178.14	0.44	10.93
	300	275.18	0.50	8.22
<b>Sugar beet pulp</b>	5	3.22	0.04	35.60
	10	6.20	0.08	33.00
	20	13.80	0.12	31.00
	40	27.60	0.25	31.00
	80	55.50	0.49	30.60
	200	147.62	1.05	26.00
	300	248.18	1.04	17.00
	400	333.17	1.34	16.70
<b>Zeolite</b>	5	3.00	0.04	40.00
	10	6.12	0.08	38.00
	20	12.20	0.16	39.00
	40	25.55	0.29	36.25
	80	52.71	0.55	34.11
	200	164.60	0.71	17.92
	300	254.17	0.92	15.27
	400	337.16	1.26	15.71
<b>Rock Phosphate</b>	5	4.00	0.02	20.00
	10	8.06	0.04	19.40
	20	16.20	0.08	19.00
	40	32.50	0.15	18.75
	80	64.80	0.30	17.00
	200	178.45	0.43	10.77
	300	275.38	0.49	8.20
	400	368.22	0.64	7.94

**Table (5). Effect of initial concentration of copper on its adsorption by sawdust, sugar beet pulp, zeolite and rock phosphate adsorbents**

<b>Sorbent material</b>	<b>Initial conc. (mg Cu/L)</b>	<b>Final conc. (mg Cu/L)</b>	<b>Sorption capacity (mg Cu /g of sorbent)</b>	<b>Removal (%)</b>
<b>Sawdust</b>	25	9.18	0.31	63.28
	50	20.00	0.60	53.38
	75	34.38	0.81	54.00
	100	45.24	1.09	54.00
	125	57.88	1.34	53.69
	200	93.49	2.13	53.25
	300	145.92	3.08	51.36
	400	225.45	3.49	43.60
<b>Sugar beet pulp</b>	25	2.23	0.45	91.10
	50	5.50	0.89	89.00
	75	9.75	1.30	87.00
	100	13.38	1.73	86.60
	125	24.98	2.00	80.00
	200	40.42	3.19	79.79
	300	77.80	4.44	74.06
	400	120.24	5.59	69.89
<b>Zeolite</b>	25	3.94	0.42	84.24
	50	8.93	0.82	82.14
	75	17.79	1.14	76.28
	100	21.96	1.56	78.04
	125	30.35	1.89	75.72
	200	52.50	2.95	73.75
	300	95.82	4.08	68.06
	400	145.40	5.09	63.65
<b>Rock Phosphate</b>	25	1.39	0.47	94.44
	50	2.22	0.95	95.44
	75	4.52	1.40	93.97
	100	5.08	1.89	94.92
	125	5.16	2.39	95.87
	200	28.45	3.43	85.77
	300	62.25	4.75	79.25
400	112.24	5.75	71.94	

**Table (6). Effect of initial concentration of chromium on its adsorption by sawdust, sugar beet pulp, zeolite and rock phosphate adsorbents**

<b>Sorbent material</b>	<b>Initial conc. (mg Cr/L)</b>	<b>Final conc. (mg Cr/L)</b>	<b>Sorption capacity (mg Cr /g of sorbent)</b>	<b>Removal (%)</b>
<b>Sawdust</b>	25	13.26	0.23	46.96
	50	27.85	0.44	44.30
	75	42.72	0.65	43.04
	100	60.60	0.79	39.40
	125	80.60	0.89	35.52
	200	132.25	1.36	33.87
	300	204.22	1.92	31.92
	400	280.20	2.40	29.95
<b>Sugar beet pulp</b>	25	9.24	0.32	63.04
	50	18.63	0.63	62.74
	75	29.36	0.91	60.80
	100	40.80	1.18	59.20
	125	56.40	1.37	54.88
	200	97.24	2.06	51.38
	300	146.20	3.08	51.26
	400	200.40	3.99	49.90
<b>Zeolite</b>	25	5.23	0.40	89.54
	50	10.28	0.79	79.44
	75	20.28	1.09	72.80
	100	32.60	1.35	67.40
	125	44.60	1.61	64.32
	200	73.60	2.53	63.20
	300	123.20	3.54	58.93
	400	180.40	4.39	54.90
<b>Rock Phosphate</b>	25	2.12	0.46	91.51
	50	4.24	0.92	91.52
	75	10.68	1.29	85.52
	100	16.00	1.68	84.00
	125	20.60	2.09	83.92
	200	42.72	3.15	78.64
	300	80.40	4.39	73.20
	400	122.25	5.56	69.43

**Table (7). Effect of initial concentration of zinc on its adsorption by sawdust, sugar beet pulp, zeolite and rock phosphate adsorbents**

<b>Sorbent material</b>	<b>Initial Conc. (mg Zn/L)</b>	<b>Final Conc. (mg Zn/L)</b>	<b>Sorption capacity (mg Zn /g of sorbent)</b>	<b>Removal (%)</b>
<b>Sawdust</b>	25	16.10	0.18	35.60
	50	34.30	0.31	31.40
	75	51.24	0.48	31.66
	100	69.00	0.62	31.00
	125	86.38	0.77	30.89
	200	138.22	1.24	30.89
	300	207.67	1.85	30.77
	400	279.36	2.41	30.16
<b>Suger beet pulp</b>	25	13.08	0.24	47.68
	50	28.32	0.43	43.36
	75	43.42	0.63	42.10
	100	59.00	0.82	41.00
	125	73.43	1.03	41.28
	200	118.68	1.63	40.00
	300	175.50	2.49	41.00
	400	247.40	3.05	38.00
<b>Zeolite</b>	25	12.82	0.24	48.72
	50	28.14	0.44	47.00
	75	39.98	0.70	46.70
	100	53.42	0.93	46.58
	125	67.50	1.15	46.00
	200	109.42	1.81	45.29
	300	169.22	2.62	43.59
	400	225.24	3.50	43.69
<b>Rock Phosphate</b>	25	8.45	0.33	66.20
	50	17.30	0.65	65.40
	75	26.25	0.98	65.00
	100	35.63	1.29	64.73
	125	46.26	1.57	62.99
	200	102.75	1.95	48.62
	300	156.40	2.87	47.86
	400	234.22	3.32	41.44

**Table (8). Effect of initial concentration of lead on its adsorption by sawdust, sugar beet pulp, zeolite and rock phosphate adsorbents**

Sorbent material	Initial conc. (mg Pb/L)	Final conc. (mg Pb/L)	Sorption capacity (mg Pb /g of sorbent)	Removal (%)
<b>Sawdust</b>	50	49.00	0.02	2.00
	100	98.60	0.03	1.40
	200	198.10	0.04	0.95
	300	297.82	0.04	0.73
	400	397.40	0.05	0.65
	500	496.92	0.06	0.62
	600	598.00	0.04	0.40
	700	697.00	0.06	0.42
<b>Sugar beet pulp</b>	50	13.07	0.74	73.86
	100	66.40	0.67	33.60
	200	145.40	1.09	27.30
	300	228.40	1.43	23.86
	400	323.28	1.53	19.18
	500	415.60	1.69	16.88
	600	512.14	1.76	14.64
	700	610.12	1.80	12.84
<b>Zeolite</b>	50	6.15	0.88	87.70
	100	20.50	1.59	79.50
	200	95.60	2.09	52.20
	300	162.60	2.75	45.80
	400	240.00	3.20	40.00
	500	368.66	2.63	26.27
	600	485.00	2.30	19.16
	700	580.00	2.40	17.14
<b>Rock Phosphate</b>	50	9.42	0.81	81.16
	100	20.62	1.59	79.38
	200	45.40	3.09	77.30
	300	106.40	3.87	64.53
	400	136.20	5.28	65.95
	500	205.14	5.90	58.97
	600	338.26	5.23	43.62
	700	393.25	6.14	43.82

**Mathematical quantifying of metal sorption**

To quantify the sorption capacity of the tested sorbents in relation to the concentration of Cd, Ni, Cu, Cr, Zn and Pb ions, the obtained experimental data were fitted to two isotherm models: Langmuir and Freundlich . The values of the various constants of the two models were calculated and represented in Table 9. This indicated that most of the experimental data fitted well to the two models. By comparing the determination coefficients ( $R^2$ ), it was observed that Freundlich isotherm gives a good model for the adsorption systems of all the tested metals with the tested adsorbents except lead with sawdust and zeolite. Also, Langmuir isotherm gives a good model for the adsorption systems of

some metals with some sorbents, which is based on monolayer sorption on to the surface restraining finite number of identical sorption sites.

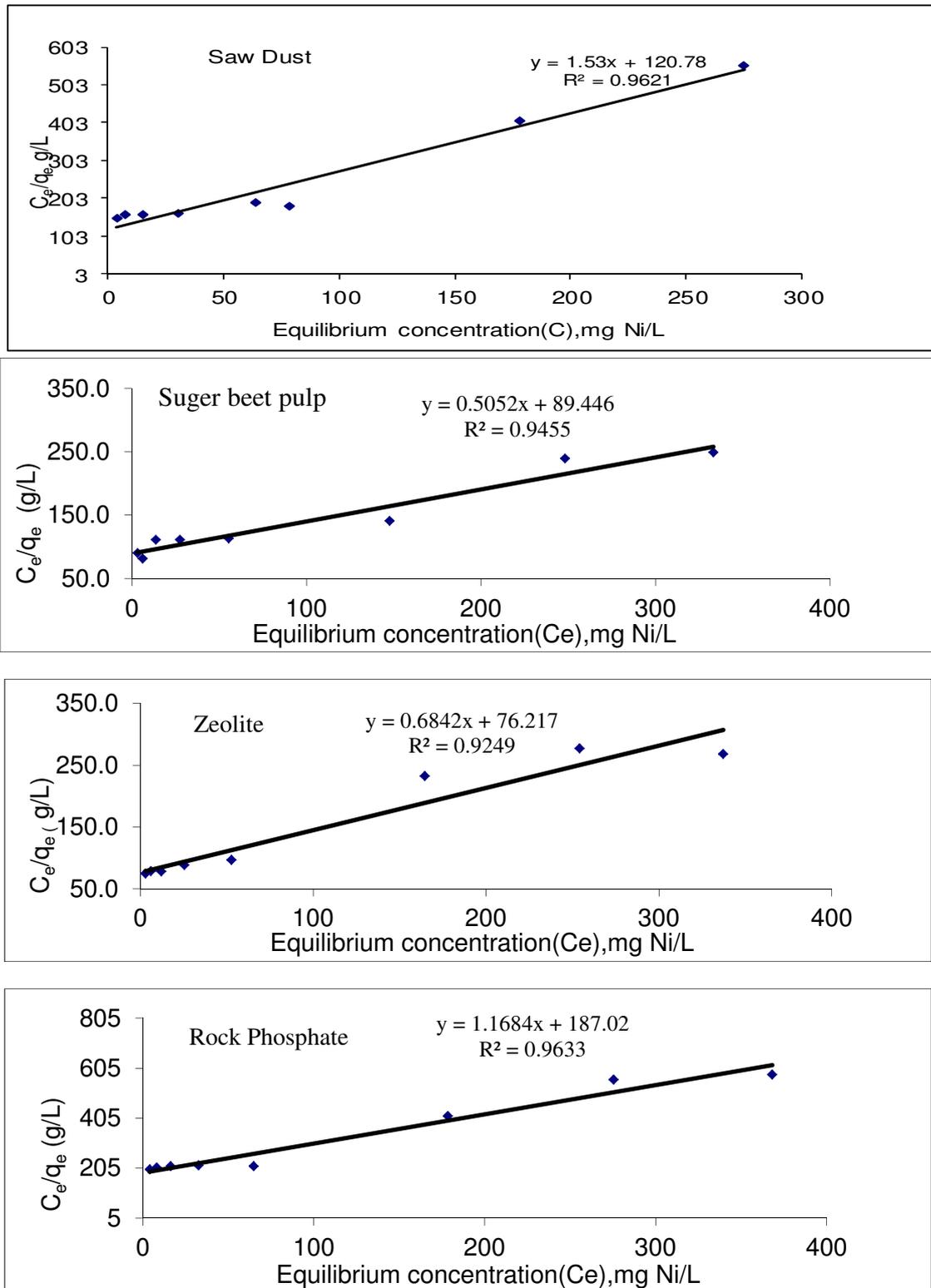
According to the linear form of Freundlich isotherm, the constant  $k_f$  and  $1/n$  were determined by linear regression from the plot of  $\ln q_e$  against  $\ln C_e$ .  $K_f$  is a measure of the degree or strength of adsorption. Low value of  $K_f$  indicates the more adsorption (Horsfall *et al.*, 2006) while  $1/n$  is used as an indication for the favorable of sorbent for removal of ions. The Freundlich constants  $k_f$  and  $1/n$  are adsorption capacity and adsorption intensity which are determined for Cd, Ni, Cu, Cr, Zn and Pb are summarized in Table 9. It can be observed from this table that the quantity  $1/n$  is less than unity for Cd, Ni, Cu, Cr, Zn and Pb adsorption which indicates adsorption isotherm favorable for adsorptive removal of Cd, Ni, Cu, Cr, Zn and Pb. The results for Cd, Ni, Cu, Cr, Zn and Pb were well represented by the linear form of Freundlich isotherms model using the four tested sorbents except Pb using sawdust and zeolite.

When the Langmuir isotherm model was applied to the obtained data of the six metals, the constants  $q_m$  and  $K_L$  these were determined from  $C_e/q$  versus  $C_e$  plot. These constants do not explain the chemical or physical properties of the adsorption process; However, the model represents the equilibrium data and indicates that there was formation of a monolayer of metal ions on the surface of the tested sorbents. A reasonable fit was obtained for the equilibrium data of both Cd, using zeolite rock phosphate and sawdust, Ni using all sorbents, Cu using sugar pulp, zeolite and rock phosphate, Cr using all sorbents, Zn using rock phosphate and sawdust and Pb using all sorbents (Table 9). When application of Langmuir model, to the equilibrium data of Cd using sugar beet, Zn using (sugar beet pulp and zeolite), the Langmuir model resulted in a large deviation from experimental data and unreasonable values of  $R^2$ . However, a very good fit for Ni sorption by the four tested sorbents was obtained using Freundlich and Langmuir models (Table 9 and Figs. 1 and 2).

The higher the  $K_L$ , the higher is the affinity of the adsorbent for metal ions,  $q_m$  can also be interpreted as the total number of binding sites that are available for adsorption (Volesky, 1995). According to Table 9, the affinity for Cd can be arranged in the order zeolite > rock phosphate > sawdust > sugar beet pulp, for Ni: is sawdust > zeolite > rock phosphate > sugar beet pulp, for Cu: is rock phosphate > sugar beet pulp > zeolite > sawdust, for Cr :is rock phosphate > zeolite > sugar beet pulp > sawdust, for Zn: is rock phosphate > sugar beet pulp > zeolite > sawdust and for Pb :is rock phosphate > zeolite > sugar beet pulp > sawdust.

In conclusion, the sorption performances of Cd , Ni, Cu, Cr and zn are strongly affected by initial metal concentrations and sorbent material type. The obtained results confirmed that the tested sorbents as a low cost materials are

able to reduce the tested ion concentrations in aqueous solutions, suggesting that sugar beet pulp, zeolite and rock phosphate could be used as a cost- useful op tion to remediate heavy metals contaminated waters.



**Fig (1). Langmuir adsorption isotherm for Ni adsorption**

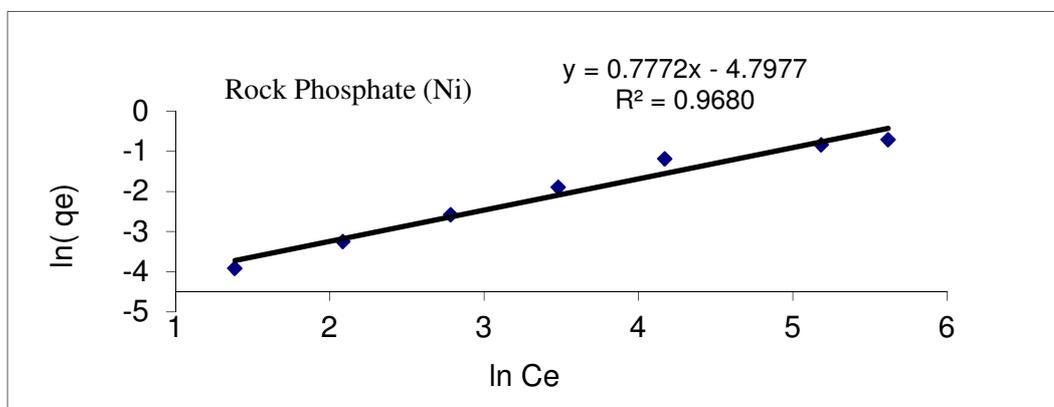
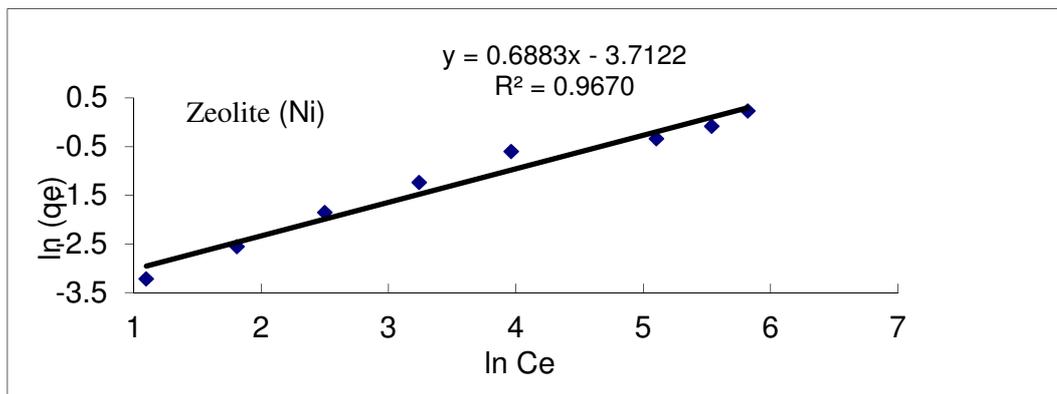
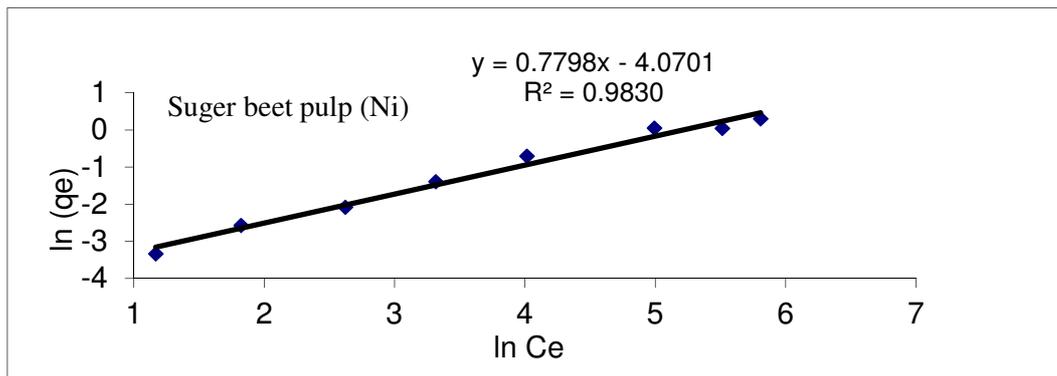
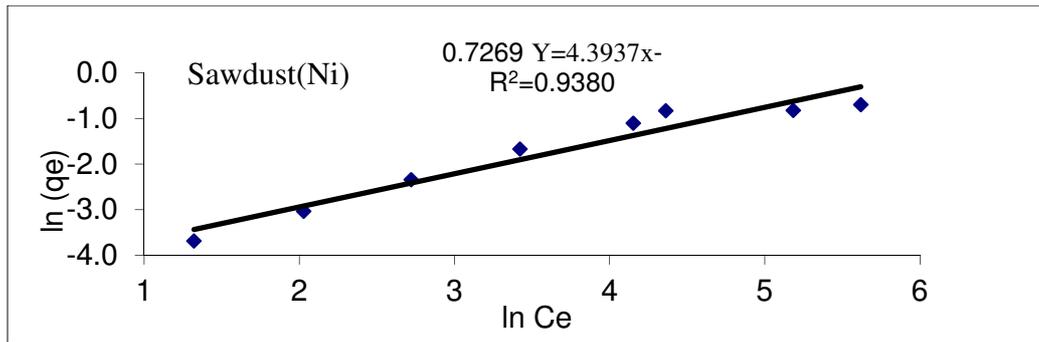


Fig (2). Freundlich adsorption isotherm for Ni adsorption.

**Table (9). Parameters and determination coefficient of Cd, Ni, Cu, Cr, Zn and Pb removal data according to the degree of correlation of Langmuir and Freundlich equations**

Metal type	Sorbent material	Langmuir parameters			Freundlich parameters		
		$q_m$ (mg/g)	$K_L$ (L/mg)	$R^2$	1/n	$K_f$	$R^2$
Cd	Sawdust	1.06	0.0068	0.8512	0.7902	0.0107	0.9631
	Sugar beet pulp	5.47	0.0013	0.4173	0.9573	0.0077	0.9844
	Zeolite	2.16	0.0155	0.9672	0.6187	0.0630	0.9850
	Rock Phosphate	1.60	0.0122	0.9465	0.6570	0.0361	0.9520
Ni	Sawdust	0.65	0.0127	0.9621	0.7269	0.0124	0.9380
	Sugar beet pulp	1.98	0.0056	0.9455	0.7798	0.0171	0.9830
	Zeolite	1.46	0.0090	0.9249	0.6883	0.0244	0.9670
	Rock Phosphate	0.86	0.0062	0.9633	0.7772	0.0082	0.9680
Cu	Sawdust	8.40	0.0034	0.7977	0.8126	0.0483	0.9858
	Sugar beet pulp	7.36	0.0216	0.9411	0.6186	0.3043	0.9904
	Zeolite	7.97	0.0113	0.9514	0.6981	0.1697	0.9930
	Rock Phosphate	6.28	0.0672	0.9835	0.4932	0.6598	0.8840
Cr	Sawdust	4.50	0.0036	0.9024	0.7453	0.0361	0.9960
	Sugar beet pulp	8.55	0.0039	0.8520	0.7953	0.0581	0.9950
	Zeolite	6.52	0.0097	0.8888	0.6541	0.1473	0.9880
	Rock Phosphate	7.07	0.0233	0.9463	0.5932	0.3308	0.9903
Zn	Sawdust	18.51	0.0004	0.4068	0.9778	0.0062	0.9990
	Sugar beet pulp	13.83	0.0012	0.6183	0.8961	0.0223	0.9970
	Zeolite	25.13	0.0007	0.4650	0.9447	0.0210	0.9970
	Rock Phosphate	4.70	0.0094	0.9561	0.6639	0.1005	0.9600
Pb	Sawdust	0.06	0.0087	0.8028	0.3391	0.0062	0.6950
	Sugar beet pulp	2.05	0.0107	0.9747	0.2785	0.2960	0.8340
	Zeolite	2.73	0.0116	0.9391	0.2217	0.7222	0.7700
	Rock Phosphate	6.82	0.0163	0.9744	0.3262	0.3262	0.9190

## REFERENCES

- AjayKumar, M., Kadirvelu, K., Mishra, G.K, Chitra, R and Nagar, P. N (2008).** Adsorptive removal of heavy metals from aqueous solution by treated Sawdust. *Journal of Hazardous Materials*, 50: 604-611.
- Amarasinghe, B.M.W.P.K. and Williams, R.A. (2007).** Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater. *Chem. Engin.*, 132: 299-309.
- Azouaou, N., Sadaoui, Z., Djaafri, A. and Mokaddem, H. (2010).** Adsorption of cadmium from aqueous solution onto untreated coffee grounds: Equilibrium, kinetics and thermodynamics. *J. Hazardous Materials*, 184: 126-134.
- Allison, L.E. (1965).** Total Carbon. In: C.A. Black et al. (ed.) *Methods of Soil Analysis. Part 2. Agronomy*. 9: 1346-1365. Am. Soc. Agron. Madison Wis. USA

- Benhima,H.,Chiban,M., Sinan,F., Seta,P. and Persin,M. (2008).**Removal of lead and Cadmium ions from aqueous solution by adsorption onto micro-particles of dry plants. *J. Colloids Surfaces*,61: 10-16.
- Bailey, S.E., Olin, T.J., Bricka, R.M., Adrian, D.D.(1999).** A review of potentially low-cost sorbents for heavy metals. *Water Res.*, 33: 2469–2479.
- Crisafully,R.,Milhome,M.A.L,Cavalcante,R.M,Selveira,E.R,Keukeleire,D and Nascimento,R.F (2008).**Removal of some polycyclic aromatic hydrocarbons from petrochemical wastewater using low-cost adsorbents of natural origin. *Journal of Bioresource Technol*, 99: 4515-4519
- Dorris, K.L., Yu, B., Zhang, Y., Shukla, A., Shukla, S.S., (2000).** The removal of heavy metals from aqueous solutions by sawdust adsorption—removal of copper. *Journal of Hazardous Materials B80*, 33–42.
- Demiral, H., Demiral, I., Tumsek, F., and Karabacakoglu, B. (2008).** “Adsorption of chromium(VI) from aqueous solution by activated carbon derived from olive bagasse and applicability of different adsorption models,” *Chem. Eng. J.* 144(2), 188-196.
- Ferda,G. and Selen,S.D. (2012).** Adsorption study on orange peel: Removal of Ni(II) ions from aqueous solution. *African J. Biotechnol*, 11: 1250-1258.
- Gulnaziya,I.,Mohamed,K.A. and Nik,M.S (2008).**Continuous adsorption of lead ions in a column packed with palm shell activated carbon. *J. Hazard Materials*, 155: 109-113.
- Gloaguen, V.and Morvan, H. J.(1997).** Removal of heavy metal ions from aqueous solution by modified barks. *Environmental Sci Health*, A32(4): 901–912.
- Horsfall,M.J.,Abia,A.A. and Spiff,A.I. (2006).** Kinetic studies on the adsorption of Cd<sup>2+</sup>,Cu<sup>2+</sup> and Zn<sup>2+</sup> ions from aqueous solutions by cassava (*Manihot sculenta cranz*)tuber bark waste. *J. Bioresource Technol*, 97: 283-291.
- Kishore,K.K,Xiaoguang,M,Christodoulatos,Cand Veera,M.B (2008).** Biosorption mechanism of nine different heavy metals onto biomatrix from rice husk. *J. Hazard. Materials*, 53: 1222-1234.
- Low, K. S.and Lee C S. (2000).** Sorption of cadmium and lead from aqueous solutions by spent grain*J. Process Biochemi*, 36: 59–64.
- Mamba, B.B, Nyembe, D.W.,and Mulaba-Bafubiandi, A.F. (2009).** Removal of Copper and Cobalt from Aqueous Solutions Using Natural Clinoptilolite. *Water SA*, 35, : 307-314.
- Marchetti, V., Clement, A., Gerardin, P., and Loubinoux, B. (2000a).** “Synthesis and use of esterified sawdusts bearing carboxyl group for removal of cadmium(II) from water,” *Wood Sci. Technol.* 34(2), 167-173.
- Ma, L. Q. and Rao, G. N.( 1999).** Aqueous Pb reduction in Pb-contaminated soils by Florida phosphate rocks: *Water Air Soil Pollut.*, 110: 1-16.
- Qin,L,Jianping,Z,Wenyi,Z,Mingmc,W and Jun,Z (2007).** Kinetic studies of adsorption of Pb(II),Cr(II) and Cu(II) from aqueous solution by sawdust and modified peanut husk: *J. Hazard Materials*, 141: 163-167.
- Rao, N. N., Kumar, A.and Kaul ,S. N. (2000).** Alkali-treated straw and insoluble straw xanthate as low cost adsorbents for heavy metal removal-preparation, characterization and application. *Bioresource Technol.* 71: 133–142.

- Shaheen, S. M., Fawzy, I. E, Khaled ,M. G. and Hala M. G.(2013).** Heavy metals removal from aqueous solutions and wastewaters by using various byproducts. J. Environ Manage. 128,514-521
- Singh, R., Kulkarni,K. and Kulkarni, A.D. (2011).** Application of appopotite in adsorption of heavy metals (Co and Ni) from wastewater. Chem. and materials Research, 2 :16-21.
- Volesky(1995).**Biosorption of heavy metals. Biotechnol. Progress, 11: 235-250.

## الملخص العربي

### إزالة بعض المعادن الثقيلة من محلول مائي بواسطة مواد ماصة منخفضة التكلفة

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تقارن هذه الدراسة قدرات نشارة الخشب ولب بنجر السكر والزيوليت والفوسفات الصخري كمواد ادمصاصيه ومدى قابليتها فى ازالة عناصر الكاديوم ،النكل ، الكروم ، النحاس، الزنك والرصاص من المحاليل المائية المحضره فردية العنصر. وقد تمت هذه الدراسه فى معمل شركه مياة الشرب بالاسكندريه وقد تم دراسة تأثير التركيز الابتدائى لأيونات هذه العناصر .وكان من الواضح أنه بزيادة تركيز العنصر فى المحلول المائى، كانت الكميته المدمصه لوحده الوزن من الماده الادمصاصيه تزيد وفى نفس الوقت تقل نسبة الازاله. ويعمل ارتباط بين البيانات التجريبية لتوازن الإزالة لأيونات هذه العناصر باستخدام كلا معادلة لانجموير و معادلة فريندليش، أثبتت النتائج أن نموذج فريندليش أعطى أفضل تفسيراً مقبولاً للبيانات التجريبية لمعظم العناصر التي تم اختبارها عن معادلة لانجموير ضمن نطاق التركيز المستخدم. على العكس من ذلك، فرضت معادلة لانجموير ملاءمة أفضل للبيانات التجريبية لكل من النحاس باستخدام صخر الفوسفات والرصاص باستخدام نشارة الخشب، لب بنجر السكر والزيوليت وصخر الفوسفات عن معادلة فرويندليش. وأشارت البيانات أيضا إلى أن لب بنجر السكر والزيوليت وفوسفات الصخرى كانت أكثر قدره على ازالة أيونات الكاديوم والنكل والكروم و الرصاص والنحاس. ويمكن القول بصورة عامه فالمواد الادمصاصيه التي تم اختبارها كمواد منخفضة التكلفة قادرة على تقليل تركيزات الأيونات المختبرة في المحاليل المائية، مما يوضح أن لب بنجر السكر والزيوليت وفوسفات الصخور يمكن أن يستخدم كخيار قليل التكلفة لمعالجة المياه الملوثة بالعناصر الثقيلة .