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Adsorption of Cadmium, Copper and Lead from aqueous solution by using some food industrial wastes

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ABSTRACT

Most available technologies applied in the removal of metal contaminants in aqueous systems are the established processes of adsorption. Adsorbents currently are either too expensive or not readily available for aqueous system. There is a need to develop new adsorbents which are readily available at low cost to remove metal contaminants. In this work, some food industrial wastes like sugar beet factory lime (SBFL), rice husk (RH) and pomegranate peel (PP) were used as a potential adsorption of Cadmium, Copper and Lead removal from various aqueous solutions. Characteristics analysis of (SBFL), (RH) and (PP) were investigated. The amount of Cd, Cu, and Pb sorbed either in the mono or competitive sorption experiment and distribution coefficient were calculated. It was found that pH values varied from 3.66 in pomegranate peel to 6.50 in rice husk and was 12.59 in sugar beet. On the other hand the highest value of organic matter observed in PP which score 47.80 % flowed by SB which value was 40.18 %, while lowest value was 34.90 % in RH. The contents of acid detergent fiber (ADF), lignin, cellulose and hemicellulose were 46.05, 4.313, 25.23 and 15.58% respectively in rice husk. The highest R^2 in mono-sorption system was in Cu by using rice husk as sorbent which score 0.92 while the highest R^2 in competitive system was 0.90. Cd removal percentage by SBFL was the highest percentages which score 99.15 % in mono-sorption system and 98.93 % in competitive sorption system. Cu removal percentage by the BSFL was the highest percentage either in mono-or competitive sorption system which values were 98.76 and 97.37 % respectively. This work proved that sugar beet factory lime and rice husk can be used as an efficient adsorbent materials for removal of heavy metals from various aqueous solutions.

Key words: Toxic metals, contaminated water, agricultural wastes, sorption experiments.

Introduction

Water, air and soil contamination with heavy metals is hazardous to plants, animals, microorganism and mankind (Boddu e*t al*., 2008; Francisco e*t al*., 2008). These metals are not only non-biodegradable but also they tend to accumulate in living organisms, resulting in deterioration of public health and causing various diseases and disorders (Krishnapriya and Kandaswamy, 2009; Kannamba e*t al*., 2010). Heavy metals are known that 10 metals namely Pb, Cr, Hg, Ur, Se, Zn, As, Cd, Co and Ni out of the 20 classified metals are referred to as toxic and are released into the environment in quantities which pose serious risks to human health (Johnson e*t al* .,2008). Toxic effects of cadmium are kidney dysfunction, hypertension, hepatic injury and lung damage (John and Jeanne, 1994). Cadmium chloride at teratogenicity dose induced significant alterations in the detoxification enzymes in the liver and the kidney (Reddy and Yellamma, 1996).

Copper is a hazardous heavy metal used in various industries. This toxicity refers to the consequences of excess of copper in the body. In living organisms copper intake in excess causes its accumulation in the liver and leads to gastrointestinal disorders, damage to kidneys and anemia (Bhattacharyya and Gupta, 2011). Lead is a metabolic poison and a neurotoxin that binds to essential enzymes and several other cellular components and inactivates them (Cunningham and Saigo, 1997). Toxic effects of lead are seen on haemopoietic, nervous, gastrointestinal and renal systems (Baykov *et al*., 1996). Recently many studies have focused on the introduced the remove of toxic metals in aqueous solutions from the expensive chemical treatment to the low cost biosorption. The low cost

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adsorbents used to practice adsorption activities were usually waste products from another production like agriculture, industrial and food production, which can be obtained abundantly (Gupta *et al.,* 2009; Zaharin and Phing, 2013). The main advantages gained by using biomass as abiosorbent and/or alternative sorbent, i.e., it is environmentally friendly (waste for waste treatment), locally available in large amounts, low economic value, and attached metals can be easily recovered while biosorbent may be reusable (Babel and Kurniawan, 2003; Lesmana *et al.,* 2009). The agricultural waste products have the ability to remove the metals in aqueous solutions effectively (Wu *et al.,* 2013). Among the agricultural wastes, which were popularly used to remove heavy metals were rice husk, fruit shell and fruit peels (Johan *et al.,* 2011; Lim *et al.,* 2012; Olu-owolabi *et al.,* 2012; Omri and Benzina 2013; Sugashini and Begum, 2013). Sugar beet factories lime (SBFL) have traditionally stockpiled factory lime near them which produced during the sugar beet juice purification process. This factory lime meets the definition of a liming product and can be used for remediation of metal contaminated soils and waters (Dutton and Huijbregts, 2006). Removal of potentially toxic metals by using natural limestone has been investigated by several researchers (Aziz *et al.,* 2008; Sdiri *et al.,* 2012). However, the efficiency of limestone in removal of metals is usually low for intensive remediation operations. Sugar beet factory lime due to its alkalinity and finer texture is expected to be more efficient in heavy metals sorption compared to limestone. Rice husk (RH) is the by-product of the rice milling industry which produced in large quantities. Generally, farmers and rice processors often burn rice husk as wastes, and this is what releases carbon dioxide (CO_2) into the atmosphere (Noor and Rohasliney*,* 2012). For decontamination of heavy metals from drinking water treated adsorbent rice husk is comparatively better than untreated one, because untreated adsorbent can further generate the problems such as low adsorption capacity, high chemical oxygen demand, biological oxygen demand, total organic carbon due to release of soluble organic compounds in plant material (Ngah and Hanafiah, 2008). Rice husk mainly consists of 35% cellulose, 25% hemicelluloses, 20% lignin, 17% ash (including silica) and 3% crude protein. This composition is associated with many chelating ligands and functional groups those make it suitable for metallic cations fixation (Chauhan, 2015). Pomegranate peel (PP) is an inedible part obtained during processing of pomegranate juice. Pomegranate peel is a rich source of tannins, flavonoids and other phenolic compounds (Li *et al.,* 2006). Pomegranate peel is a good source of crude fibers (11.22%) and carbohydrates (80.50%) (Rowayshed *et al.,* 2013).

Materials and Methods

Materials:

Peel of pomegranate (PP)

Mature pomegranate fruits were washed with double distilled water (DDW) till the water was clear of all coloration and cut manually to separate the seeds and peel. The peels cut into small pieces using a sharp knife and dried in an air oven at 105±2ºC for 6 hrs. Dried pieces were cooled, powdered in a laboratory disc mill (Moulinex, model No 205, made in France) to pass through 150-300 μm mesh sieve. The adsorbent was packed in high density polyethylene bags and stored at ambient temperature until use (Singh and Sethi, 2003 ; Devatkal and Naveena, 2010).

Rice husk (RH)

Rice husk was obtained from private rice mill, El-Gharbiya Governorate, Egypt. To prepare the powder, they are initially ground and homogenized using a food blender with steel blades for 10 min, the ground husks were stored in polyethylene bags.

Sugar beet factory lime (SBFL)

Sugar beet lime was obtained from the Delta sugar beet factory in El-Hamoul, Kafr El-Sheikh governorate, Egypt. The received SBFL was kept in desiccator all the time of experiments.

Sorption experiments:

Mono-sorption system:

A batch equilibrium experiment was conducted using Cd, Cu and Pb solutions in a mono sorption system as follows: 2 g of every studied sorbents was equilibrated with 40 mL of 0.01 M $CaCl_2$ solutions containing 50, 75, 100, 125, 150, 175 and 200 Cd, Cu and Pb mg L^{-1} in chloride form, then samples transfereed in 50-mL centrifuge tubes (pre-weighed) for 24 h on a reciprocating shaker at room temperature. Some drops of toluene were added to suppress microbial activity.

A relatively high initial metals concentration range was used in this study, because after a preliminary experiment it was shown that the large initial metals concentrations range were necessary especially with Pb for the alkaline sorbent with high metals sorption capacity. After equilibration the samples were centrifuged and the supernatant was filtered through a Whatman No. 42 filter paper. Three replicates were used for collecting each data point. Cd, Cu, and Pb concentrations in the supernatant were measured by atomic absorption spectrometry (GBC Avanta E, Victoria, Australia; Ser. No. A5616), according to Standard Methods for the Examination of Water and Wastewater (APHA, 2005).

Competitive sorption system:

A batch equilibrium experiment was conducted using Cd, Cu, and Pb in a competitive sorption system with metal concentrations in solution ranging from 50 to 200 mg L^{-1} for all metal solutions as follows: 2 g of every studied sorbents was equilibrated with 40 mL of 0.01 M $CaCl_2$ solutions containing 50, 75, 100, 125, 150, 175 and 200 mgL^{-1}, of Cd, Cu, and Pb, respectively as a chloride salts in 50-mL centrifuge tubes (pre-weighed) for 24 h on a reciprocating shaker at room temperature. Some drops of toluene were added to suppress microbial activity. After equilibration the samples were centrifuged and the supernatant was filtered through a Whatman No. 42 filter paper. Three replicates were used for collecting each data point. Metals concentrations in the supernatant were measured by atomic absorption spectrometry (GBC Avanta E, Victoria, Australia; Ser. No. A5616), according to Standard Methods for the Examination of Water and Wastewater (APHA, 2005).

Treatment of data with Freundlich equation:

The amount of Cd, Cu, and Pb sorbed either in the mono or competitive sorption experiment was calculated as the difference between the initial and final concentration. Cadmium, Cu, and Pb sorption data were fitted to Freundlich equation using the formula:

$$q = k_f \ c^n \qquad Eq. \ 1$$

Where: q is the sorbed metal amount in mg kg^{-1}; c is the equilibrium solution concentration in mg L^{-1}. From this equation, the following sorption parameters were determined: k_f, which represents the metal sorbed at $c = 1$ mg L^{-1}, n which is an empirical parameter expressing the metal sorption intensity. To fit the data, the model was linearized by using the logarithmic transformation resulting in the predictive equation $\log (q) = \log (K_f) + n \log(c)$. The linearized model fitted to each sorbent using analysis of covariance to estimate $\log (K_f)$ and n and test if the $\log (K_f)$ and n coefficients differed across the tested treatments. Estimates of K_f were obtained using $\exp (\log (K_f))$.

Calculation of distribution coefficient (K_d):

The distribution coefficient (K_d) is defined as the ratio of the metal concentration in the solid phase to that in the equilibrium solution after a specified reaction time and is calculated according to (Alloway, 1995; Anderson and Christensen, 1988; Gomes *et al.,* 2001) by using the sorption equations. The distribution coefficients (K_d) is a useful parameter for comparing the sorptive capacities of different sorbents for any particular ion, when measured under the same experimental

conditions. The distribution coefficient (K_d) values were calculated according to (Alloway, 1995; Anderson and Christensen; 1988; Gomes *et al.,* 2001) by using the formula:

Distribution coefficient (K_d) = $q/c = k_f c^n/c = k_f c^{n-1}$ *Eq.2*

Where K_d was estimated by the values of K_f and n obtained as described above. The distribution coefficient (K_d) calculate over the whole range of the added concentrations of metal studied. Also, the sorption selectivity sequence of metal by sorbent could be established at $K_{d\ medium}$ values to obtain one comparable value for each metal and each sorbent (Vega *et al.,* 2006; Shaheen *et al.,* 2009a,b; Tsadilas *et al.,* 2009; Shaheen *et al.,* 2012; Shaheen and Tsadilas, 2012).

Analytical methods:

Cationic composition:

The samples were dry mineralized in quartz crucibles muffle furnace (VULCAN, Model No.A-550, USA). It was later filtered and its volume made up to 50ml with the ash was solubilized in 6mol/l hydrochloric acid and quantitatively transferred to laboratory deionized water .Determinations were carried out using a Pye Unicam Atomic Absorption Spectrophotometer (Model No. SP-192, England). All absorption measurements were performed under the following operating conditions: wavelength, 228.8 nm -Cd and Cu at 324.7 nm and 217 nm- Pb, as described by A.O.A.C. (2005).

Organic matter content:

The organic matter content of samples was determined as mentioned in A.S.T.M.(2010). Determined and recorded the mass of an empty, clean, and dry porcelain dish (MP). Place a part of dry sample, determined and recorded the mass of the dish and sample specimen (MPDS). Place the dish in a muffle furnace (VULCAN, ModelNo.A-550, USA). Gradually increased the temperature in the furnace to 440° C. Leave the specimen in the furnace overnight. Determined and recorded the mass of the dish containing the ash (MPA). The organic matter content in the sample calculated using equation:

OM= MO/ MD x 100

Where, MO = MD - MA (determine the mass of organic matter).
MD=MPDS-MP (determine the mass of the dry sample).
MA=MPA-MP (determine the mass of the ashed).

Fiber Fraction:

Raw Fiber Analyzers (VELP, Scientifica, Italy) was used to determine hemicellulose, cellulose, neutral detergent fiber (NDF), acid detergent fiber (ADF) and lignin (ADL) according to the method of Van Soest and Robertson, (1979) as follow:

Determination of neutral detergent fiber (NDF)

Neutral detergent fiber (NDF) was determined as follows:

A- Grind the dried sample to pass 1 mm screen.
B- Weight in a crucible 1 g of grinded sample.
C- Add 100 ml of neutral detergent solution at room temperature into crucible with 0.5 g of sodium sulfite and some drops of n-octanol.
D- Heat to boiling and reflux 60 minutes from onset of boiling.
E- Filter and wash 3 times with boiling water, then twice with acetone.
F- Dry 8 hrs at 105^{0}C and weighted.
G-Calculate NDF% = (weight of crucible + weight of residue) – weight of crucible / weight of sample x 100.

Determination of Acid Detergent Fiber (ADF)

The difference between NDF and ADF is given mostly by hemicelluloses.

Acid detergent fiber (ADF) was determined as follows:

A- Grind the dried sample to pass 1 mm screen.
B- Weight in a crucible 1 g of grinded sample.
C- Add 100 ml of Acid detergent solution at room temperature and some drops of n-octanol.
D- Heat to boiling and reflux 60 minutes from onset of boiling.
E- Filter and wash 3 times with boiling water, then twice with acetone.
F- Dry 8 hours at 105^0C and Weighted.
G- Calculate ADF% = (weight of crucible + weight of residue) – weight of crucible / weight of sample x 100.

Determination of Acid Detergent Lignin (ADL)

The method is based on the solubilization of cellulose by 72% sulfuric acid and gives a "raw lignin".

Acid detergent lignin (ADL) was determined as follows:
A- Start using the residue of ADF determination.
B- Add 25 ml about of 72% sulfuric acid at room temperature and carry on cool extraction during 3 hrs, stirring every hour.
C- Filter and wash 3 times with boiling water.
D- Dry 8 hrs at 105^0C and weighted.
E- Calculate ADL% = (weight of crucible + weight of residue) – weight of crucible / weight of sample x 100.

Calcium carbonate:

A procedure to determine calcium carbonate by the neutralizing capacity of a calcareous material as mentioned in A.S.T.M. (2010). 25 mL of 1.0 N hydrochloric acid (HCl) solution was added up to sample into the flask. About five minutes after the addition of the 1.0 N HCl solutions the excess acid in the flask is titrated with 0.5 N sodium hydroxide (NaOH) solution using phenolphthalein as indicator. The volume of NaOH solution required for the titration of the excess acid was measured. The calcium carbonate content in the sample calculated using equation:

$$\% \text{ CaCO}_3 = \frac{5.0045(V_1N_1 - V_2N_2)}{W} \times 100$$

Where:
V_1 = Volume of the HCl solution used.
N_1 = Normality of the HCl solution.
V_2 = Volume of the NaOH solution required for titration of the excess acid in mL.
N_2 = Normality of the NaOH solution.
W = Weight of the sample in grams.

Physical properties:

Surface Area Analysis:

The surface areas of samples were determined using the ethylene glycol method described by Joseph and Philomena (2011), as follow: 1g of each sample was weighed and transferred into different beakers. 3ml of ethylene glycol was measured and gently added. The mixtures were swirled carefully until uniform slurry was formed. The slurry was placed in Auto vacuum desiccators (EQ-SP,

Model No. VC-3, USA) having anhydrous calcium chloride and ethylene glycol as desiccant. The mixtures were weighed at intervals of 12 hrs and weight was taken as the final slurry weight. The final slurry weight of samples was obtained after 108 hrs, which was used for the calculations. The specific surface area (SSA) was calculated using equation:

$$SSA = (WFS-WS)/0.000286 = WA/0.000286$$

Where
SSA = Specific surface area.
WFS = weight of final slurry.
WS = weight of Sample.
WA = weight of ethylene glycol retained by the sample in grams.
0.000286 = a constant representing the weight of ethylene glycol required to form a mono molecular layer on a square meter surface per gram of adsorbent (m^2/g).

pH value

The pH values of samples were determined according to the method described by Alkarkhi *et al*. (2010). Ten grams of the sample was shaken with 100ml distilled water, filtered and the pH of filtrate was measured at room temperature, using a digital pH- meter (JENWAY, Model No. 3510, UK).

Quality control and statistical analysis:

In all measurements, blanks, triplicate measurements of metals in extracts, and analysis of certified reference materials for each metal (Merck) were routinely included for quality control according to ISO 17025 requirements for laboratory accreditation. The figures were carried out using Oringin Pro 8G (Origin Lab corporation, Northampton, USA).

Results and Discussion

The results of selected characteristics and total metals concentration in the studied sorbents are presented in Table (1). pH plays an important role in affecting the adsorption rate, pH values varied from 3.66 in pomegranate peel to 6.50 in rice husk and was 12.59 in sugar beet , on the other hand the highest value of organic matter observed in PP which score 47.80 % flowed by SB which value was 40.18 %, the lowest value was 34.90 % in RH.

Table 1: Selected characteristics and total metals concentration in the studied sorbents

Properties	*PP	RH	SBFL
pH	3.66	6.50	12.59
Organic matter, %	47.80	34.90	4.18
Total CaCo₃,%	**nd	nd	82.04
Surface area, m^2g^{-1}	0.214	0.198	2.435
Total metal concentrations, $mgkg^{-1}$			
Cd	nd	0.015	0.027
Cu	4.68	5.49	13.82
Pb	0.18	0.062	0.084

*PP: Pomegranate Peel ; RH: Rice Husk; and SBFL: Sugar Beet Factory Lime, **nd: not detected.

The same Table indicated that SBFL only contain high amount of calcium carbonate which value was 82.04 % while PP and RH were free from it .Also the highest surface area (2.435 m^2g^{-1}) was in SBFL while values were 0.214 and 0.198 m^2g^{-1} in PP and RH respectively.

Total metal concentrations which contain (Cd, Cu and Pb) indicated that same table, Cd not found in PP while values were 0.015 and 0.027 $mgkg^{-1}$ in RH and SBFL, on the other hand the highest value of Cu was 13.82 $mgkg^{-1}$ in SP while decreased to 5.49 and 4.68 $mgkg^{-1}$ in RH and SBFL respectively. From the same table, it could be reported that, pb score 0.18, 0.062, and 0.084 $mgkg^{-1}$ in PP, RH and SBFL respectively. Shaheen *et al.* (2013) characterized SBLF and found that it contain 81.56 % $CaCO_3$ and pH value 12.59 , on the other hand it contain 0.13 mg/ kg Cd and 11.93 mg/kg Cu while Pb not detected in SBFL.

Fibers can be considered as potential ingredients of adsorbents. Data presented in Table (2) demonstrate the fiber fraction of the studied sorbents in the form of NDF (neutral detergent fibre), ADF (acid detergent fibre). ADL (acid detergent lignin), Lignin, cellulose and hemicellulose.

From the obtained results of Table (2), it could be noticed that, the average value of NDF (neutral detergent fibre) was 53.99% and 21.60 % for ADL (acid detergent lignin) in rice husk. The same table showed that, the contents of ADF, lignin, cellulose and hemicellulose were 46.05, 4.313, 25.23 and 15.58% respectively in rice husk. In the current study, PP contained 16.05%NDF, 11.86%ADF, 7.23%cellulose, 1.77% lignin and 5.87% hemicellulose. Rowayshed *et al.* (2013) reported that, pomegranate fruits peel (PP) contained a higher content of crude fiber (11.22%).

Table 2: Fiber fraction in the studied sorbents (as %dry weight basis)

Sorbents	NDF	ADF	ADL	Lignin	cellulose	hemi cellulose
Rice husk	53.99	46.05	21.60	4.313	25.23	15.58
Pomegranate peel	16.05	11.86	3.95	1.77	7.23	5.87

ADF= acid detergent fibre.   NDF= neutral detergent fibre.   ADL= acid detergent lignin.

Data in Table (3) showed that R^2 value and K_d value varied between mono- sorption and competitive system, the highest R^2 in mono-sorption system was in Cu by using rice husk as sorbent which score 0.92 while the highest R^2 in competitive system was 0.90. According to reported by Shaheen *et al.* (2013), R^2 value were higher than 0.85 in the mono-metal and 0.76 in the competitive sorption system.

Also, Kolodynska, (2011); Shaheen *et al.*, (2012) observed that the effective of Freundlich equation in characterizing Cd, Pb, Cu and Zn sorption using natural and industrial sorbents. On the other hand the same table reveals that K_d values which different by using different sorbents. The high K_d value refer that high metal retention by the solid phase through chemical reaction resulting in low metal solubility.

Table 3: Calculated Freundlich parameters (K_f and *n*) and mean values of distribution coefficients (K_d) for the sorption isotherm of Cd, Cu, Pb by the studied sorbents under mono and competitive sorption system

Metal	Mono sorption system				Competitive sorption system			
	Kf, L kg^{-1}	N	R$_2$	Kd, L kg^{-1}	Kf, L kg^{-1}	n	R$_2$	Kd, L kg^{-1}
Pomegranate Peel								
Cd	15.60	0.89	0.42	9.72	24.95	0,86	0.50	134.23
Cu	97.45	0.72	0.81	34.65	253.28	0.71	0,82	112.18
Pb	1634.18	0.04	0.00	138.87	547.65	0.52	0.46	171.65
Rice Husk								
Cd	512.86	0.51	0.51	147.24	910.75	0,21	0.53	113.25
Cu	161.77	0.69	0.92	57.79	402.16	0.67	0.90	183.65
Pb	2177.21	0.08	0.01	1919.16	4102.99	0.42	0.33	9907.66
Sugar Beet Factory Lime								
Cd	1631.17	-0.16	0.27	43641.17	2231.00	-0.06	0.01	3848.06
Cu	2229.46	0.06	0.00	2237.80	2943.74	-0.35	0.20	1444.07
Pb	1201.99	0.19	0.08	92.96	2256.32	0.06	0.02	3604.29

Data recorded in Table (4) and figures (1- 6), noted that value of K_d varied in the metal sorption system, the highest K_d value observed when using SBFL as natural adsorbent either in mono-sorption or competitive system. Which medium score of K_d were 43641.17 and 3848.06 respectively by using SBFL. at the same trend for Cu which highest K_d value noted when SBFL are used in mono or competitive system which values were 2237.80 and 1444.07 respectively , the lowest value of K_d noted when PP used as adsorbent which the value for Cd and Cu were 9.72 and 34.65 in mono-sorption system and 134.23 and 112.18 in competitive system.

On contrast rice husk had a highest K_d for removal Pb in mono- and competitive system which values were 1919.16 and 9907.66 respectively .These results are agreement with reported by Shaheen *et al.* (2013), for using SBFL to remove Cu at the same concentration which medium K_d was 4451.1, the high efficacy of SBFL in sorption metal may be due to its high alkalinity (pH =12.59), high

content of calcium carbonate (82.40%), the same results obtained by Shaheen and Tsadilas (2013) its can be used SBFL to increase solution pH ,reducing metal solubility due to enhanced sorption or precipitation (Hal *et al*., 2012).

Table 4: The distribution coefficient, K_d (L kg^{-1}) calculated for each added metal concentration and $K_{d\ medium}$ for the studied materials under the mono and competitive sorption system
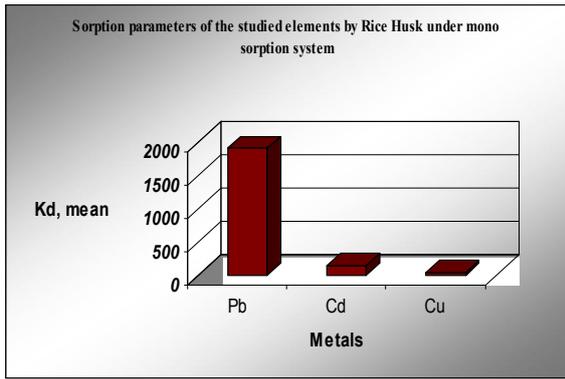
Mono sorption system K_d (L kg^{-1})				Competitive sorption system K_d (L kg^{-1})			
Conc., Mg L^{-1}	*PP	RH	SBFL	Conc., mg L^{-1}	PP	RH	SBFL
Cd							
50	10.34	188.63	515.37	50	105.52	241.96	6053.01
75	10.56	201.94	68251.10	75	103.84	169.40	1648.99
100	9.85	169.31	7782.70	100	117.35	210.90	991.09
125	9.55	163.57	42642.61	125	129.73	60.85	1978.47
150	9.36	85.95	152512.15	150	150.47	55.62	1075.76
175	9.35	124.09	26642.68	175	165.81	28.99	2903.22
200	9.06	97.19	7141.61	200	166.92	25.06	12285.92
$K_{d\ medium}$	**9.72**	**147.24**	**43641.17**	$K_{d\ medium}$	**134.23**	**113.25**	**3848.06**
Cu							
50	44.68	77.47	1954.99	50	134.36	235.67	1124.34
75	38.93	64.06	2626.50	75	134.80	233.41	620.11
100	37.38	64.73	1049.04	100	123.21	204.18	512.63
125	30.80	54.22	2885.59	125	114.72	172.28	532.22
150	31.29	51.05	2198.48	150	96.27	160.75	488.97
175	30.95	48.43	4122.46	175	94.32	141.39	2065.74
200	28.54	44.60	827.54	200	87.57	137.85	4764.50
$K_{d\ medium}$	**34.65**	**57.79**	**2237.80**	$K_{d\ medium}$	**112.18**	**183.65**	**1444.07**
Pb							
50	107.66	1081.23	572.23	50	182.66	10435.25	2849.91
75	128.84	3904.51	369.50	75	263.26	12330.13	4328.81
100	265.09	1454.77	334.54	100	231.73	11092.83	1181.62
125	145.19	1404.82	1895.14	125	149.75	11466.74	1010.64
150	47.35	3330.48	113.61	150	126.87	13397.18	10243.13
175	245.62	535.84	209.37	175	133.77	5267.57	4988.16
200	32.34	1722.49	270.67	200	113.49	5363.93	627.77
$K_{d\ medium}$	**138.87**	**1919.16**	**537.86**	$K_{d\ medium}$	**171.65**	**9907.66**	**3604.29**

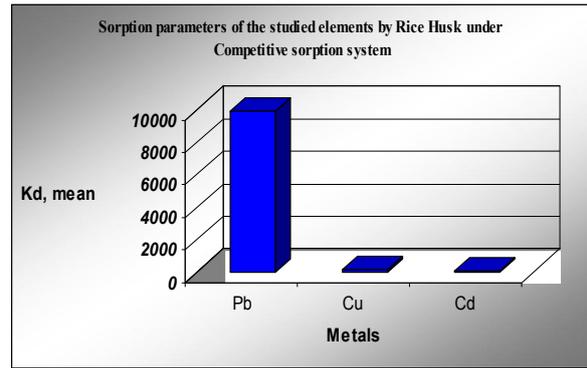*PP: Pomegranate Peel; RH: Rice Husk; SBFL: Sugar Beet Factory Lime*
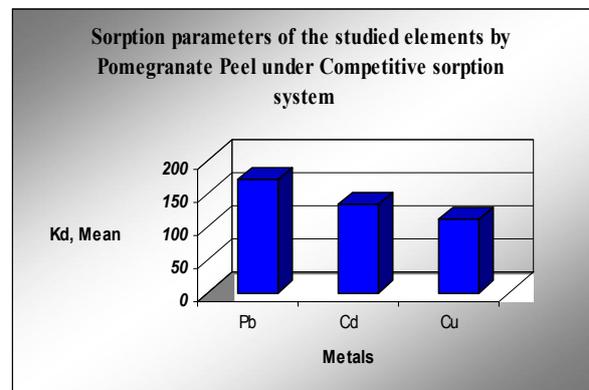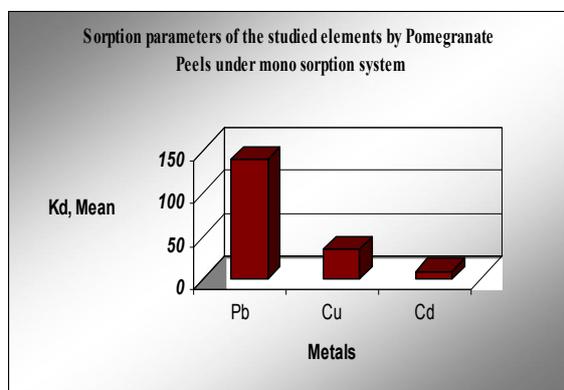
Fig. (1a): The distribution coefficient for each added metal concentration for Pomegranate Peel under the mono sorption system
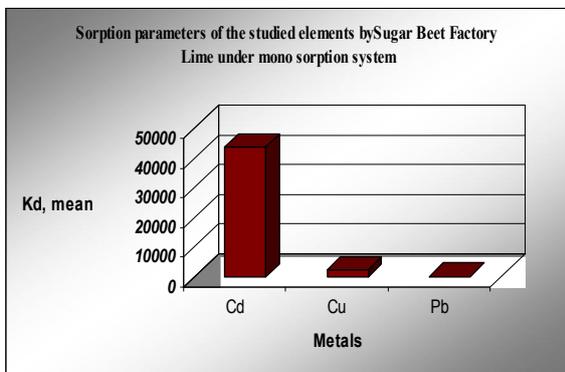
Fig.(1b): The distribution coefficient for each added metal concentration for Pomegranate Peel under the competitive sorption system
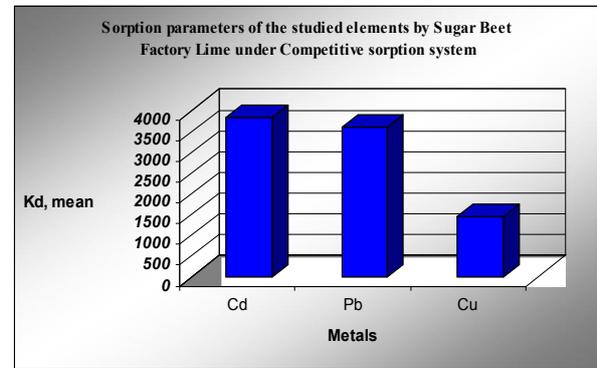
Fig. 2a: The distribution coefficient for each added metal concentration for Rice Husk under the mono sorption system.
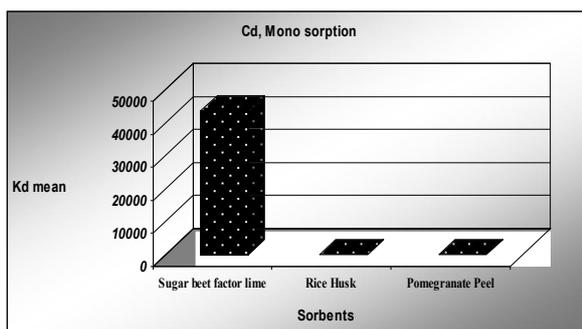

Fig. 2b: The distribution coefficient for each added metal concentration for Rice Husk under the competitive sorption system.
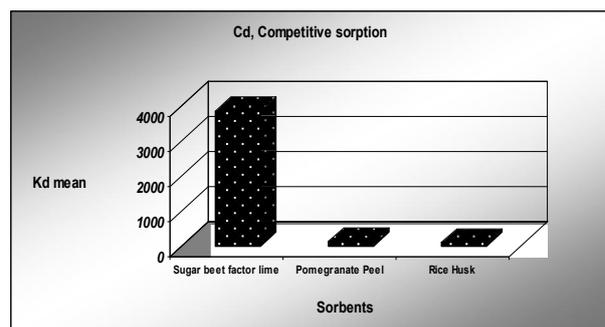

Fig. 3a: The distribution coefficient for each added metal concentration for Sugar Beet Factory Lime under the mono sorption system.
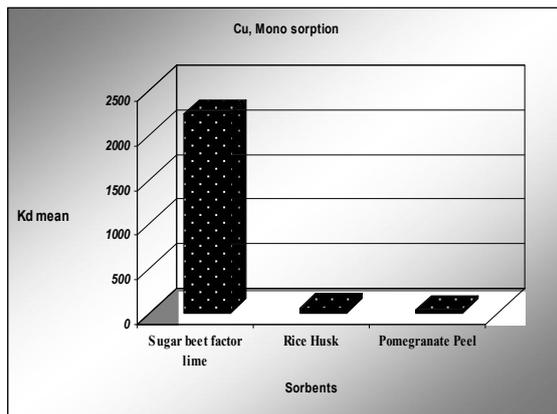

Fig. 3b: The distribution coefficient for each added metal concentration Sugar Beet Factory Lime under the competitive sorption system.
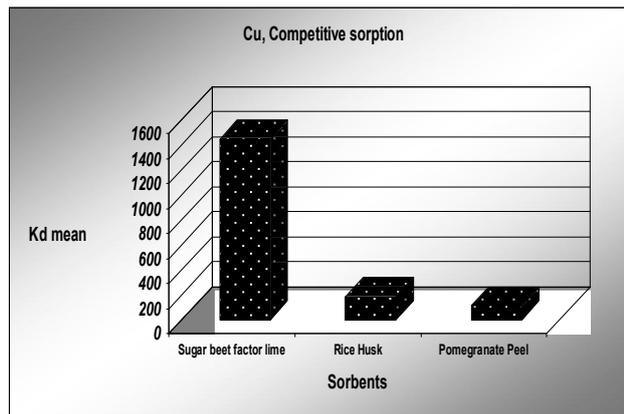

Fig. 4a: The distribution coefficient for Cd concentration for studied sorbents under the mono sorption system

Fig. 4b: The distribution coefficient for Cd concentration for studied sorbents under the competitive sorption system

Fig. 5a: The distribution coefficient for Cu concentration for studied sorbents under the mono sorption system.

Fig. 5b: The distribution coefficient for Cu concentration for studied sorbents under the competitive sorption system.

Fig. 6a: The distribution coefficient for Pb concentration for studied sorbents under the mono sorption system
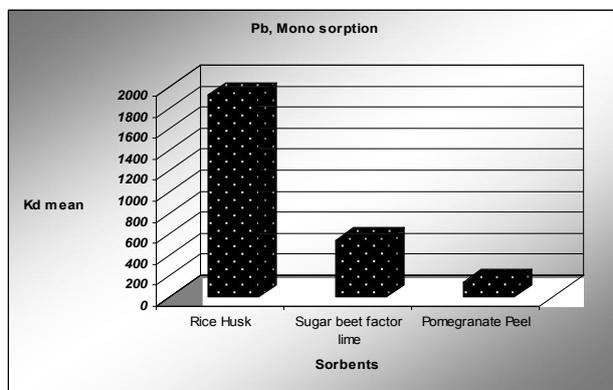
Fig. 6b: The distribution coefficient for Pb concentration for studied sorbents under the competitive sorption system
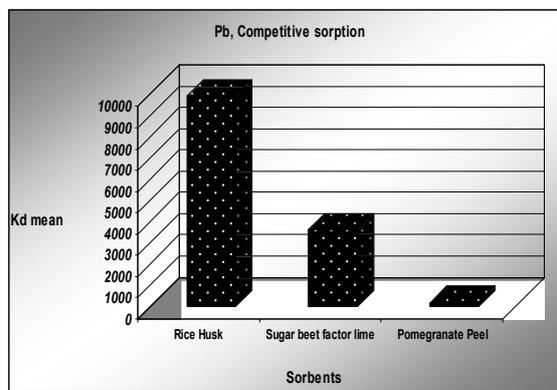
Several factors such as pH, temperature, initial concentration, and contact time affect the adsorption kinetics (Zaharin and Phing, 2013). Table (5 and 6) and figures (1- 6),indicated that metal removal percentage of Cd, Cu, and Pb varied between PP, RH, and SBFL. It noted that Cd removal percentage by SBFL was the highest percentage which score 99.15 % in mono-sorption system and 98.93 % in competitive sorption system. Similar results for Cd sorption has been observed by Hasany and Ahmed (2006) and Janos *et al*. (2007).

At the same trend Cu removal percentage by the BSFL was the highest percentage either in mono-or competitive sorption system which values were 98.76 and 97.37 % respectively. On the other hand the highest metal removal percentage of Pb noted. In the case of using RH as a natural adsorbent in mono- and competitive sorption system which values were 98.3 and 99.76 % respectively, it may be due to the average value of NDF (neutral detergent fibre) was 53.99% and 21.60 % for ADL (acid detergent lignin) in RH. This composition is associated with many chelating ligands and functional groups those make it suitable for metallic cations fixation. Foo and Hameed (2011) suggested that the activated rice husk treated with KOH and K2CO3 had proven that the adsorption capacity was 441.52 mg/g, which is higher compared to the other absorbent such as bamboo, cotton stalk, pine wood powder, coffee ground, and durian peel, figures (1- 6).

Table 5: The distribution coefficient, Kd (L kg-1) calculated for each added metal concentration, Kd medium for the studied materials and percentage of metal removal from samples by the sorbents under the mono sorption system.

Conc., mg L⁻¹	*PP		RH		SBFL	
	K_d (L kg⁻¹)	Metal removal Percentage %	K_d (L kg⁻¹)	Metal removal Percentage %	K_d (L kg⁻¹)	Metal removal Percentage %
Mono sorption						
Cd						
50	10.34	16.2	188.63	84.60	515.37	94.6
75	10.56	53.87	201.94	91.07	68251.10	99.95
100	9.85	34.6	169.31	90.4	7782.70	99.74
125	9.55	30.64	163.57	91.76	42642.61	99.95
150	9.36	30.40	85.95	74.47	152512.15	99.99
175	9.35	40.23	124.09	89.66	26642.68	99.95
200	9.06	30	97.19	85.10	7141.61	99.86
Medium	**9.72**	**33.71**	**147.24**	**86.72**	**43641.17**	**99.15**
Cu						
50	44.68	67.6	77.47	78.5	1954.99	97.7
75	38.93	64.67	64.06	73.53	2626.50	98.88
100	37.38	69.35	64.73	80.8	1049.04	97.77
125	30.80	51.04	54.22	72.8	2885.59	99.39
150	31.29	61.47	51.05	72.47	2198.48	99.32
175	30.95	65.63	48.43	72.03	4122.46	99.70
200	28.54	59.83	44.60	68.08	827.54	98.57
Medium	**34.65**	**62.80**	**57.79**	**74.03**	**2237.80**	**98.76**
Pb						
50	107.66	66.00	1081.23	95.72	572.23	95
75	128.84	81.20	3904.51	99.29	369.50	94.28
100	265.09	93.35	1454.77	98.45	334.54	95.15
125	145.19	90.04	1404.82	98.71	1895.14	99.54
150	47.35	73.33	3330.48	99.58	113.61	87.73
175	245.62	95.89	535.84	97.38	209.37	95.06
200	32.34	70.25	1722.49	99.36	270.67	96.85
Medium	**138.87**	**81.44**	**1919.16**	**98.3**	**537.86**	**94.80**

Table 6: The distribution coefficient, Kd (L kg-1) calculated for each added metal concentration, Kd medium for the studied materials and percentage of metal removal from samples by the sorbents under the competitive sorption system.

Conc., mg L⁻¹	PP		RH		SBFL	
	K_d (L kg⁻¹)	Metal removal Percentage %	K_d (L kg⁻¹)	Metal removal Percentage %	K_d (L kg⁻¹)	Metal removal Percentage %
Competitive sorption system						
Cd						
50	105.52	24.4	241.96	89.40	6053.01	99.22
75	103.84	51.6	169.40	88.93	1648.99	98.23
100	117.35	50.6	210.90	93.70	991.09	97.85
125	129.73	49.12	60.85	75.92	1978.47	99.104
150	150.47	38.4	55.62	77.53	1075.76	98.67
175	165.81	32.57	28.99	56.29	2903.22	99.55
200	166.92	40	25.06	54.05	12285.92	99.9
Medium	**134.23**	**40.96**	**113.25**	**76.55**	**3848.06**	**98.93**

Cu					
50	134.36	82.2	235.67	89.9	1124.34	95.92
75	134.80	88.27	233.41	93.07	620.11	95.77
100	123.21	88.00	204.18	92.20	512.63	96.35
125	114.72	87.72	172.28	89.56	532.22	97.16
150	96.27	81.27	160.75	89.27	488.97	97.48
175	94.32	82.77	141.39	86.43	2065.74	99.26
200	87.57	80.53	137.85	87.18	4764.50	99.65
Medium	**112.18**	**84.39**	**183.65**	**89.66**	**1444.07**	**97.37**
Pb					
50	182.66	80.3	10435.25	99.6	2849.91	98.44
75	263.26	93.87	12330.13	99.8	4328.81	99.33
100	231.73	94	11092.83	99.82	1181.62	98.01
125	149.75	88.08	11466.74	99.86	1010.64	98.12
150	126.87	85.97	13397.18	99.913	10243.13	99.87
175	133.77	89.23	5267.57	99.63	4988.16	99.75
200	113.49	86.73	5363.93	99.69	627.77	98.05
Medium	**171.65**	**88.31**	**9907.66**	**99.76**	**3604.29**	**98.80**

*PP: Pomegranate Peel; RH: Rice Husk; SBFL: Sugar Beet Factory Lime.

Conclusion

From the above discussion, it could be concluded that a low cost adsorbents like Sugar beet factory lime BSFL, Rice husk RH and Pomegranate peel PP are environmentally friendly product, which can be introduced to remove toxic metals in aqueous solutions. They can be pre-treated or modified to improve the current efficiency in order to produce a marketable product for the manufacturing industries.

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