Pomegranate (Punica graantum) Peels as an Agricultural Waste for Removing of CD(II), CR(VI), CU(II), NI(II), PB(II) and ZN(II) from Their Aqueous Solutions

G. M. Taha
South Valley University, Aswan

A. E. Arifien
South Valley University, Aswan

S. El-Nahas
South Valley University, Qena

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G.M.Taha[1]*, A.E.Arifien[1] and S. El-Nahas[2]

[1]Chemistry Dept., Aswan Faculty of Science, South Valley University, Aswan, Egypt.
[2]Chemistry Dept., Qena- Faculty of Science, South Valley University, Qena, Egypt.

ABSTRACT

Pomegranate (Punica Graantum) peels as an agricultural waste was used as an adsorbent for removal of Cd, Cr, Cu, Ni, Pb and Zn ions from simulated aqueous solutions. The adsorption process was carried out using the batch method. Various effective parameters such as pH, initial metal ion concentration, and adsorbent dose, shaking time, particle size and temperature were investigated. Fouier Transform Infrared (FTIR) and Scanning Electron Microscopy (SEM) of Punica Graantum peels were done. The efficiency of Punica Graantum peels toward removal of metal ions was ordered as $Pb^{2+} < Cr^{6+} < Cu^{2+} < Cd^{2+} < Zn^{2+} < Ni^{2+}$, with the corresponding values of 92.8%, 84.6%, 52.8%, 38%, 25.4% and 22.8%, respectively.
Keywords: heavy metal removal, biosorption isotherm, pomegranate, Punica Graantum peels.

INTRODUCTION

Since the rise of the Industrial Revolution, efforts to control pollution by removing man-made pollutants from the environment have been unable to keep pace with the increasing amounts of waste materials and a growing population that further aggravates the situation. With the technology advancement, two groups of substances, in particular, have been found to be an effective power on the particularly disruptive to the natural balance in aquatic ecosystems:

(i) Nutrients, which promote unrestricted biological growth and, in turn, oxygen depletion.

(ii) As well as, sparingly difficult to degradable synthetic chemicals and other waste substances which often contribute to multiple harmful effects on the aquatic ecosystem.

In general, a strong relationship between contaminated drinking water with heavy metals and chronic diseases such as renal failure, liver cirrhosis, hair loss and chronic anemia has been identified (Salem et al., 2000). These diseases are apparently related to the contamination of drinking water with heavy metals. Of these heavy metals, Cd, Cu, Cr, Ni and Pb. Renal failure is related to the contamination of drinking water with Cd and Pb, liver cirrhosis to the contamination with Cu and molybdenum, hair loss to the contamination with Cr and Ni and chronic anemia to the contamination with Cd and Cu.

In addition, examples of chronic health effects include cancer, birth defects, organ damage, disorders of nervous system and damage of immune system (USGAO, 2000).

Cd. Cu, Co, Cr, Mn, Ni, Pb and Zn are toxigenic and carcinogenic agents consistently found as contaminants in human drinking water supplies in many areas around the world (Groopman et al., 1985).

Contamination of drinking water with some heavy metals (e.g., Cd, Cu, Ni and Pb) resulting in populations' health threat as follows:

CADMIUM:

Cadmium appears to accumulate with age progress especially in the kidney and it is considered as carcinogenic. It was reported that (Webb, 1979) the geochemical implications of Cd in human health related to bone and renal failure in populations drinking a contaminated water.

COPPER:

Chronic exposure to contaminated drinking water with copper can result in the development of anemia, liver and kidney damage (Madsen, 1990).In small children, diarrhea could be also occurred. Copper in large doses is very dangerous for infants and peoples with certain metabolic disorders.

NICKEL:

It is regarded as an essential trace metal but toxic in large amounts. It is considered as carcinogenic to human. Toxicity of nickel is enhanced in presence of some other metals in drinking water. Of these, Co, Cu, Fe and Zn. Kaaber et al., 1979 was reported worsening of eczema for human exposed to high level of nickel. Hair loss and derma toxicity in hypersensitive are related to contaminated drinking water with nickel.

LEAD:

Exposure to lead is cumulative over time. High concentration of lead in the body can cause death or permanent damage to the central nervous system, the brain and kidney (Jennings et al., 1996). The damage commonly results in behavior and learning problems. Such problems are hyperactivity, memory and concentration problems, high blood pressure, hearing problems, headaches, slowed growth, reproductive problems in men and women, digestive problems, muscle and joint pain.

Lead is considered the most health threat for children and the effect of lead poisoning can last a lifetime.

There are a variety of established methods for the removal of metal ions from aquatic ecosystems such as, reduction and precipitation, coagulation, flotation, ion-exchange, reverse osmosis or electro dialysis and adsorption. Among of these methods, the most commonly used are the reduction and precipitation as well as the coagulation techniques. These methods have some disadvantages, however, with disadvantages such as, low efficiency and creation of an, often, hazardous sludge. However, ion exchange and reverse osmosis, that applied in few industrial settings, even while technologies due to energy and materials costs effective are expensive (Shukla et al., 2006).

Basically, adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid adsorbent, and strongly bounded by physical and/or chemical interactions (Kurniawan, et al., 2006). Because this can make the contaminant easier to contain and does not require additional energy inputs. Recently, research has been focused on discovering for low-cost adsorbents with high

adsorption capacities has been intensified. Materials which are locally available in large quantities such as natural materials by-products of manufacturing or food processing by-products, and/or agricultural waste or industrial by-products can be utilized as low-cost adsorbents. These sorbents have several advantages, as they are inexpensive raw materials or waste products from industries. Furthermore, most of the waste's masses can be used as a cleaning agent for the environment.

Researchers have investigated several adsorbent materials for the removal of metal ions from aqueous system, particularly agricultural wastes such as: rice bran (Farajzadeh and Vardast, 2003 a,b), wheat bran (Farajzadeh and Monji, 2004) , coir fibers (from coconut husks)(Shukla et al., 2006) , natural and oxidized corncob (Leyva-Ramos, et al., 2005) , by-products of the tea-industry (Cay et al.,2004), petiolar felt-sheath of palm (Iqbal et al., 2002), carbonized jackfruit peel (Indbaraj and Sulochana, 2004) , sugar beet pulp and fly ash (Pehlivan et al., 2006; Taha, 2006; Gupta and Ali, 2000), palm kernel fiber (Ho and Ofomaja, 2006), papaya wood (Saeed, et al., 2005b) , coir pith (Parab, et al., 2006).

The present research was conducted to evaluate the best conditions for removing the heavy metals, Cd(II), Cr(VI), Cu(II), Ni(II), Pb(II) and Zn(II) from their aqueous solutions through the uses of Punica Graantum peels, as no-or low-cost adsorbent material, commonly available in our own environment as an industrial by-product.

METHODOLOGY
REAGENTS
All chemicals used in the experiments were of analytical grade. The stock solutions of Cd(II), Cr(VI), Cu(II), Ni(II), Pb(II) and Zn(II) with concentration of 1000 mg/L were purchased from Specrosol, BDH Chemicals Ltd., Poole, England. Working solutions of metal ions were prepared by dilutions from the stock solutions. The pHs of solutions were adjusted to the required values by using 0.2M HCl or 0.2M NaOH.

PRETREATMENT OF ADSORBENT MATERIAL:
The origin fruit of Punica Graantum peels were collected from local market at Aswan city (Upper Egypt). The Punica Graantum peels were washed several times with tap water, to remove dust and soluble impurities, then with deionized water and then allowed to dry at room temperature .Thereafter, the cleaned peels were kept in oven at 80 °C over night until a constant weight was obtained. The dried peels were crushed by electrical grinder and sieved to obtain different particle sizes (<125µm, 125-250µm, 250-500µm and 500µm to 1nm).

INSTRUMENTATION
The metal concentrations in each sample were determined by atomic adsorption spectrophotometer (solar 969) with a hollow cathode lamp at recommended conditions for each metal, England. A pH-meter (Consort, P901, Belgium) was used for pH adjustment.

Agitating of the samples was performed using a Wirst-action mechanical and thermostated shaker (Burrell Corp. Scientific Instruments, Germany). For the

34   *International Journal of Global Health and Health Disparities*

characterization of the Punica Graantum peels, FTIR analysis and SEM Micrographs were achieved.

The FTIR analysis in solid phase was performed by KBr technique using a Nicolet Fourier Transform Infrared Spectrometer model Magna-FTIR-560 (USA). SEM Micrographs were taken using a model JEM-1010 Jeol Microscope (Japan) operating at 80 KV and 60 µA.

ADSORPTION STUDIES:

Sorption studies were carried out in batch technique in which, 25-ml of each metal ions solution with different initial concentrations (25-400 ppm) was added in a conical flask pre-containing 0.5 g of dried adsorbent material (of varying particle size). The mixture was mechanically shaking with an electrical shaker at various pH values (2-10) for 2h at the predetermined temperature (20-50 °C). Then, the mixture was filtered off and the final concentration in the supernatant of each metal ion was determined by the atomic adsorption spectrophotometer.

For the kinetic studies, 25-mL of 100 ppm of metal ions concentrations was shaken with 0.5 g of dried adsorbent material (with particle size from 250µm to 500 µm) over a period of time expanded from 0 to 180 min. The % of removal for metal ion concentration was calculated by the following equation:

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

Also, the amount of adsorption (mg/L) was calculated by following equation:

$$q = \frac{C_0 - C_e}{W} \times \frac{V}{1000}$$

where C_O and C_e are the initial and equilibrium concentrations (mg/L), W the mass of adsorbent material (g) and V is the volume of the solution (ml).

STATISTICAL ANALYSIS

Different models (Freundlich, Langmuir, Pseudo-first order and Pseudo-second order) were examined to fit the experimental data and all constants were calculated using Microrigin 5.0 and Excel 2000 programs.

RESULTS AND DISCUSSION

PHYSICAL CHARACTERIZATION:

FOURIER TRANSFORM INFRARED (FTIR):

Most adsorbent materials, derived from agricultural wastes contain hemicelluloses and lignin with surface functional groups such as carboxylic, carbonyl and hydroxyl groups, which possess high affinity for the removal of heavy metal ions (Kurniawan, et al., 2006). The FTIR spectra of Punica Graantum peels are presented in Fig (1).
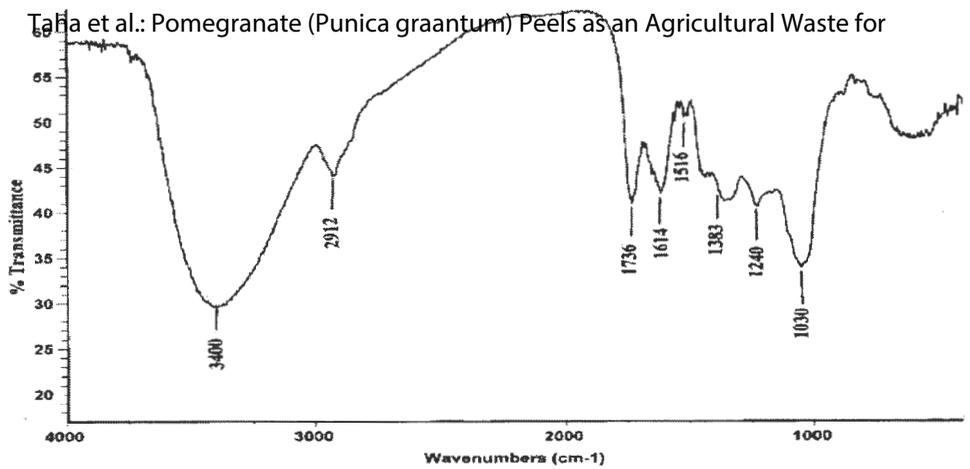
FIG (1): THE FTIR SPECTRA OF PUNICA GRAANTUM PEELS

The above spectrum exhibits a number of absorption bands, indicating the complex nature of the examined material. The FTIR spectrum indicates a broad band at 3400 cm^{-1} representing bonded –OH groups. The band observed at about 2912 cm^{-1} could be assigned to the stretching C-H bond of CH_2 group. In addition, the band around 1736 cm^{-1} is corresponding to the C=O of –COOH group. While, the bands around 1614-1516 cm^{-1} is assigned to the aromatic skeletal (ring breathing) vibrations of Punica Graantum peels structure. It seems that these types of functional groups are likely to participate in metal binding as reported by Malkoc and Nuhoglu, 2005. Also, It is obvious from the FTIR spectrum that the structure of Punica Graantum peels have a large number of polar and non-polar functional groups, which can bind metal ions to their surface through formation of chemisorptive bonds or through ion exchange mechanism.
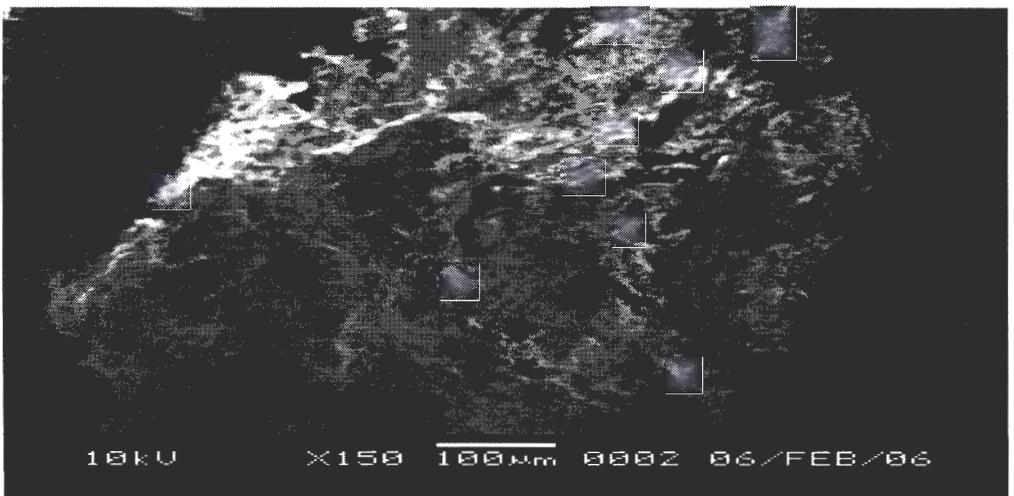

FIG (2): SCANNING ELECTRON MICROSCOPY (SEM) OF PUNICA GRAANTUM PEELS POWDER

Figure 2 shows the complex texture and porosity of the adsorbent materials. Pores and internal surface are requisite for an efficient adsorbent (Mohan et al., 2006). The powder was an assemblage of fine particles, and did not have regular, fixed shape or size. All particles were of various dimensions and all of them contained a large number of steps and kinks on the external surface, with broken edges.

EFFECT OF pH:

The influence of pH values is considered as one of the most critical parameter controlling the adsorption process of metal ion in aqueous solutions. Different metal ions may have different pH optima, possibly due to the different solution chemistry of the species (Parab et al., 2006). Figure 3, shows that the percentage of metal ions sorbet from solution versus different pH values (2-10).

As seen, the removal of metal ions increases by increasing pH and reached to a maximum value. The maximum percentage removal reached 69 % for Cd(II) at pH 6; 79.7 % for Cr(VI) at pH 4; 53.6 % for Cu(II) at pH 4; 45 % for Ni(II) at pH 8; 79.1 % for Pb(II) at pH 4 and 66.8 % for Zn(II) at pH 4. At higher pH values, above 7, most of metals show a trend of declining in adsorption.

The relatively low metal adsorption at lower values of pH may be explained by the fact that at low pH values the H^+ concentration is high and therefore can competes with the metal cations (M^{n+}) on the available surface sites.

On the other hand, the declining in the biosorption of metals at pH above 7 may be attributed to their precipitation forms as hydroxides (Saeed et al., 2005 a and b; Parab, et al, 2006; Özer, and Pirincci, 2006).

When the pH values increase, there will be a decrease in the positive surface charge (since the deprotonation of the sorbent functional groups could be occur), resulting in a lower electrostatic repulsion between the positively charged metal ions and the surface of the adsorbent material, favouring adsorption of metal ions (Martinez, et al., 2006).
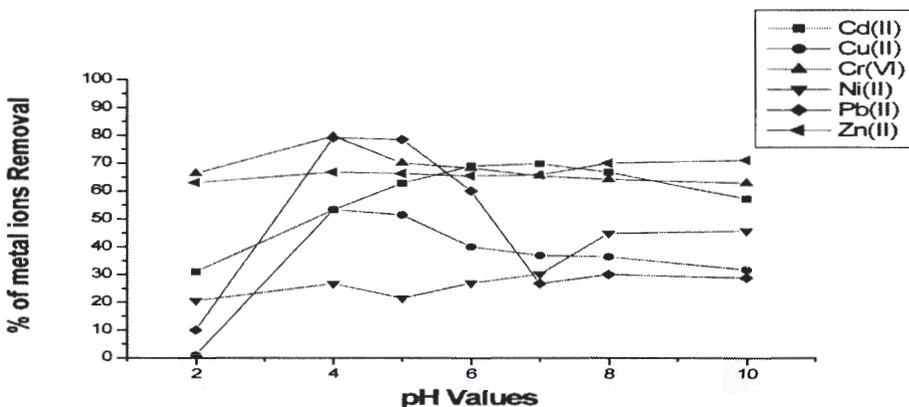

FIG (3): EFFECT OF pH VALUES ON % REMOVAL OF METAL IONS.

The equilibrium time is considered to be one of the most important parameters for economical wastewater treatment plant application of new adsorbent technologies (Madhava-Rao, et al., 2006).

Figure 4 shows the effect of contact time on the adsorption of the studied metal ions at initial concentration of 100 ppm for a period of time extended up to 180 min. One can noticed, the percentage of metal ions removal at the beginning progressed rapidly with increasing the time until it reached the equilibrium within about 30 min for (Cr and Ni ions); 60 min for (Cd , Pb and Zn ions).

Once equilibrium was attained, the percent of metal ions removal did not increase with increasing the shaking time. The early rapid stage removal may be due to the abundant availability of active sites on the adsorbent surface. On saturation of these sites, the sorption becomes less effective. The relatively short contact time necessary to achieve equilibrium conditions is considered as an initial indicator that the adsorption is a chemical-reaction controlled process rather than diffusion controlled process (Perez-Marin, et al., 2007).

The resulting data are compatible with many other works, e.g.; Sharma et al., 2006; Bulut and Baysal, 2006; Pehlivan, et al., 2006; Ho and Ofomafa, 2006.
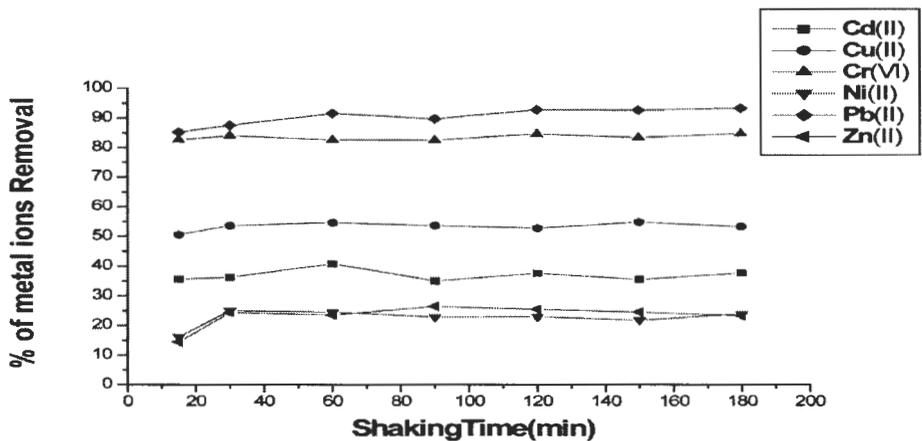

FIG (4): EFFECT OF SHACKING TIME ON % REMOVAL OF METAL IONS.

EFFECT OF INITIAL METAL IONS CONCENTRATION

The initial concentration of metal ions provides an important driving force to overcome mass transfer resistance of metals between the aqueous medium and solid phases (Malkoc and Nuddogu, 2005).

In Case of Ni and Zn ions, percent metal removal increased with increasing the initial concentration as shown in Figure (5). At the beginning, a large surface area of peels is available for the adsorption process which allows the adsorbate to forms a thick monolayer. Then the capacity of the adsorbents gets exhausted and the uptake rate is controlled by the rate at which the adsorbed ions are transported from the exterior to interior sites of adsorbent (Malkoc and Nuddogu, 2005).

38   *International Journal of Global Health and Health Disparities*

In case of Cr and Pb ions, the % metal removal increases sharply with increasing metal concentration until an optimal level and then remains constant. This may be attributed to the saturation of the adsorption sites (Das and Kumar, 2006). The percentage removal of Cd, and Cu ions, were decreased with increasing their concentrations.

This may be ascribed to the fact that, at low metal concentration and fixed adsorbent dose the adsorption of metal ions involves the high-energy sites. As the metal ion concentration increased the higher energy sites saturated and the adsorption continued on the lower energy sites, resulting in a decrease in adsorption efficiencies (Erdem and Özverdi 2005).
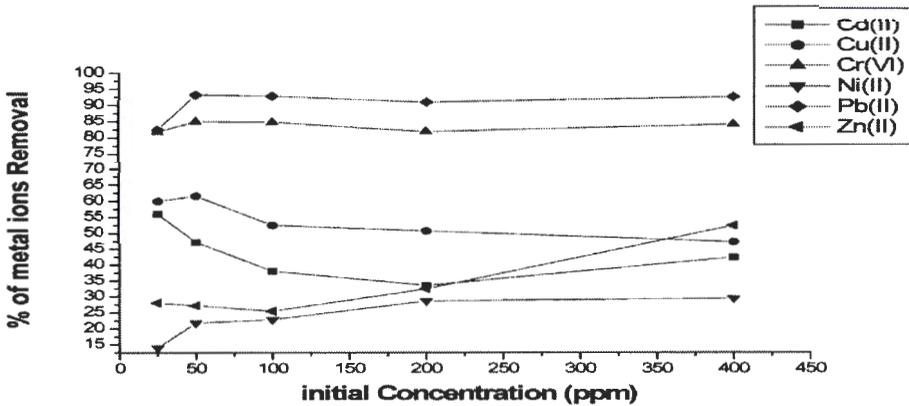

FIGURE (5): EFFECT OF INITIAL METAL IONS CONCENTRATION (25 – 400 MG/L) ON % REMOVAL

EFFECT OF ADSORBENT DOSE:

Adsorbent dose reflects the capacity of an adsorbent for a given initial concentration of an adsorbate. The experimental data represented in Figure (6) is carried out at initial metal ion concentration of 100 mg/L, where the adsorbent dose is varied from 4 to 40 g/L at room temperature. 20g/L was the best dose for all the studied cations which gives adsorption uptake of 38 %, 84.7 %, 52 %, 23 %, 93 %, and 25 % for Cu(II); Cd(II); Cr(VI); Ni(II); Pb(II) and Zn(II), respectively.

. Figure(6) also shows that the percent of metal ions removal of most metals under investigation increase sharply, at the beginning, with increasing the adsorbent dose and then it become almost constant. This may be attributed to the greater availability of exchangeable of surface area sites at higher adsorbent dose (Pehlivan, et al., 2006).
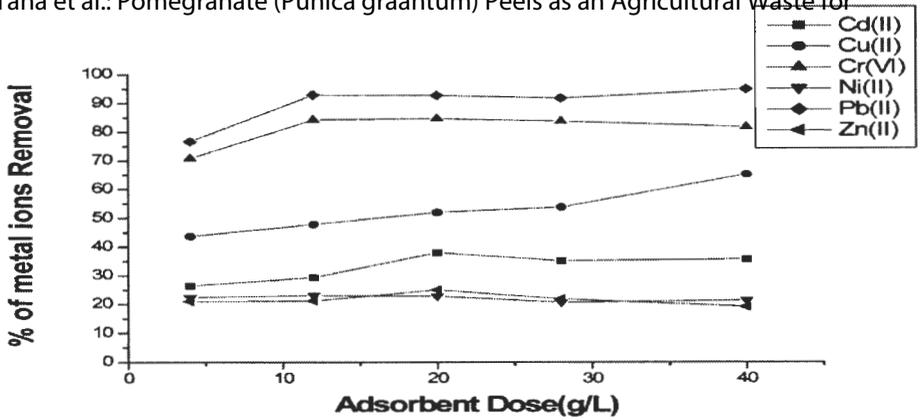
FIG (6): EFFECT OF ADSORBENT DOSE ON % REMOVAL OF METAL IONS

EFFECT OF ADSORBENT PARTICLE SIZE:

Figure (7) shows that the particle size of Punica Graantum peels has no influence on the adsorption of most metal ions under test. Because of some problems in milling, gradation and for the simplicity of filtration, the particle size 500μm-1nm was chosen in this study).
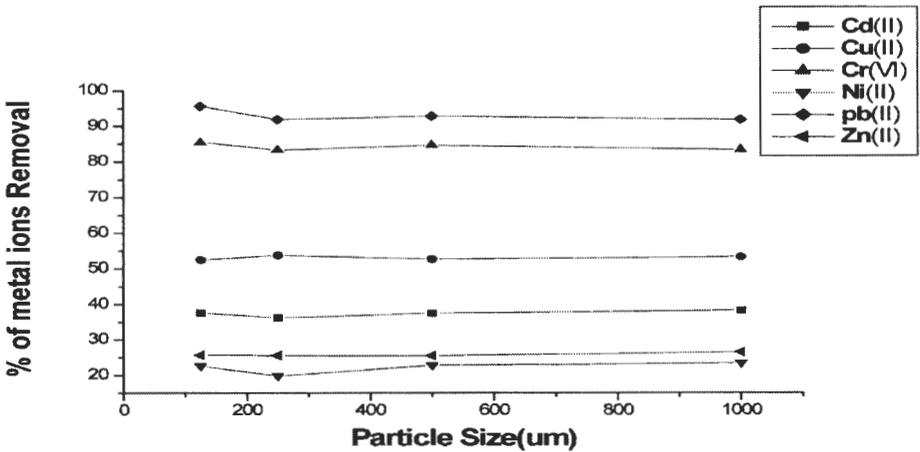

FIG (7): EFFECT OF ADSORBENT PARTICLE SIZE ON % REMOVAL OF METAL IONS

EFFECT OF TEMPERATURE:

The effect of temperature on the adsorption of metal ions under investigation is presented in Figure (8). The results revealed that adsorption uptake of metal ions [except for Cr(VI)] increases from 38 to 61 % for Cd(II); 53 to 66.9 % for Cu(II); 23 to 28 % for Ni(II); 91.5 to 92 % for Pb(II) and 25.8 to 38.81 % for Zn(II) with increasing of temperature from 20-40°C. These increases in metal ions uptake may be due to increase the mobility of the metal cations (as a result of decreasing in solution viscosity

40   *International Journal of Global Health and Health Disparities*

and increasing in metals activity). Furthermore, increasing temperature may produce a swelling effect within the internal structure of the adsorbent enabling metal cations to further penetrate the adsorbent material. In addition, increasing temperature may cause changes in the size of the pores of the adsorbent material (Bulut and Baysal, 2006). In general, increase in metal ions uptake with increasing temperature suggests that the sorption is an endothermic process and may be not only be a physical but also a chemical sorption process (Aksu, 2002).

On further increasing in temperatures from 40 to 50°C, there is a slight decrease in metal ions uptake, from 61.4 to 58 % for Cd(II); from 66.9 to 65 % for Cu(II); from 28 to 27 % for Ni(II); from 92 to 91 % for Pb(II) and from 38.8 to 37.5 % for Zn(II). This decreases may be due to the damage of active binding site in the biomass (Özer, A and Özer, D., 2003). On the other hand, the increase in temperature was accompanied by a decrease in sorption of Cr ions from 84.7 to 76 % and this may be due to the weakening of adsorptive force between the active sites of the adsorbents and adsorbate species and also between the adjacent molecules of the adsorbed phase (Singh et al., 2006). This behavior indicates that the sorption of Cr ions is an exothermic process as was mentioned by Bhattacharyya and Sharma, 2004.
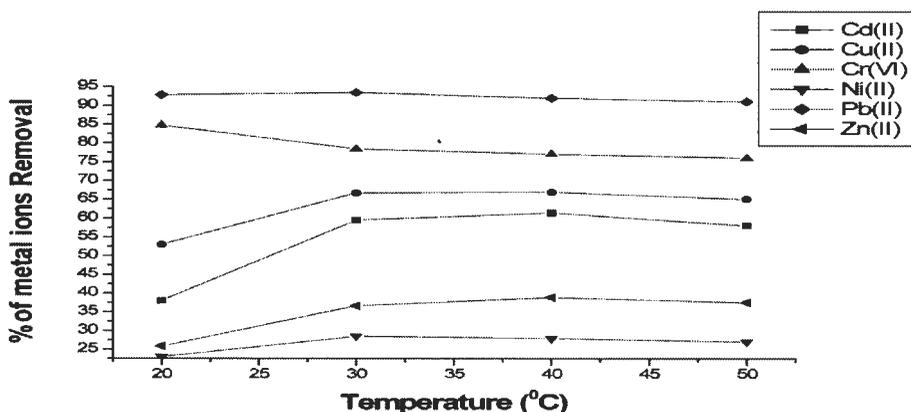

FIG (8): Effect of Temperature on % Removal of Metal Ions

EQUILIBRIUM STUDIES:

Equilibrium studies are described by adsorption isotherms that characterized by certain constants whose values express the surface properties and affinity of the adsorbent. The adsorption isotherms, are usually the ratio between the quantities adsorbed from the adsorbate and that remaining in the solution at fixed temperature at the equilibrium (Han et al., 2005). The most commonly used equilibrium models are Freundlich and Langmuir isotherms, where the temperature is a fixed parameter, and different initial metal ions concentrations are used.

a- Freundlich Isotherm Equation:

The empirical Freundlich isotherm is based on the adsorption on a heterogeneous surface and is expressed by:

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

Which has the logarithmic linear form of:

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

where q_e is the equilibrium sorption capacity (mg/g), Ce is the equilibrium concentration in the liquid phase (mg/L) while K_f and n are Freundlich constants, related to adsorption capacity and intensity, respectively (Özer, A. and Pirincci, H., 2006).

Freundlich isotherm plots are presented in Figure (9), and the calculated Freundlich constants are tabulated in Table 1.

TABLE 1: FREUNDLICH ISOTHERM CONSTANTS AND CORRELATION COEFFICIENT (R^2) VALUES FOR THE METAL IONS UNDERSTUDY.

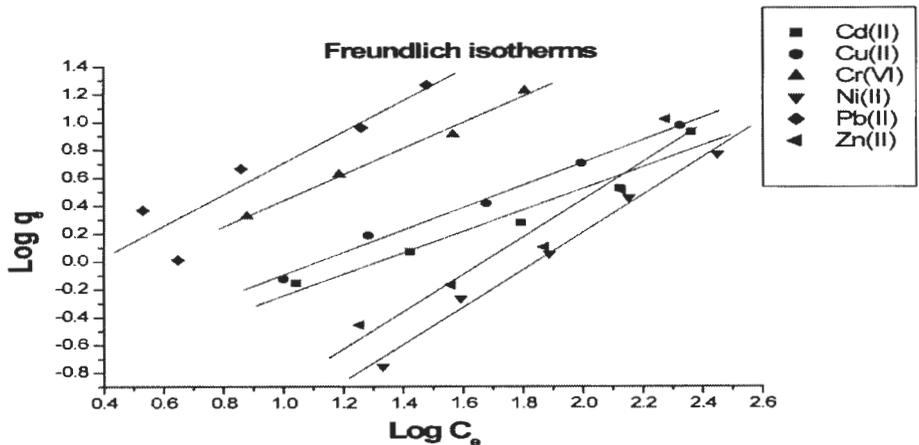| r^2	K_f	n	Metal ion
0.975	0.0969	1.30	Cd (II)
0.997	0.1258	1.24	Cu (II)
0.995	0.2462	0.994	Cr (IV)
0.995	0.0034	0.745	Ni (II)
0.924	0.381	0.890	Pb (II)
0.965	0.0058	0.745	Zn (II)

FIG (9): FREUNDLICH ISOTHERM PLOTS FOR THE ADSORPTION OF THE METAL IONS UNDER STUDY

Freundlich plots have high linearity, (r^2) between 0.997 for Cu(II) and 0.924 for Pb(II). These results indicate that the adsorption process confirmed the empirical Freundlich pattern. Freundlich coefficient (n) is between 1.3 for Cd(II) and 0.745 for Zn(II). Since 1< n< 10, this indicates that the Cd(II) and Zn(II) are the favorably adsorbed of metal ions by this adsorbent material (Han et al., 2005). The other values of Freundlich coefficient (K_f, represent the adsorption capacity) are in the range 0.0034 for Ni(II) and 0.381 for Pb(II).

42   *International Journal of Global Health and Health Disparities*

B-LANGMUIR ISOTHERM:

The Langmuir adsorption isotherm is, probably, the most widely applied model. In addition, it is often used to describe the maximum adsorption capacity of adsorbent material, which is the most important parameter for an adsorption system. The Langmuir equation is described by:

$$q_e = \frac{q_m \times K_a \times C_e}{1 + K_a \times C_e}$$

or in a linear form as:

$$\frac{1}{q_e} = \left[\frac{1}{q_m \times K_a}\right] * \frac{1}{C_e} + \frac{1}{q_m}$$

Where qe is the equilibrium sorption capacity (mg/g), Ce is the concentration of the equilibrium liquid phase (mg/L), q_m is the monolayer capacity (the maximum adsorption capacity which denotes a practical limiting adsorption capacity when the surface of adsorbent is completely covered with adsobate) and Ka (L/mg) the sorption equilibrium constant related to the affinity of binding sites or binding energy (Özer and Pirincci, 2006).

In addition, the essential characteristic of the Langmuir isotherm is the dimensionless constant separation factor or equilibrium parameter, R_L, which is expressed as:

$$R_L = \frac{1}{1 + K_a C_0}$$

The parameter R_L indicates the shape of the isotherm where R_L can takes so many values. Such values are $0 < R_L < 1$; $R_L > 1$; $R_L = 1$ or $R_L = 0$ which denotes to favorable, unfavorable, linear or irreversible adsorption process (Vadivelan and Kumar, 2005). Langmuir constants (qm and Ka) calculated from the plots in Figure (10) are presented in Table 2.
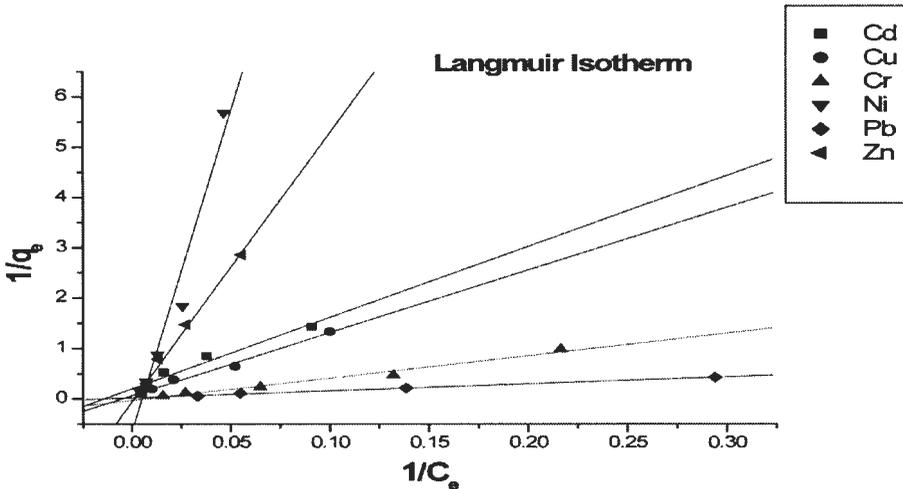

FIG (10): LANGMUIR ISOTHERMS FOR ADSORPTION OF THE METAL IONS UNDERSTUDY.

International Journal of Global Health and Health Disparities   43

TABLE 2: LANGMUIR ISOTHERMS CONSTANTS AND THE CORRELATION COEFFICIENT (R^2) VALUES FOR THE METAL IONS UNDER STUDY.

r^2	K_a	q_m	Metal ion
0.978	0.0142	4.97	Cd (II)
0.996	0.0053	15.24	Cu (II)
0.990	0.0068	33.11	Cr (VI)
0.978	0.0051	1.544	Ni (II)
0.998	0.0148	48.33	Pb (II)
0.996	0.0011	16.37	Zn (II)

As illustrated by correlation coefficients values in Table 2, all curves have good linearity. The correlation coefficients are varied from 0.998 for Pb ions and 0.978 for both Cd and Ni ions.

The magnitudes of Langmuir constants, Ka, indicate the affinity for the binding of metal ions under investigation (Han et al., 2005). Pb(II) and Cd(II) have the highest values of Ka (0.0148 and 0.0148, respectively). While Zn(II) has the lowest Ka (0.0011).Comparing of the q_m values, presented in Table 2 for metal ions under consideration, one can noticed, the adsorption capacities increase in the following order Pb(II)>Cr(IV)>Zn(II)>Cu(II)>Cd(II)> Ni(II).

The favorability of the adsorption process is confirmed by calculating the R_L values, Table (3), at different initial concentrations. As the R_L values for the adsorption of the metal ions, under investigation, are in the range $0<R_L<1$ this indicates favorable of the adsorption process of metal ions with Punica Graantum peels. From the results in Table 3, it is clear that the values of R_L are decreasing with increase in the initial metal ions concentrations. This behavior indicates that the adsorption is most favorable at higher initial metal ions concentrations(Özer and Pirincci, 2006).

TABLE (3): THE R_L VALUES CALCULATED AT DIFFERENT INITIAL METAL ION CONCENTRATIONS.

R_L Values						Co, ppm
Zn^{2+}	Pb^{2+}	Ni^{2+}	Cr^{6+}	Cu^{2+}	Cd^{2+}	
0.972	0.979	0.887	0.854	0.883	0.738	25
0.945	0.959	0.797	0.745	0.791	0.584	50
0.897	0.922	0.662	0.594	0.655	0.413	100
0.813	0.856	0.495	0.423	0.487	0.260	200
0.686	0.748	0.329	0.268	0.321	0.149	400

KINETIC STUDIES:

In practice to design a funcutional adsorption reactor, it is necessary to determine adsorption rate constant, where the adsorption process is time dependant (Özer and Pirincci, 2006). The mechanism of adsorption often involves the chemical reaction between functional groups present on the adsorbent surface and the metal ions. This involves, in most cases, formation of metal-organic complexes or cation exchange reactions.

The order of the adsorbate-adsorbent interactions has been described by using the pseudo-first order derived by Lagergren and pseudo-second order. These models were examined to fit the experimental data for the studied metal ions.

A- LAGERGREN PSEUDO- FIRST ORDER KINETIC MODEL:

The linear form of the Lagergren pseudo- first order equation is expressed as:

$$\log(q_e - q_t) = \log q_e - \frac{K_{ads}}{2.303} t$$

Where, q_e is the amount of metal ion sorbed at equilibrium (mg/g); q_t is the amount of metal ion sorbed (mg/g) at time t and $K_1 (1/\min)$ is the rate constant of Lagergens pseudo- first order equation.
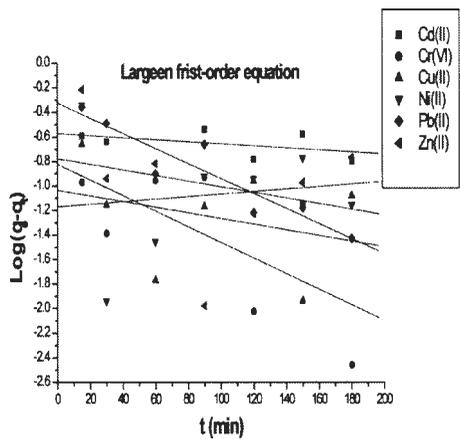
b-Pseudo- Second order kinetic model:

The pseudo second order reaction is greatly influenced by the amount of metal ions on the adsorbent's surface and the amount of metal ions adsorbed at equilibrium. The pseudo second order equation that expressed for the sorption system of divalent metal ions can be written as

$$\frac{t}{q_t} = \frac{1}{K_2 \cdot q_e^2} + \frac{1}{qe} \cdot t$$

Where, qe is the amount of metal ion sorbed at equilibrium (mg/g); qt is the amount of metal ions sorbed (mg/g) at time t and K_2 is the rate constant of pseudo-second order equation (Ho and Ofomaja, 2005).
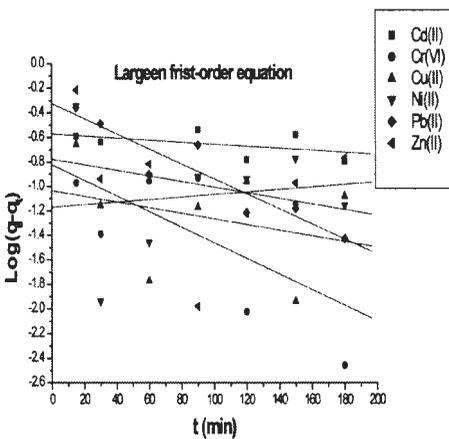
FIG(11): PSEUDO-FIRST ORDER KINETIC PLOTS.

FIG(12): PSEUDO-SECOND ORDER KINETIC PLOTS.

The two models were applied to fit the experimental data. It was observed that, Lagergren pseudo-first order equation is not adequate to describe the adsorption process for most metal ions under study, where the correlation coefficients (r^2) derived from Lagergren pseudo-first order equation are 0.49 for Cd(II); 0.65 for Cr(VI); 0.31 for Cu(II); 0.13 for Ni(II); 0.93 for Pb(II) and 0.26 for Zn(II) . While, the correlation coefficients (r^2) for these plots derived from pseudo-second order equation are superior in most cases (> 0.99) and almost equal to 1, as shown in Figure (12) and presented in Table (4). Accordingly, the sorption process can be considered as pseudo-second order. In this model, the rate-limiting step is a chemical sorption between the adsorbate and adsorbent (Martinez et al., 2006; Mohan et al., 2006).

TABLE (4): THE PSEUDO-SECOND ORDER KINETIC PARAMETERS AND THE CALCULATED (R^2).

r^2	K_2	q_e	Metal ions
0.998	2.21	1.84	Cd (II)
0.999	1.541	2.69	Cu (II)
0.999	0.275	4.23	Cr (VI)
0.996	0.518	1.16	Ni (II)
0.999	0.094	4.70	Pb (II)
0.994	0.363	1.23	Zn (II)

CONCLUSIONS

This work demonstrates that Punica Graantum peels, which considered as no-cost and nontoxic agriculture waste available in many communities, have significant higher adsorption capacities for removing of heavy toxic metal ions from their aqueous solutions. As there is no needs for adsorbent regeneration, there would be significant and hence saving of time and money. In addition, the main advantages of this procedure are the ease and simplicity of preparation of adsorbent, sensitivity and rapid attainment of phase equilibration with good enrichment.

The metal ions adsorption capacity of Punica Graantum peels, as discovered by this work, followed the order Pb(II)> Cr(VI)>Cu(II)>Cd(II)>Zn(II)>Ni(II).

The adsorption process is highly dependent on pH, initial concentration, shacking time, adsorbent dose and temperature. On the other hand, it is independent on adsorbent particle size.

The adsorption process follows both Langmuir and Freundlich models. The adsorption process is very fast and reaches the equilibrium state within 30-60 min. Also, the kinetic sorption process is well fitted to pseudo second order model which supports the hypothesis that that chemisorption is the rate-limiting step for the adsorption process.

The sorption process is effectively dependent on pH, initial concentration, shaking time, adsorbent dose and temperature (endothermic process in case of Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II), while it is an exothermic process with respect to Cr(VI). The adsorption process in this work is adsorbent particle size independent.

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