BatchHeavy MetalsBiosorption by Punica granatum Peels: Equilibrium andKinetic Studies

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ABSTRACT

This research was conducted to study the feasibility of using fruit peels as biosorbent for removal of Pb^{+2}, Cu^{+2} and Zn^{+2} ions from simulated wastewater. A waste biomass of Pomegranate Peel or Punicagranatum L. (P. granatum L.) was chosen as neutral biosorbent in this study.Fourier transformation infrared (FTIR) was used to characterize the surface of PGP, the results confirm that amino, carboxylic, hydroxyl and carbonyl group on the surface of PGP. Different parameters such as initial concentration range between (25-200) mg/L, pH (3-7), contact time (1-2) hour, amount of sorbent (0.1- 4) gm, agitation speed range (200- 500) rpm and temperature (25- 50^{o}C), influencing the sorptive process were examined. Sorption equilibrium isotherm and kinetic data fit well by the Langmuir isotherm and the pseudo-second-order kinetic model, respectively. Sorption processes were spontaneous and exothermic in nature according to the thermodynamic results and the equilibrium was attained within 60 minute. The amount of sorbed metal ions was calculated as 9.9, 9.5 and 7.75 mg/g dry PGP for Pb^{+2}, Cu^{+2} and Zn^{+2}ions, respectively, at pH 5; temperature 25^{o}C; contact time 1hr and 4 gm of peels.

Keywords: heavy metals;wastewater; sorption; PGP; kinetics.

ازالة المعادن الثقيلة من المياه الصناعيه بطريقة الامتزاز بأستعمال قشور الرمان: دراسة حركية الأتزان

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الخلاصه

أجري هذا البحثلدراسةإمكانية استخدامقشورالفاكهةكوسط مازلإزالةالمعادن الثقيلة. في هذه الدراسة تم اختيار قشرة ثمرة الرمان كوسط طبيعي لأمتزاز عناصر النحاس و الرصاص و الخارصين من مياه الصرف الصحي المحاكاة. و قد تم أولا اجراء فحص التحليل الكيفي لقشرة ثمرة الرمان باستخدام جهاز الأشعة تحت الحمراء لغرض دراسة المركبات الكيميائية و المركبات المؤكسدة و معرفة المجموعات الفعالة للمركبات العضوية مثل المجموعات الأمينية،الكربوكسيلية، الهيدروكسيل و الكربونيل. كما تمت دراسة العوامل المؤثرة على عملية الأمتزاز مثل قيمة الدالة الحامضية (4- 5), كمية القشور المستعملة (0.1- 4) غم \ لتر , زمن التماس بين المادة الممتزة و السطح الماز (1- 2) ساعة, التركيز الأولي للعناصر الملوثة (25- 50) ملغم \ لتر ,سرعة الأهتزاز (200- 500) دورة لكل دقيقة و درجة الحرارة (25- 50) درجة مئوية. تم تحليل البيانات الناتجة من عملية الأمتزاز بواسطة موديلات

لانكمير و فريندلج. أظهرت النتائج أن موديل لانكمير هو المفضل أكثر لامتزاز أيونات النحاس و الرصاص و الخارصين على سطح قشرة ثمرة الرمان مقارنة بموديل فريندلج تحت نفس الظروف . وتم اختبار البيانات الحركية من الدرجة الاولى و الثانية , تبين انها ملائمة مع الدرجة الثانية اكثر من ملائمتها مع الدرجة الاولى للنظام المفرد. وكانتعمليات الامتزازتلقائيةوذات طابع طاردة للحرارة وفقا لنتائجالحراريةوقد تحققالتوازنفي غضون 60دقيقة. تم ايجاد السعة القصوى للأمتزاز للنظام المفرد ليكون (9.9 , 9.5, و 7.75) ملغم \ غم لكل من الرصاص و النحاس و الخارصين على التوالي.النتائج تشير الى ان قشرة الرمانيمكن استخدامه بكفاءة عالية لازالة المعادن الثقيلة من المياه.

الكلمات الرئيسية:المعادن الثقيلة؛ مياه الصرف؛ الامتزاز؛ قشور الرمان؛حركية.

1. INTRODUCTION

As a result of industrial activities and technological development, the amount of heavy metal ions discharged into streams and rivers by industrial and municipal wastewater have been increasing incessantly. Heavy metals are member of a loosely-defined subset of elements that exhibit metallic properties, which mainly includes the transition metals, some metalloids, lanthanides, and actinides. Heavy metals such as copper, lead and zinc are main toxic pollutants in industrial wastewater, and they also become major surface and ground water contaminants. Heavy metals are discharged by various industries such as metal purification, metal finishing, chemical manufacturing, mining operations, smelting, battery manufacturing, and electroplating, **lssabayeva et al., 2010**. Removal of heavy metals from industrial wastewater is of primary importance because they are not only causing contamination of water bodies and are also toxic to many life forms. During the last years, increasing attention has been focused on the separation, pre- concentration and/ or determination of the trace heavy metal ions in the environment. The removal of these hazardous materials may be performed using various techniques, including chemical precipitation, electro coagulation, solvent extraction, ion exchange, membrane filtration, adsorption, and flotation separation processes. Of these, adsorption has proved to be an effective technique, but it may suffer from economic limitations owing to difficulties encountered in separating sorbent from suspension in order to be regenerated, **Lu and Gibb, 2007**. Therefore, attempts have been made to develop separation techniques.In recent years, special attention has been focused on the use of natural sorbents as an alternative to replace the conventional adsorbents, based on both the environmental and economical points of view. Natural materials that are available in large quantities, or certain waste products from industrial or agriculture operations, may have potential as an inexpensive sorbents. Due to their low cost, when these materials are at the end of their lifetime, they can be disposed without expensive regeneration. The abundance and availability of agricultural by- products make them good source of raw materials for natural sorbents, **Hanan et al., 2010**.Although the adsorption of heavy metals by activated carbon is another powerful technology; its high cost has prevented its application at least in developing countries. Alternatively, some low cost biomass, such as rice husk, coconut shell, hazelnut shell, walnut shell, cotton seed hull, Bagasse pitch, tea factory waste, etc., **Sudet et al., 2008;Wasewaret et al., 2008**, are being paid more attention to recently.

Those biomass seem to be viable option for heavy metal removal because of their economic and eco-friendly traits due to natural chemical composition, availability in abundance, low cost, high efficiency of heavy metals removal from diluted solutions, regeneration of the bio-adsorbent, and the possibility of metal recovery, **Altun et al.,**

2007. In this paper, Pb^{+2}, Cu^{+2} and Zn^{+2} ions were chosen as a model pollutant in simulated waste water to carry out an investigation on pomegranate peel sorption action. In order to understand the nature of the sorption, equilibrium isotherms, kinetic data, and thermodynamic parameters have been evaluated.

2. EXPERIMENTAL

2.1 Materials

Analytical grade reagents were used in experimental studies. Copper Sulfate pent hydrated ($CuSO_4.5H_2O$), Lead Nitrate (Pb $(NO_3)_2$) and Zinc Chloride ($ZnCl_2$) from (E. MERK, Denmark) were used for preparing synthetic solutions. The properties of metal salts are given in **Table 1**.pH adjustments were carried out by using 0.1N HCl and 0.1N NaOH. Pomegranate peel was used as a biosorbent for the removal of heavy metals. Pomegranate peel was washed with tap water then distilled water, dried at 105^oC for 24 hours in the oven to remove the moisture content until constant weight. The dried peel was milled and sieved, and particles sizes 0.6 mm were selected for investigation in order to obtain more homogenous particle size.

2.2 Apparatus

GBC933 plus Atomic Absorption Spectrometer AAS (GBC scientific equipment Pty Ltd commenced operations in 1978) was used to measure concentrations of soluble copper, zinc and lead. Batch experiments were carried out in Lap Mixer (Cole Parmer, USA).wtw series ion lab pH-meter used for pH measurements.

2.3 Sorption Experiments

Batch sorption experiments have been carried out to find the optimum pH, contact time, and equilibrium isotherms. 2 L flask was employed. The procedure involved filling the flask with 1 L of heavy metal ions solution of (25 - 200) ppm. About (0.1-4) g of adsorbent was added into flask, adsorbents and solution dumped into a flask and mixing at (200-500) rpm mixer speed, the solution and adsorbents allowed for equilibrium in the mixer. Experiments were carried out at initial pH values ranging from 3 to 7; suitable aliquots were analyzed by Atomic Absorption Spectrometer (AAS).The percent removal of sorptive (%) was calculated using Eq. (1).

$$Removal\ \% = \frac{Ci-Cf}{Ci} \times 100 \tag{1}$$

Where $C_i$and C_f(mg/ L) are initial and final concentrations of heavy metal ions.

2.4 Sorption Isotherms

Sorption isotherms are very important tools for the analysis of sorption process. Establish the relationship between the equilibrium concentration and the amount of adsorbate adsorbed by the unit mass of adsorbent at a constant temperature, **Sevgi, 2007**. Langmuir and Freundlich isotherms models are widely used to investigate the sorption process. The model parameters can be construed further, providing understanding on sorption mechanism, surface properties and an affinity of the adsorbent, **Pehlivan and Altun, 2006.**

2.4.1 Langmuir isotherm model

The Langmuir adsorption model is valid for single-layer adsorption. It is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, that the energy of adsorption is constant, and that there is no transmigration of adsorbate in the plane of the surface, **Lucas and Cocero, 2004**. The Langmuir isotherm equation is:

$$q_e = \frac{q_m b C_e}{(1 + bC_e)} \qquad (2)$$

The linear form of Eq. (2) is:

$$\frac{C_e}{q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0} \qquad (3)$$

Where: q_e is the sorbed metal ions on the biomass (mg/g), q_m is the maximum sorption capacity for monolayer coverage (mg/g), b is the constant related to the affinity of the binding site (L/mg), and C_e is metal ions concentration in the solution at equilibrium (mg /L).The Langmuir isotherm is used most frequently to describe the adsorption isotherm which is limited by the assumptions of uniform energies of adsorption on the surface of adsorbent.

2.4.2 Freundlich isotherm model

Freundlich equation is derived to model the multilayer sorption and for the sorption on heterogeneous surfaces. The Freundlich isotherm theory says that the ratio of the amount of solute adsorbed onto a given mass of sorbent to the concentration of the solute in the solution is not constant at different concentrations, **Zhihuiet et al., 2009**. The equation may be written as:

$$q_e = KC_e^{1/n} \qquad (4)$$

The linear form of Eq. (4) is:

$$log q_e = log K + \frac{1}{n} log C_e \qquad (5)$$

Where: Kis the constant indicative of the relative adsorption capacity of the adsorbent (mg/g). 1/n is the constant indicative of the intensity of the adsorption. Both K and n are constants, being indicative of the extent of adsorption and the degree of non-linearity between solution and concentration, respectively. The linear Freundlich plots are obtained by plotting log q_e versus log C_e from which the adsorption coefficients.

2.5 Sorption Kinetics

The kinetics describes the solute uptake rate which in turn controls the residence time of sorbate uptake at the solid–solution interface. Therefore, it is important to be able to predict the rate at which sorbate is removed from aqueous solutions in order to design appropriate sorption treatment processes, **Puraniket, et al., 2005**.The sorption kinetics, thus, constitute a major principle in the determination of the interest of sorption processes. Two kinetic models such as the Lagergren-first order, pseudo-second-order used to describe the biosorption kinetics. The Lagergren-first order kinetic model equation, **Lagergren, 1989,** is:

$$ln\left(q_{eq} - q_t\right) = ln\, q_e \; - k_1 t \tag{6}$$

The Pseudo-second order reaction kinetic can be expressed as, **Ho and Mckay, 1999**:

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_{eq}^2} + \frac{t}{q_{eq}}\right) \tag{7}$$

Where q_{eq} is the amount of metal sorbed at equilibrium (mg/g); q_t is the amount of metal sorbed at time t (mg/g); and k_1 is the equilibrium rate constant of pseudo first sorption (1/min) and k_2 is the pseudo-second order rate constant (g/mg h).

2.6 Thermodynamic Study

The amounts of sorption of single metal ions by Pomegranate peel (PGP) were carried out at temperatures of 25°C, 40°C and 50°C. Thermodynamic parameters were calculated for the system by using the equation, **Khanet, et al., 1995:**

$$lnK_d = \left(\frac{\Delta S^{\circ}}{R}\right) - \left(\frac{\Delta H^{\circ}}{RT}\right) \tag{8}$$

Where K_d is the distribution coefficient; ΔH, ΔS, and T the enthalpy, entropy, and temperature in Kelvin, respectively; R is the gas constant. Gibbs free energy (ΔG) was calculated using the following equation, **Colaket et al.,2009:**

$$\Delta G^{\circ} = \Delta H^{\circ} - \Delta S^{\circ} T \tag{9}$$

The thermodynamic parameters, Gibbs free energy change ΔG^0, standard enthalpy change ΔH^0, and standard entropy change ΔS^0 used to understand the effect of temperature on the biosorption, **Hasanyet, et al.,2002.**The Gibbs free energy indicates the degree of spontaneity of the adsorption process, where more negative values reflect a more energetically favorable adsorption process, **Colaket et al.,2009.**The decrease in the value of the free energy with increase in temperature indicates that the biosorption process is endothermic and it is thereby favored with increase in temperature. While the increase in the value of the free energy with increase in temperature indicates that the biosorption process is exothermic and it is thereby favored with decrease in temperature, **Hasanyet, et al.,2002.**

2.8 Modified of natural sorbent

In general, chemically modified agricultural waste peels exhibit higher biosorption capacities than unmodified forms. Numerous chemicals have been used for modifications which include mineral and organic acids, bases, oxidizing agent, organic compounds, etc., agriculture peel or husk in its natural state contains a high proportion of cellulose, hemicelluloses, lignin and mineral ash, **Wan, et al., 2007,** and this cellulosic surface will becomes partially negatively charged when immersed in water and hence, produce columbic interaction with cationic species in water, **Laszlo, et al., 1994 and Baig et al., 1999** studied on the binding of Pb^{+2}, Cu^{+2}, Ni^{+2}, Cd^{+2}, Zn^{+2}, $Cr^{+2}$and Cr^{+2}ions to the inactivated biomass of Solanumelaeagnifolium and suggested that carboxyl groups (—COOH) are responsible to some extent for the binding of metal ions. This means that metal binding can be enhanced by increasing the number of carboxylate ligands in the biomass. In this review, some of a fine powder of pomegranate peel was treated with sodium hydroxide (0.1 M) to improve the biosorption capacities to copper, lead, and zinc ions. 10 gm of dried PGP soaked in solution 50 mL NaOH (0.1 M) for 4 hr. by filtration, the sodium hydroxide modified Pomegranate peel (MPGP) was washed with distilled water until the pH value of the solution reached 7.0, and then dried. This (MPGP) is tested in sorption stage.

3. RESULTS AND DISCUSSION

3.1 FTIR Result

In order to understand the possible biosorbent- metal ion interactions, it is essential to identify the functional groups present on the biomass involved in this process. The main effective binding sites can be identified by FTIR spectral comparison of the biosorbent, copper (II) ions- loaded biosorbent, lead (II) ions- loaded biosorbent, and zinc (II) ions- loaded biosorbent. Biosorbent were examined using (SHIMADZO FTIR, 800 series spectra- photometer).All samples were analyzed in the laboratory of Ibn Sina/ college of science/ University of Baghdad.Three flasks of 250 ml were filled with 100 ml of each metal solution 50 mg/L and 1gm of dried Pomegranate peel (PGP). The flasks were then placed on a shaker and agitated continuously for 3hr at 200 rpm. Samples of each flask were dried in oven at 50 C^0 for 48 hr., from **Fig.1**. The FTIR spectral indicates the presence of amino, carboxylic, hydroxyl and carbonyl groups. Contribution of each functional group in this process is summarized in Table 2. Pb^{+2} have greatest changes in the peak values of bands than Zn^{+2} and Cu^{+2}, while Zn^{+2} was the lowest one. It can be concluded that functional groups of PGP biomass prefers Pb^{+2} than other metals.

3.2 Effect of pH

The pH is an important factor affecting the removal of metal ions from aqueous solutions. Dependence of metal sorption on pH is related to both the metal chemistry in the solution and the ionization state of functional groups of the adsorbent which affects the availability of binding sites, **Heidari, et al., 2009.** In order to evaluate the influence of pH on sorption of the metal ions, the experiments were carried out in the pH range of 3–7 for Pb^{+2}, Cu^{+2} and Zn^{+2} ions. The pH ranges were chosen as mentioned ranges in order to avoid precipitation of metal ions in the form of metal hydroxides, initial metal concentration 50 mg/L, adsorbent dose 4 g/L, at 25^oC. The effect of pH on removal efficiencies is shown in **Fig.2**, the percentage sorption increases with increase in pH. The minimum sorption was observed at low pH. This behavior may be due to the fact that the presence of higher concentration and higher mobility of H^+ ions favored sorption compared to M (II) on the other hand in the acidic medium due to high solubility and ionization of metal ions. The surface of the adsorbent becomes more positively charged at high H^+ concentration such that the attraction between adsorbents and metal cations is reduced. In reverse with increase in pH the negatively charged surface area becomes more thus facilitating greater metal removal and then at very high pH also the percentage removal decreases, **Onundiet, et al., 2010.** The maximum sorption was observed within the pH range 4 to 7 which might be due to partial hydrolysis of metal ions. Further increase in pH i.e., above 7 of the solution causes precipitation of metal ions on the surface of the adsorbent by nucleation. To achieve high extraction efficiency without metal hydroxide precipitation, pH of 4.0 for Pb^{+2} and pH of 5.0 for Cu^{+2} and Zn^{+2}were selected for subsequent experiments. Similar optimum pH value was also reported for sorption of Cu^{+2}ions by other natural materials, such as sunflower leaves used in the investigation of **Benaïssa and Elouchdi, 2006**, rubber leaves in the study carried out by **Ngah and Hanafiah, 2007**, orange peel utilized in the study by **Liang and Tian, 2010.**

3.3 Effect of Contact Time

The removal of metal ions (Cu^{+2}, Pb^{+2}, and Zn^{+2} ions) from aqueous solution was studied as function of contact time in the time interval (0-120) min at 50 mg/L initial metal concentrations, pH (4-5), 4g/L adsorbent, and room temperature. The effect of contact time on removal of metal ions is shown in **Fig. 3**, it was observed that the rate of metal ions removal was higher at the beginning until 60 min and, after that, the sorption rate become practically very slow and after 120 min. it starts decreasing. The difference in the degree of sorption may be due to the existence of greater number of sorbent sites available for the sorption of metal ions. As the remaining vacant surface sites decreasing, the sorption rate slowed down due to the formation of repulsive forces between the metals on the solid surface and in the liquid phase, the same behavior was noticed by **Qassim, 2013.** Based on these results 60 min was considered as the optimum time for the rest of the experiments.

3.4 Effect of Pomegranate Peel Dose

The effect of sorbent dose on the removal of metal ions was studied using PGP concentrations of 0.1-4 g/L by shaking 500 rpm with 50 mg/L of (Cu^{+2}, Pb^{+2}, and Zn^{+2} ions) concentrations for 1 hr, at 25°C, and pH (4- 5). The results are shown in **Fig.4**. It was found that the retention of metals increased with increasing amount of sorbent dose up to 4 g/L this value was taken as the optimum amount for other trials. Sorption of metal ions was increased as the sorbent amount increased. The results were expected because for a fixed initial metal concentration, increasing adsorbent amount provides greater surface area or sorption site, **Heidariet et al., 2009.** The removal efficiency of Pb^{+2} is higher than that of Cu^{+2} and Zn^{+2}. This may be due to the physical and chemical properties of lead to be more favorable to be adsorbed than zinc and copper. This could be explained on the basis of ionic radii. Ionic radii of Pb, Cu, and Zn are 1.54, 1.45, and 1.42 $\mathring{A}$, respectively. Pb^{+2} having higher ionic radii, therefore, the Pb^{+2} ions will be removed more efficient. Furthermore, the molecular weight of Pb^{+2}, Cu^{+2}, and Zn^{+2} are

331.2, 249.70, and 136.28 respectively. As the uptake related to the molecular weight of metals and as the molecular weight increases the uptake rate increases and Pb^{+2} having higher molecular weight, **Nawar, 2012.**

3.5 Effect of Initial Metal Concentration

The initial concentration of Pb^{+2}, Cu^{+2}, and Zn^{+2} ions provides an important driving force to outweigh all mass transfer resistance of metal between the aqueous and solid phases. Removal of these ions for various initial concentrations (25 to 200 mg/L) by PGP dose (4g/L) at 60 min contact time and at pH (4-5) have depicted in the **Fig.5**. The percentage removal of copper increased 9.8% to 79%, for lead 20.13% to 83.3%, and 4.43% to 68% for zinc, with decrease in initial concentration from 200mg/L to 25 mg/L. According to **Kumar et al., 2010**, at lower metal ions concentration, the percentage uptake was higher due to larger surface area of sorbent being available for sorption. When the concentration of metal ions became higher, the percentage removal decreased since the available sites for sorption became less due to saturation of sorption sites. At a higher concentration of metal ions, the ratio of initial number of moles of metal ions to the sorption sites available was higher, resulting in lower sorption percentage.

3.6 Effect of Temperature

In order to investigate the effect of temperature on metal sorption onto (PGP) in a single component systems, experiments were carried out with initial concentrations of Pb^{+2}, Cu^{+2}, and Zn^{+2} ions of 50 mg/L at 60 min. contact time and 4 g/ L Pomegranate peel at best pH for each metal, at temperature range (25, 40 and 50°C) and a constant stirring speed of 500 rpm. The results are plotted in **Fig.6** for copper, zinc and lead respectively. From this figure it can be seen that sorption decrease with increasing temperature, suggesting that the process is exothermic in nature. The removal efficiency of copper decreased from 74% to 33.18%, zinc from 62% to 29.36%, and lead decreased from 76% to 50.5% with increasing temperature from 25 to 50°C. The same behavior was noticed by **Mabrouk and Mourad, 2010** for Pb(II) adsorption by Tunisian clay, **Sha et al.,2010** for Cu (II)adsorption by orange peel, **Tushar and Dustin, 2011** for Zn (II) adsorption by natural Bentonite. The explanation of this behavior due to fewer active sites is available on the surface of adsorbents or due to the mobility of metal ions in the solution increases with increase in temperature, **Liang et al., 2010.Table 3** summarizes the distribution coefficients from a series of batch experiments at different temperatures.

3.6.1 Thermodynamic study

The amounts of sorption of Pb^{+2}, Cu^{+2}, and Zn^{+2} ions by Pomegranate peel (PGP) were carried out at temperatures of 25°C, 40°C and 50°C. The thermodynamic parameters such as $\Delta G°$, $\Delta H°$ and $\Delta S°$, describing lead, copper and zinc ions uptake by PGP, were calculated using the thermodynamic equations described in section (2.6). The values of enthalpy and entropy were obtained from the slope and intercept of $\ln K_d$ versus 1000/T **Fig. 7**. The distribution coefficients and thermodynamic parameters (Gibbs free energy change ΔG^o, standard enthalpy change ΔH^o, and standard entropy change ΔS^o) for the sorption of metal ions on Pomegranate peel (PGP) at different temperature are given in **Table 4**. The negative values of ΔGat all studied temperatures indicated that sorption process is spontaneous. The negative value of ΔH, indicating the exothermic nature of the process, which further explain the fact that sorption efficiency decreased with the increase of temperature. The positive value of ΔSindicatesan increase in randomness at the solid/solution interface during the biosorption of Pb^{+2}, Cu^{+2}, and Zn^{+2} ions Pomegranate peels.

3.7 Sorption Isotherm Parameters

The calculated parameters of the Langmuir, Freundlich isotherms (section 2.4) for the sorption of copper, lead and zinc onto P. granatum L. peels are listed in **Table 5**. The Langmuir model described the sorption data slightly better than Freundlich model depending on the value of correlation coefficients.

3.8 Sorption Kinetic Parameters

The Lagergren first-order, pseudo-second-order diffusion models have been applied for the experimental data to analyze the sorption kinetics of Pb^{+2}, Cu^{+2}, and Zn^{+2} ions (section 2.5). The slopes and intercept of ln (q_e-q_t) versus t plot **Fig. 8a** were used to determine the pseudo first order rate constants (k_1) and q_e, compiled in Table 6 along with correlation coefficients (R^2) values.A plot of t/qt versus **Fig. 8b** was used to determine the pseudo-second-order rate, constantk_2 and $q_e$values from the slope and intercept, **Table 6**. The values of correlation coefficient (R^2) indicate a better fit of pseudo- second- order model with the experimental data compared to pseudo- first- order model. The values of q_e calculated from the second order kinetic model agreed very well with the experimental values, and the regression coefficients are over 0.956. Therefore, the second-order model can be applied for Cu^{+2}, Pb^{+2} and Zn^{+2}ions sorption process. The first- order kinetic model was used for reversible reaction with an equilibrium being established between liquid and solid phases. Whereas, the second order kinetic model assumed that the rate limiting step may be chemical sorption, **Yuaet et al., 2009.**

3.9 Results of Modification PGP

In order to investigate the effect of treated sorbent on removal of Pb^{+2}, Cu^{+2}, and Zn^{+2}ions; 1L of 50 mg/L (for each individual ions) metal solution was used. The experiments were performed in pH range 4-5; the treated PGP 4 g; contact time 2hr and stirred speed 500rpm. The effect of treated PGP on removal efficiency is shown in the **Fig. 9**. An increase of percentage removal of lead, copper, and zinc ions were obtained after modification of the sorbent, the removal percentage in raw material reached 78%, 76%, and 62%, whereas in treated material it reached 95.78%, 85.7%, and 70% for Pb, Cu, and Zn, respectively. This could be attributed to impurities of treated adsorbents, which could be removed by modification and more exchangeable surface area becoming available, **Hananet et al., 2010.**

4. CONCLUSIONS

The following results have been obtained:

1. According to the experimental results, PGP seems to be an effective, low cost and alternative adsorbent precursor for the removal of heavy metal ions from aqueous solutions.

2. The equilibrium isotherm data showed that pH value plays an important factor in the sorption efficiency. The best pH values for removal were (4- 5) for copper, zinc and lead.
3. The linear Langmuir and Freundlich isotherms were used to represent the experimental data and the data could be relatively well interpreted by Langmuir isotherms.
4. The sorption processes for copper (II), zinc (II), and lead (II) ions are spontaneous since the calculated standard Gibbs free energy values are all negative. The negative values of ΔHsuggest that the nature of sorption is exothermic.
5. The experimental data showed that the sorption of three metals well fitted the pseudo-second-order kinetic model.
6. An increase in the sorbent dosage (0.1- 4 gm) resulted in higher metal ions removal efficiency and by increasing the sorbent dosage the contact time that required to reach equilibrium decrease.
7. The results of FTIR analysis showed that Pb^{+2} made a greater change in the functional groups of PGP biomass revealed high affinity of PGP toward this metal, the wave numbers of the amino and hydroxyl groups on the biosorbent were changed after the biosorption of Cu^{+2}, Pb^{+2} and Zn^{+2} ions due to the interaction between biosorbent and these metals.
8. The usability of P. granatum L. peels was also examined in the simulated wastewater samples after treated with NaOH (0.1M). The results indicate that the sorption yields for Cu^{+2}, Pb^{+2} and Zn^{+2} ions are very high. The modification enhanced the sorption efficiency by about (18%).

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Table 1. Properties of metal salts.

Property	**Lead nitrate** **$Pb(NO_3)_2$**	**Copper sulfate** **$CuSO_4.5H_2O$**	**Zinc chloride** **$ZnCl_2$**
Molar mass g/mol	331.2	249.70	136.28
Atomic weight g/mol	207.2	63.546	65.208
Appearance	White crystals	Blue	White crystals
Density g/cm^3	4.53	2.284	2.907

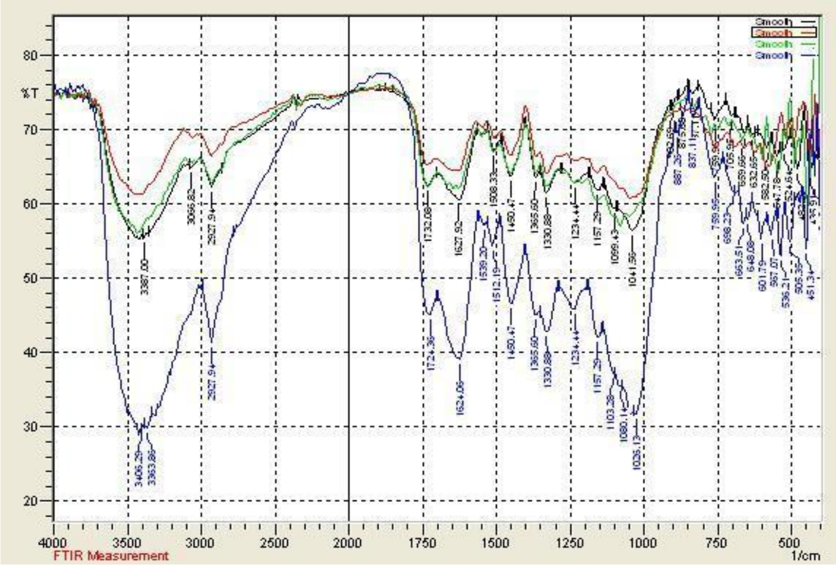


Figure 1. FTIR spectrums of PGP (black line) raw PGP, (blue line) Pb loaded PGP, (green line) Cu loaded PGP, and (red line) Zn loaded PGP.

Table 2. Function groups before and after PGP biomass loaded with Cu (II), Pb (II) and Zn (II) ions in single systems.

Wave number before sorption cm^{-1}	**Assignment groups**	**After sorption of Cu^{+2} cm^{-1}**	**After sorption of Pb^{+2} cm^{-1}**	**After sorption of Zn^{+2} cm^{-1}**
3406.00	Carboxylic, Amides, Amine	3429.43	3452.58	3406.29
3387.00	Carboxylic acid, Amides	3336.85	3387.00	3363.86
3066.82	Carboxylic acid, Hydroxyle, Alkenes	3059.10	3059.10	3059.10
2927.94	Carboxylic acid	2924.09	2927.94	2927.94
1732.08	Carboxylic	1732.08	1735.93	1724.36
1627.92	Carboxylic, Hydroxyle, Alkanes	1627.92	1627.92	1624.06
1508.38	Carboxylic	1512.19	1508.33	1512.19
1365.60	Nitro groups	1365.60	1365.60	1365.60
1330.88	Nitro groups	1330.88	1330.88	1330.88
1234.44	Carboxylic acid	1234.44	1230.58	1234.44
1157.29	Carboxylic acid	1153.43	1157.29	1157.29
1041.56	Carboxylic acid	1049.28	1045.42	1042.13
875.86	Aromatic	879.54	865.39	887.28

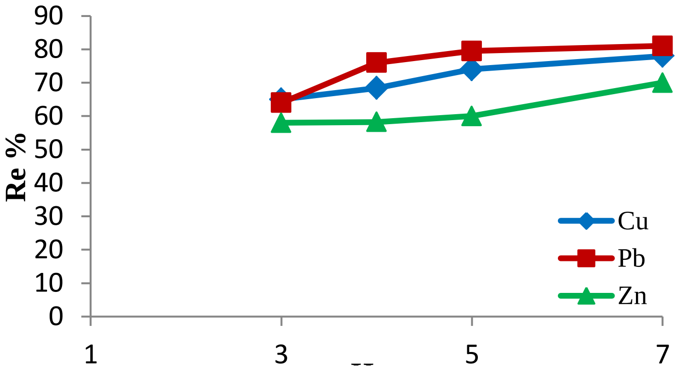


Figure 2. Effect of pH on the removal of Cu^{+2}, Pb^{+2}, and Zn^{+2}ions using Pomegranate peel (W=4 g/L; T=25°C;C_i= 50 mg/L; rpm =500).

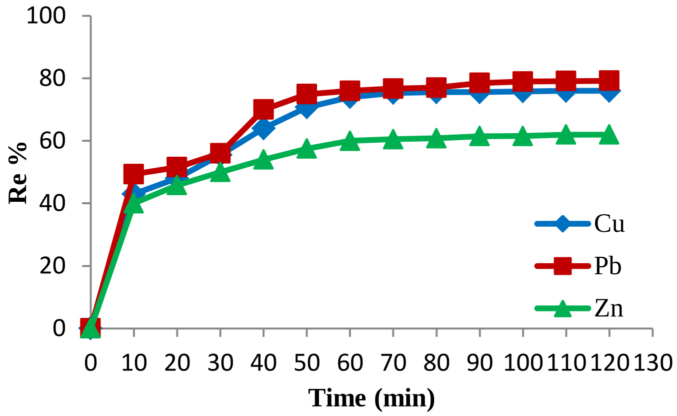


Figure 3. Effect of contact time on the removal of Cu^{+2}, Pb^{+2}, and Zn^{+2}ions using Pomegranate peel (W=4 g/L; pH 4-5; T=25°C;C_i= 50 mg/L; rpm =500).

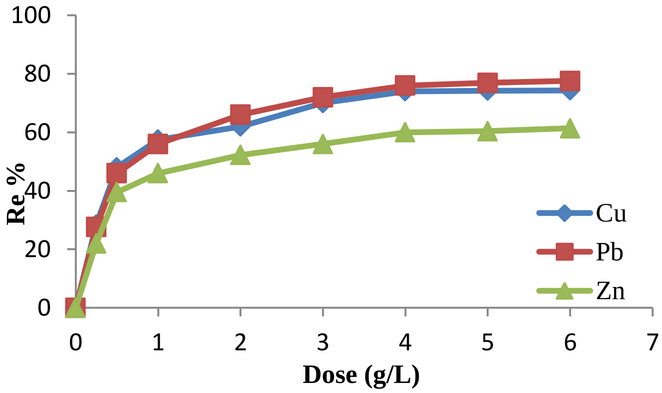
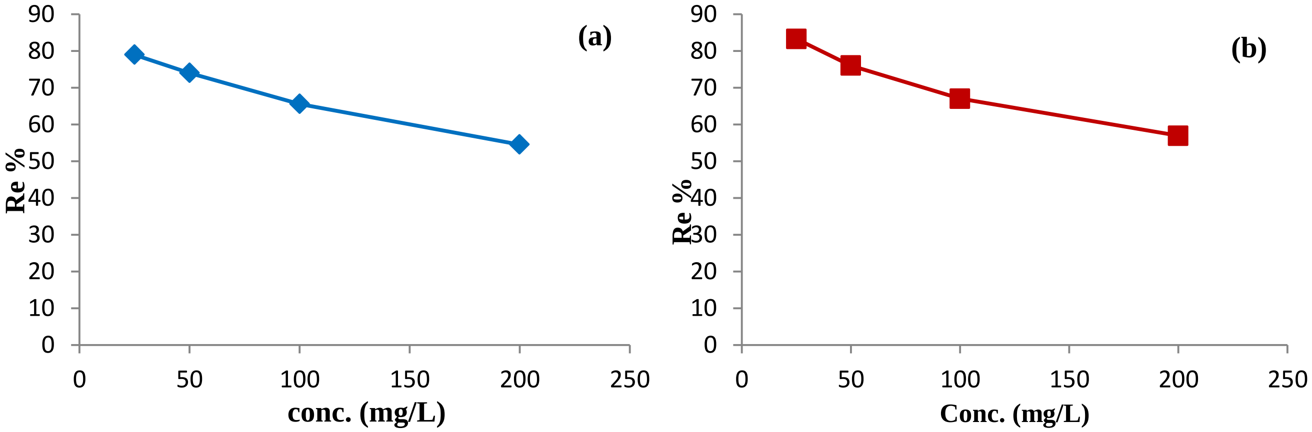


Figure 4: Effect of PGP dose on the removal of Cu^{+2}, Pb^{+2}, and Zn^{+2}ions (pH 4-5; T=25°C;C_i = 50 mg/L; rpm =500)



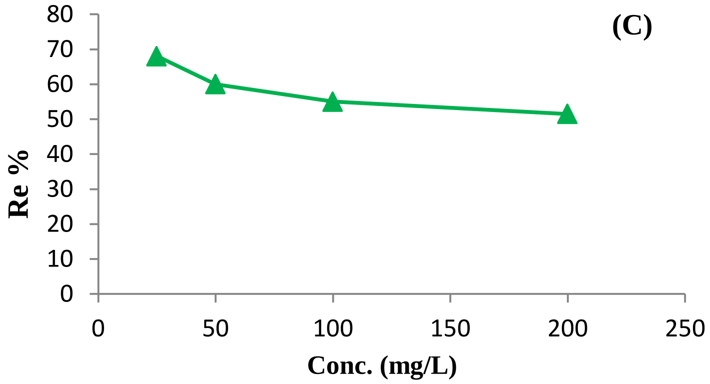


Figure 5. Effect of initial metal concentration on the removal of (a) Cu^{+2} (b) Pb^{+2} (c) Zn^{+2} ions using Pomegranate peel (pH 4-5; W=4g/L; T=25°C; rpm=500).

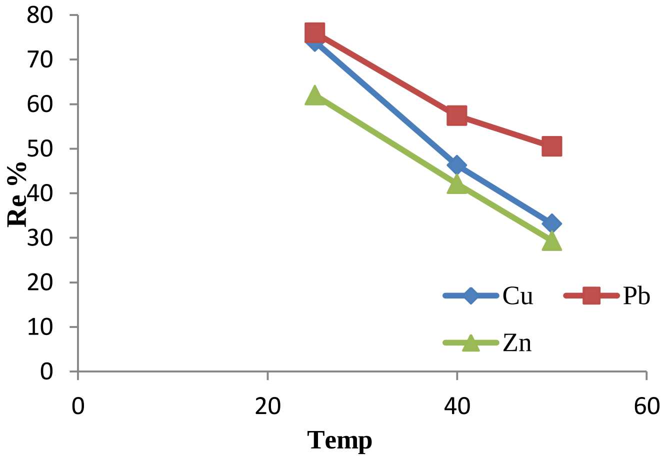
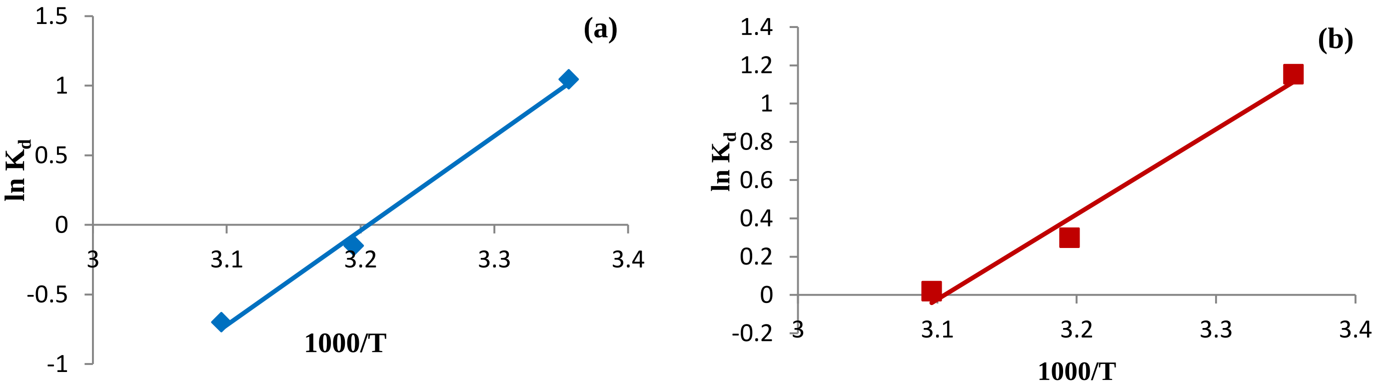


Figure 6. Effect of temperature on the removal of Pb^{+2}, Cu^{+2}, and Zn^{+2}ions using PGP (pH 4-5; W= 4g/L; rpm =500).



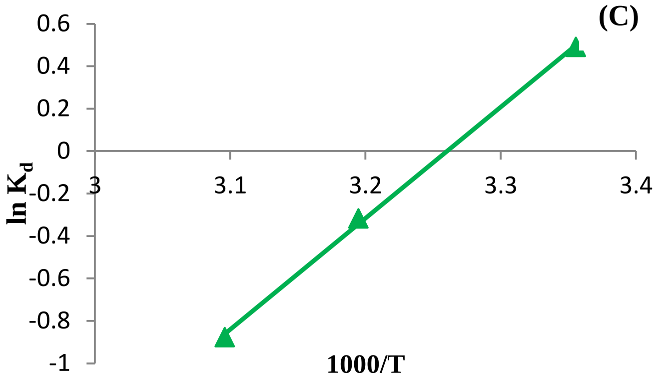


Figure 7. Distribution coefficient versus 1000/T for (a) Cu^{+2} (b) Pb^{+2} (C) Zn^{+2} ions.

Table 3. The distribution coefficients at different temperature.

Metal	**k_d**			**R^2**
	298k	**313k**	**323k**	
Copper (II)	2.846154	0.860811	0.496558	0.994
Lead (II)	3.166667	1.34852	1.020202	0.978
Zinc (II)	1.631579	0.727116	0.415629	0.999

Table 4. The thermodynamic parameters for the sorption of Pb^{+2}, Cu^{+2}, and Zn^{+2}ions on Pomegranate peel (PGP).

Metal	**ΔH (J/mol)**	**ΔS(J/mol K)**	**ΔG(kJ/mol)**		
			298K	**313K**	**323K**
Copper	-56.460	181.000	-53.995	-56.710	-60.330
Lead	-37.014	114.900	-34.277	-36.001	-38.300
Zinc	-43.582	142.086	-42.385	-44.517	-47.358

Table 5. Parameters of the Langmuir, Freundlich isotherms for the sorption of Pb^{+2}, Cu^{+2}, and Zn^{+2} ions onto P. granatum L. peels

Model	**Parameters**	**Copper**	**Lead**	**Zinc**	**Model**	**Parameters**	**Copper**	**Lead**	**Zinc**
Langmuir Eq. 2	q_m (mg/g)	25.925	28.969	19.175	Freundlich Eq. 3	q_m (mg/g)	2.427	2.339	1.824
	b (l/mg)	0.0424	0.0354	0.0370		1/n	0.525	0.542	0.500
	R^2	0.984	0.975	0.979		R^2	0.967	0.957	0.921

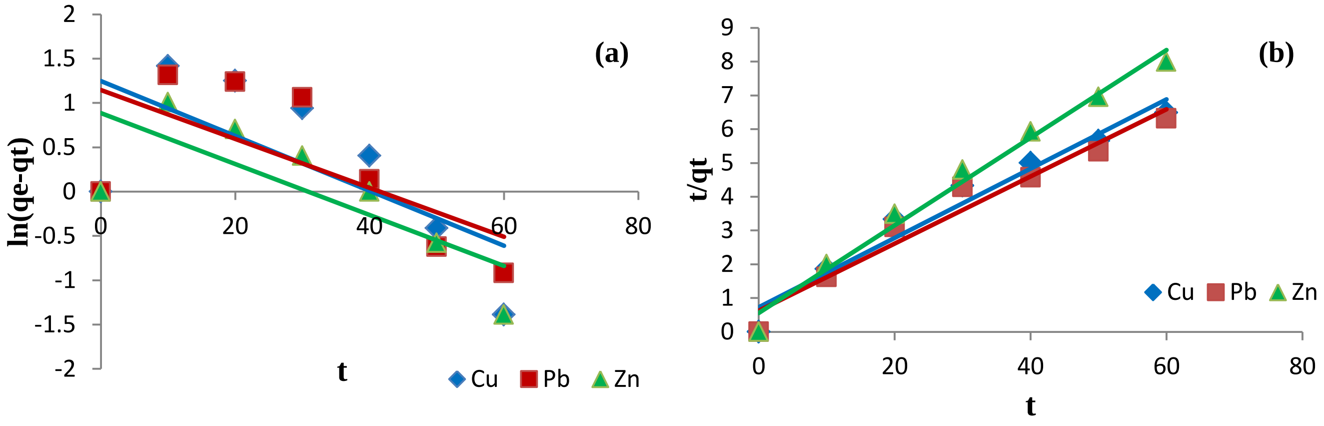


Figure 8.(a) Pseudo-first-order (b) Pseudo-second-order for sorption of Cu^{+2}, Pb^{+2}, and Zn^{+2} ions using PGP (pH 4-5; W= 4g/L; T=25°C; rpm =500).

Table 6. Comparison of sorption rate constants, experimental and calculated q_e values for the pseudo-first- and –second-order reaction kinetics for component systems.

Metal	**$q_{e experimental}$ mg/g**	**Pseudo-first-order**			**Pseudo-second-order**		
		k_1 1/min	**$q_{e calculated}$ mg/g**	**R^2**	**k_2g/mg.min**	**$q_{e calculated}$ mg/g**	**R^2**
Copper	9.500	0.0550	5.841572	0.925	0.014233	9.803922	0.956
Lead	9.900	0.0500	5.11921	0.924	0.015783	10.10101	0.957
Zinc	7.750	0.0460	3.277235	0.957	0.0298	7.751938	0.984

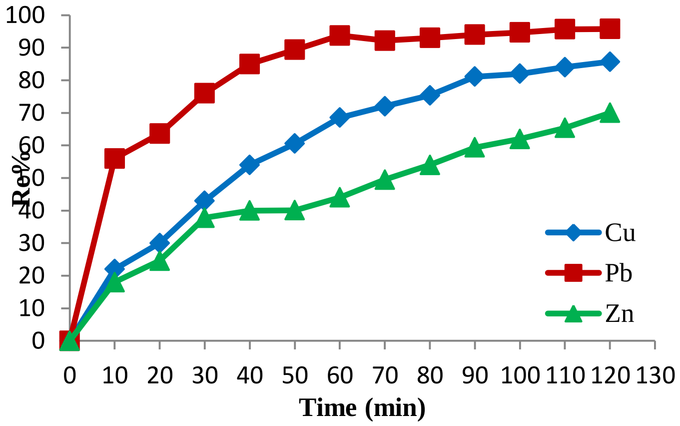


Figure 9. Effect of modification PGP on the removal of Cu^{+2}, Pb^{+2}, and Zn^{+2}ions (pH 4-5; W= 4g/L; T=25°C; rpm =500)