CHAPTER-4

Adsorption of Heavy Metals on Pomgranate (*Punica granatum*) peel: Removal and Recovery of Cr(VI) from Multimetal System
4.1. Introduction

The contamination of water by toxic heavy metals through the discharge of industrial wastewater is worldwide environmental problem. The environmental impact due to their toxicity has led to the enforcement of stringent standards for the maximum allowable limits of their discharge into open landscape and water bodies [1]. Authorities enforcing these standards further require the treatment procedure to be environment friendly [2]. Different methods used for the removal of metals are filtration, chemical precipitation, coagulation, solvent extraction, electro dialysis, ion-exchange, membrane process and adsorption [3]. Ion-exchange and adsorption are the most common and effective processes for this purpose. Activated carbon and different type of ion-exchange resins are very often used. However, their high price and regeneration cost have encouraged research work to find low-cost adsorbing materials for the removal of heavy metals. Several materials in this category have been successfully used for the removal of heavy metal ions from industrial wastewater [4-11].

Copper is generally considered to be toxic to man at concentration exceeding 5 mg/L, imparts color and undesirable taste. The World health Organization’s guide line for drinking water based on its staining properties is 1mg/L [12]. Beyond the permissible level, copper causes acute and chronic disorders in human beings such as gastrointestinal catarrh, cramps in the calves, hemochomatosis and skin dermatitis brasschills usually accompanied by high fever [13-14]. Industries discharging copper in the wastewater are electroplating industries, pulp and paper mills, fertilizer plants, steel work foundries, petroleum refineries, aircraft and finishing, motor vehicles and non-ferrous metalwork [15-17]. Pomegranate peel, a by-product of the pomegranate
juice industry is an inexpensive material. It is composed of several constituents, including polyphenols, ellagic tannin and Gallic and ellagic acids [18-19]. Ashtoukhy [20] has used pomegranate peel as an adsorbent for Pb(II) and Cu(II) and compared its properties with activated carbon prepared from it. This paper describes the adsorption properties of pomegranate peel for Cu(II), Cd(II), Ni(II), Zn(II) and Cr(VI).
4.2. Experimental procedure

4.2.1. Adsorbent

Fruit peel of pomegranate was dried, crushed and washed several times with double distilled water (DDW) till the water was clear of all coloration and finally dried in an air oven at 60°C for 24 hrs. After drying the adsorbent was sieved through 150-300 µm mesh size and used as such.

4.2.2. Adsorbate solution

Stock solution of Cu(II) was prepared (1000 mg/L) by dissolving the desired quantity of copper nitrate (AR grade) in double distilled water (DDW). Solutions of other metal ions were prepared (1000 mg/L) by dissolving their chlorides or nitrates in double distilled water. K$_2$Cr$_2$O$_7$ was used to prepare Cr(VI) solution.

4.2.3. Determination of Point of zero charge (pH$_{PZC}$)

The zero surface charge characteristics of the pomegranate peel were determined by using the solid addition method [21] as described in chapter 2.

4.2.4. Determination of surface active sites

Acidic sites on pomegranate peel were determined by acid-base titration method [22]. 0.5 g adsorbent was treated separately with 50 mL each 0.1N NaOH, 0.1N Na$_2$CO$_3$ and 0.1N NaHCO$_3$ in 250 mL conical flasks. The flasks were agitated at constant temperature (20°C) and left there for 5 days. Afterwards a sample of 10mL was titrated with 0.1N HCl solution using pH meter.
4.2.5. Adsorption studies

Adsorption studies were carried out by batch process. 0.5 g adsorbent was placed in a conical flask, 50 mL solution of metal ions of desired concentration was added and the mixture was shaken in shaker incubator for 24 hrs. The mixture was then filtered by whatman filter paper No. 41 and final concentration of metal ions was determined in the filtrate by atomic absorption spectrometry (AAS) (GBC 902). The amount of metal ions adsorbed was calculated by subtracting final concentration from initial concentration.

4.2.6. Effect of pH

The effect of pH on the adsorption of Cu(II) was studied as follows. 100 mL of Cu(II) solution was taken in a beaker. The pH of solution was adjusted by adding 0.1N HCl or 0.1N NaOH solution. The concentration of Cu(II) in this solution was then determined (initial concentration). 50 mL of this solution was taken in conical flask and treated with 0.5 g adsorbent for 24 hrs in shaker incubator. The mixture was then filtered and final concentration of Cu(II) in filtrate was determined as described above.

4.2.7. Effect of time

A series of 250 mL conical flasks, each having 0.5 g adsorbent and 50 mL solution of known Cu(II) concentration were shaken in a shaker incubator and at the predetermined intervals, the solution of the specified flask was taken out and filtered. The concentration of Cu(II) in the filtrate was determined by AAS and the amount of Cu(II) adsorbed in each case was then determined as described above.
4.2.8. Effect of adsorbent dose

A series of 250 mL conical flasks, each containing 50 mL of Cu(II) solution of 50 mg/L concentration were treated at 20°C with varying amount of adsorbent (0.1-1.0 g). The conical flasks were shaken in a shaker incubator for 5 min since adsorption is completed in 5 min. The solutions were then filtered and amount of Cu(II) adsorbed in each case was calculated as described above. The same procedure was repeated at 30 and 40°C.

4.2.9. Desorption of Cu(II) by Batch Process

Attempts were made to desorb Cu(II) by batch process. 0.5 g adsorbent was treated with 50 mL of Cu(II) solution (50 mg/L) for 5 min. The adsorbent was washed several times with DDW to remove excess of Cu(II) ions. Adsorbent was then treated with 50 mL 0.1N HCl solution and after 24 hrs the amount of Cu(II) desorbed was determined. The same procedure was repeated with different desorbing solutions.

4.2.10. Treatment of electroplating wastewater by batch process

In another experiment 0.5 g adsorbent was treated with 50 mL electroplating wastewater in a conical flask and after 5min. the concentrations of Cu(II), Ni(II), Zn(II) and Cr(VI) in the supernatant liquid were determined. The adsorbent was then washed with DDW several times and then treated with 50 mL 0.1 N HCl solution for 24 hrs. The metal ions desorbed were then determined by AAS.

4.2.11. Desorption of Cu(II) by Column process

0.5 g of adsorbent was taken in a glass column (0.6 cm internal diameter) with glass wool support and 50 mL of Cu(II) solution (50 mg/L initial concentration) was
passed through the column with the flow rate of 1mL/min. It was washed several times with double distilled water in order to remove any unadsorbed Cu(II), then 0.1N HCl solution was passed through the column with a flow rate of 1mL/min. The effluent was collected in 10 mL fractions and Cu(II) desorbed was determined in each fraction by AAS.

4.2.12. Breakthrough capacity

0.5 g of adsorbent was taken in a glass column (0.6 cm internal diameter) with glass wool support. 1000 mL of Cu(II) solution with 50 mg/L initial concentration (C₀) was then passed through the column with a flow rate of 1mL/min. The effluent was collected in 50 mL fractions and the amount of Cu(II) was determined in each fraction with the help of AAS. The breakthrough curve was obtained by plotting C/C₀ verses volume of the effluent. Same procedure was applied to determine breakthrough capacities of Zn(II), Cd(II), Ni(II) and Cr(VI) by passing 1000 mL solution containing the mixture of Zn(II), Cd(II), Ni(II) and Cr(VI) (10 mg/L each) through the column.

4.2.13. Treatment of electroplating wastewater by column process

100 mL of electroplating wastewater was passed through the column containing 0.5 g adsorbent under identical conditions. The flow rate was maintained at 1mL/min through out the experiment. Effluent was collected in 10 mL fractions and these metals ions were determined in each fraction by AAS.
4.3. Results and discussion

Pomegranate peel shows high affinity towards Cu(II), Cd(II), Ni(II) and Zn(II) at pH 4.5. Cu(II) and Cd(II) are equally adsorbed (Fig. 4.1) followed by Zn(II) and Ni(II). However, adsorption of Cr(VI) is least at pH 4.5. Adsorption of Cu(II) is also high in presence of Cd(II), Ni(II), Zn(II) and Cr(VI) at pH 4.5.

4.3.1. Effect of concentration and contact time

The effect of concentration on the adsorption of Cu(II) was carried out at initial concentrations of 0.157, 0.314, 0.472, 0.629, 0.787 mmol/L. These results are shown in Fig. 4.2. The adsorption capacity increases with increase in initial concentration since concentration gradient between bulk and surface of the adsorbent increases with increase in concentration which results in the increase of driving force responsible for high uptake of metal ions at high concentration. The maximum adsorption of Cu(II) was 0.0677 mmol/g at 0.787 mmol/L initial Cu(II) concentration. Adsorption of Cu(II) ions increases rapidly and sharply with time in the initial stage (0 to 2 min range) and then increases gradually to reach equilibrium in 5 min. Further increase in contact time has no significant effect on the uptake amount. Therefore shaking time was kept 5 min. for all other batch experiments.

4.3.2. Effect of pH

Adsorption of Cu(II) increases with increase in initial pH. The maximum adsorption occurs at pH 4 (Fig. 4.3) and there after increase in pH has negligible effect. Acidic solution (low pH) inhibits metal uptake because of the high concentration of H⁺ ions competing with Cu(II) ions due to the protonation of various functional groups (carboxylic and phenolic) present on the surface of the adsorbent.
The final pH (pHₐ) is the pH of the solution at equilibrium. It is also an important factor since many sorption reactions are explained at equilibrium. It has been observed that when initial pH is 2, the final pH is not affected (pHₐ = 2.2) showing that solution is acidic and contains fairly high concentration of H⁺ ions therefore H⁺ ions compete and adsorption of Cu(II) is minimum (0.017 mmol/g). When initial pH is adjusted to 3 then final pH increases sharply (pHₐ = 5.8) and at the same time adsorption of Cu(II) increases (0.072 mmol/g) showing that large quantity of Cu(II) ions are adsorbed along with the H⁺ ions resulting a decrease in H⁺ ions in the solution and this results an increase in final pH at equilibrium. The adsorption of Cu(II) continues to increase with increase in pH and then becomes constant at and above pH 4. The surface of the adsorbent is positive at pH < pHₚzc, neutral at pH = pHₚzc and negative at pH > pHₚzc. The pHₚzc of pomegranate peel is 7 (Fig. 4.4) showing that the surface is negatively charge above this pH hence fairly large amount of Cu(II) ions are adsorbed. The amount of total acidic sites (carboxylic, phenolic and lactonic) on the surface of the adsorbent is 0.208 meq/g. These acidic sites are protonated in acidic medium resulting low adsorption of metal ions by pomegranate peel at low pH.

4.3.3. Adsorption isotherms

The adsorption isotherm data were analyzed with Langmuir and Freundlich isotherm equations [4]. The linear form of Langmuir isotherm is represented as

\[
\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{b} \times \frac{1}{C_e} + \frac{1}{q_m} \quad \text{------------------ (1)}
\]

Where \( q_e \) is the amount of metal adsorbed per unit weight of adsorbent, \( q_m \) is the maximum sorption capacity (mmol/g) determined by the number of reactive surface sites in an ideal monolayer system, \( C_e \) is the concentration of metals ions (mmol/L) at
equilibrium and b is a constant related to bonding energy associated with pH dependent equilibrium constant. A plot of $1/q_e$ verses $1/C_e$ gave straight line at different temperatures (Fig. 4.5). The values of b and qm at different temperatures are reported in Table 4.1. Fig. 4.6 represents non-linear Langmuir isotherms at different temperatures. It is found that $q_e$ calculated from the model (designated as $(q_{e(cal)})$ are very close to $q_e$ determined experimentally (designated as $(q_{e(exp)})$ at 20°C but when temperature is increased these values differ appreciably showing that Langmuir isotherm is fitted at 20°C and deviates with increase in temperature. A chi-square test ($\chi^2$) was also applied to this model. The advantage of $\chi^2$ is that $q_{e(cal)}$ from the model and $q_{e(exp)}$ values can be compared on the same abscissa and ordinate [23]. If data from model were similar to the experimental data, $\chi^2$ would be small and vice versa. Values of $\chi^2$ were calculated using the following relation.

$$\chi^2 = \sum \frac{(q_{e(exp)} - q_{e(cal)})^2}{q_{e(cal)}} \quad (2)$$

The value of $\chi^2$ is least at 20°C (Table 4.1) and also the regression coefficient ($R^2$) is high showing that Langmuir isotherm is best fitted at 20°C.

The Linear form of Freundlich isotherm can be represented as

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (3)$$

Where $K_f$ is Freundlich constant and n is another constant that informs about the heterogeneity degree of the surface sites. When n approaches zero, the surface site heterogeneity increases. A plot of $\log q_e$ verses $\log C_e$ gave straight line (Fig. 4.7). Values of Freundlich constants are reported in Table 4.1. Fig. 4.8 represents non-linear Freundlich isotherms at different temperatures. It is found that Freundlich isotherm is also obeyed at 20°C since $q_{e(exp)}$ values are very close $q_{e(cal)}$. The values of
\( \chi^2 \) at different temperature are also shown in Table 4.1. The least value of \( \chi^2 \) at 20°C and high correlation coefficient (R^2) indicates that Freundlich isotherm is also obeyed at 20°C but deviates as temperature increases. However, the value of \( K_f \) increases with increase in temperature showing that adsorption is favored at high temperature. When Langmuir and Freundlich (non-linear) isotherms are compared at 20°C, the \( \chi^2 \) value for Freundlich isotherm is slightly lower (0.011) than that obtained from Langmuir isotherm (0.025) hence it can be concluded that both Langmuir and Freundlich models are obeyed by the system at 20°C but Freundlich model is a better fit.

The essential characteristic of Langmuir isotherm can be expressed in term of dimensionless constant separation factor or equilibrium parameter R_L, given by

\[
R_L = \frac{1}{1 + b \times C_0}
\]  

(4)

R_L value predicts the shape of the isotherm. If R_L >1 unfavorable, R_L = 1 linear, 0< R_L <1 favorable and R_L = 0 for irreversible adsorption [24]. The R_L values at 20, 30 and 40°C are shown in Table 4.1. The values of R_L in the range 0-1 at all these temperatures show favorable adsorption of Cu(II) on Pomegranate peel.

4.3.4. Thermodynamic studies

The temperature range used in this study was 30-50°C. The equilibrium constants (Kc) at 30, 40 and 50°C were calculated from the following relation [25].

\[
Kc = \frac{C_A C}{C_e}
\]  

(5)
Where $C_{AC}$ and $C_e$ are the equilibrium concentrations (mg/L) of Cu(II) on the adsorbent and in solution, respectively

$$
\Delta G^\circ = -RT \ln Kc \quad \text{------------------------} (6)
$$

Where $T$ is the temperature in Kelvin, $R$ is gas constant and $\Delta G^\circ$ is the standard free energy change. The value of enthalpy change ($\Delta H^\circ$) and entropy change ($\Delta S^\circ$) were calculated from the following relation.

$$
\log Kc = (\Delta S^\circ/2.303R) - (\Delta H^\circ/2.303R) \times (1/T) \quad \text{------------------------} (7)
$$

$\Delta S^\circ$ and $\Delta H^\circ$ were calculated from the slope and intercept of linear plot of log $Kc$ verses $1/T$ (Fig. 4.9). The values of $Kc$, $\Delta H^\circ$, $\Delta S^\circ$ and $\Delta G^\circ$ are reported in Table 4.2. The positive value of $\Delta H^\circ$ indicates the process is endothermic. The negative values of $\Delta G^\circ$ indicate that the process is spontaneous and spontaneity increases with increase in temperature. The positive value of $\Delta S^\circ$ suggests increase randomness at the solid-liquid interface during adsorption.

The Dubinin-Redush Kevich isotherm [26] is based on the heterogeneous nature of the adsorbent surface, was used to predict the physical or chemical nature of the adsorption process. The D-R equation may be given as

$$
\ln q_e = \ln q_m - \beta \varepsilon^2 \quad \text{------------------------} (8)
$$

Where, $q_e$ is the adsorption capacity (mol/g) and $q_m$ is the maximum adsorption capacity (mol/g), $\beta$ is the activity coefficient constant and $\varepsilon$ is the Polanyi potential which is given as

$$
\varepsilon = RT \ln (1+1/C_e) \quad \text{------------------------} (9)
$$
Where, \( R \) is the gas constant (kJ/mol) and \( T \) is the temperature in Kelvin. \( C_e \) is the equilibrium concentration (mol/L). The values of \( q_m \) and \( \beta^2 \) can be obtained from the intercept and slope of the plot of \( \ln q_e \) verses \( \varepsilon^2 \) (Fig. 4.10). The mean free energy of adsorption \( E \) can be calculated from the following equation

\[
E = 1/ (-2\beta)^{1/2} \quad \text{------------------------- (10)}
\]

The D-R parameters and mean free energy are given in Table 4.3. The values of \( E \) obtained are between 9.6 and 10 kJ/mol, which are in the energy range of chemisorption reaction [27].

### 4.3.5. Adsorption kinetics

The rate constants were calculated by using pseudo-first-order & pseudo-second-order equations. The pseudo-first order [28] and pseudo-second order [29] reactions are based on solution concentration. The pseudo-first-order expression is given by equation.

\[
\log (q_e - q_t) = \log q_e - (K_1/2.303) \times t \quad \text{------------------------- (11)}
\]

Where \( q_e \) is the amount adsorbed at equilibrium, \( q_t \) is the amount adsorbed at time \((t)\) and \( K_1 \) is the pseudo-first-order adsorption rate constant. A linear plot of \( \log (q_e - q_t) \) verses \( t \) is observed. The regression coefficients \((R^2)\) and rate constant for first-order kinetic at various concentrations are reported in Table 4.4.

The pseudo-second-order adsorption kinetics rate equation is

\[
t /q_t = 1/h + (1/q_e) \times t \quad \text{----------------------------- (12)}
\]

Where \( h = K_2 \times q_e^2 \)
K₂ is the adsorption rate constant for pseudo-second-order reaction and h is the initial adsorption rate. The values of K₂ were calculated from the slope of the linear plots of \( \frac{t}{q} \) verses t (Fig. 4.11). These values are reported in Table 4.4. A comparison of the experimental adsorption capacities (\( q_{e(\text{exp})} \)) and calculated values (\( q_{e(\text{cal})} \)) obtained from Equation (11) and (12) show that \( q_{e(\text{cal})} \) values obtained from pseudo-first order kinetics model differed largely from \( q_{e(\text{exp})} \) values. However, in pseudo-second-order kinetics, \( q_{e(\text{cal})} \) values were very close to \( q_{e(\text{exp})} \) and also the high value of the correlation coefficient (\( R^2 \)) confirmed the applicability of the pseudo-second-order kinetics.

4.3.6. Adsorption and desorption studies

**Batch Process**

In order to make the process more economical, desorption studies were carried out by batch as well as by column process. Table 4.5 represents desorption of Cu(II) from pomegranate peel with various salt solutions by batch process. The results indicate that Cu(II) is strongly adsorbed on pomegranate peel and cannot be recovered by different salt solutions. However 79.5% of Cu(II) could be recovered when 0.1N HCl is used. This behavior shows that Cu(II) can be removed from industrial wastewater containing other dissolved salts, since presence of these salts will not affect the adsorption of Cu(II) ions. Attempts were made to desorb various metal ions from electroplating wastewater by treating 50 mL wastewater with 0.5 g adsorbent under identical conditions. The analysis of electroplating wastewater collected from one of the lock factory in Aligarh city is reported in Table 4.6. The analysis indicates high concentration of Cr(VI) (390 mg/g) in the electroplating wastewater. Table 4.7
shows adsorption/desorption of various metals from electroplating wastewater by batch process.

Desorption of Cu(II) by column process

Desorption of Cu(II) by column process is shown in Fig. 4.12. It has been found that 2.35 mg of Cu(II) was adsorbed and 1.87 mg was recovered with 0.1N HCl solution. Fig. 4.11 shows that desorption are rapid and maximum amount of Cu(II) can be recovered within 10 mL of the effluent.

Continuous flow fixed bed column studies

Break through curve is the most effective column process making the optimum use of the concentration gradient between the solute adsorbed by the adsorbent and that remaining in the solution. The column is operational until the metal ions in the effluent start appearing and for practical purposes the working life of the column is over called breakthrough point. This is important in process design because it directly affects the feasibility and economics of the process [30]. The breakthrough capacity of Cu(II) is shown in Fig. 4.13. It is clear from the figure that 100 mL of water containing 50 mg/L Cu(II) can be passed through the column without detecting Cu(II) in the effluent. The breakthrough capacity was found to be 10 mg/g. However, breakthrough capacity of Cu (II) is slightly reduced when a mixture of Cu(II), Ni(II), Cd(II), Zn(II) and Cr(VI) was passed through the column. The breakthrough capacity curves of Cu(II), Ni(II), Zn(II) Cd (II) and Cr(VI) are shown in Fig. 4.14. The breakthrough capacities of Cu(II), Ni(II), Cd(II), Zn(II) and Cr(VI) at pH 4.5 were calculated as 6, 2, 2, 2 and 0 mg/g respectively. However, adsorption of Cr(VI) is very less and more than 50% Cr(VI) comes out as such in the effluent. It can therefore be concluded that Cr(VI) solution containing Cu(II), Ni(II), Cd(II) and Zn(II) can be
purified by this adsorbent. This behavior of adsorbent has been utilized for the purification and recovery of Cr(VI) solution from electroplating waste water. Fig. 4.15 shows breakthrough curves of Cu(II), Ni(II), Zn(II) and Cr(VI) when 100 mL electroplating wastewater was passed through the column under identical conditions. It has been found that maximum 10 mL wastewater can be treated without detecting Cu(II), Ni(II) and Zn(II) in the effluent. The amount of Cr(VI) determined in the first 10 mL fraction was 106 mg/L. This effluent free from Cu(II), Ni(II) and Zn(II) and rich in Cr(VI) can be reused in the electroplating plant.
4.4 Conclusions

Pomegranate peel is a byproduct of pomegranate juice industry. It represents good adsorption capacity for Cu(II), Cd(II), Ni(II) and Zn(II) at pH 4.5 while adsorption of Cr(VI) is least at this pH. The order of adsorption of these metals is Cu(II) = Cd(II) > Zn(II) > Ni(II) > Cr(VI) at pH 4.5. The maximum adsorption capacity of Cu(II) was 0.0677 mmol/g at 0.787 mmol/L initial Cu(II) concentration. Adsorption process follows both Langmuir and Freundlich isotherms at 20°C but Freundlich isotherm is a better fit as indicated by χ² test. Adsorption process is endothermic the values of mean free energy indicate the chemical nature of the adsorption. Kinetics data indicate that pseudo-first order and pseudo-second order rate equations are followed but pseudo-second order rate is better obeyed since experimental values of qe agreed well with calculated values. Desorption of Cu(II) was 79.4 and 80 % by batch and column process respectively. Attempts were made to desorb Cu(II), Ni(II), Zn(II) and Cr(VI) from electroplating wastewater. Breakthrough capacity of these metals was determined in the synthetic mixture as well as in actual electroplating wastewater and it was found that 10 mL electroplating wastewater can be passed through the column (containing 0.5 g adsorbent) without detecting Cu(II), Ni(II) and Zn(II) in the effluent at pH 4.5. However, least adsorption of Cr(VI) at this pH and high adsorption of Cu(II), Ni(II), Cd (II) and Zn(II) have made it possible to recover purified Cr(VI) solution from electroplating wastewater that can be reused in the electroplating plant.
Table 4.1.
Langmuir and Freundlich isotherms parameters for the adsorption of Cu(II).

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>q_m (mmol/g)</th>
<th>b</th>
<th>R²</th>
<th>χ²</th>
<th>R_L</th>
<th>Freundlich parameters</th>
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<tbody>
<tr>
<td>20</td>
<td>0.4066</td>
<td>0.069</td>
<td>0.997</td>
<td>0.025</td>
<td>0.224</td>
<td>1.900 0.764 0.997 0.011</td>
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<tr>
<td>30</td>
<td>0.5502</td>
<td>0.079</td>
<td>0.920</td>
<td>0.803</td>
<td>0.202</td>
<td>2.973 0.677 0.880 0.283</td>
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<tr>
<td>40</td>
<td>0.2662</td>
<td>0.059</td>
<td>0.902</td>
<td>0.544</td>
<td>0.253</td>
<td>3.104 0.618 0.889 0.723</td>
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Table 4.2.
Thermodynamic parameters for the adsorption of Cu(II)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Kc</th>
<th>ΔG° (kJ/mol)</th>
<th>ΔH° (kJ/mol)</th>
<th>ΔS° (kJ/mol K)</th>
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<tr>
<td>30</td>
<td>21.7</td>
<td>-7.51</td>
<td>-8.75</td>
<td>25.84</td>
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<td>40</td>
<td>32.3</td>
<td>-8.75</td>
<td>25.84</td>
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<td>50</td>
<td>40.6</td>
<td>-9.64</td>
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Table 4.3.
D – R isotherms parameters for the adsorption of Cu(II).

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>β (mol²/kJ)</th>
<th>q_m (mol/g)</th>
<th>E (kJ/mol)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>-0.0054</td>
<td>0.00175</td>
<td>9.6</td>
<td>0.9967</td>
</tr>
<tr>
<td>30</td>
<td>-0.0053</td>
<td>0.00169</td>
<td>9.7</td>
<td>0.9940</td>
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<tr>
<td>40</td>
<td>-0.0050</td>
<td>0.00251</td>
<td>10.0</td>
<td>0.9993</td>
</tr>
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</table>
Table 4.4.
Kinetics parameters for the adsorption of Cu(II).

<table>
<thead>
<tr>
<th>Conc. (mmol/L)</th>
<th>K₁</th>
<th>qₑ(exp) (mmol/g)</th>
<th>K₂</th>
<th>h</th>
<th>qₑ(cal) (mmol/g)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.157</td>
<td>0.460</td>
<td>0.0116</td>
<td>0.958</td>
<td>0.182</td>
<td>0.0116</td>
<td>0.999</td>
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<tr>
<td>0.314</td>
<td>0.499</td>
<td>0.0259</td>
<td>0.870</td>
<td>0.123</td>
<td>0.0018</td>
<td>0.999</td>
</tr>
<tr>
<td>0.472</td>
<td>2.890</td>
<td>0.0425</td>
<td>1.000</td>
<td>0.005</td>
<td>0.0137</td>
<td>0.999</td>
</tr>
<tr>
<td>0.629</td>
<td>0.693</td>
<td>0.0566</td>
<td>1.000</td>
<td>0.003</td>
<td>0.0125</td>
<td>0.999</td>
</tr>
<tr>
<td>0.787</td>
<td>0.504</td>
<td>0.0677</td>
<td>0.860</td>
<td>0.001</td>
<td>0.0061</td>
<td>0.999</td>
</tr>
</tbody>
</table>

Table 4.5.
Adsorption and desorption of Cu(II) by batch process (Amount of Cu(II) loaded =2.5mg).

<table>
<thead>
<tr>
<th>SNo.</th>
<th>Eluent</th>
<th>Amount adsorbed (mg)</th>
<th>Desorption (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Distilled Water</td>
<td>0.00</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>0.05M Acetic acid</td>
<td>2.20</td>
<td>29.5</td>
</tr>
<tr>
<td>3</td>
<td>0.1M Acetic acid</td>
<td>2.20</td>
<td>36.3</td>
</tr>
<tr>
<td>4</td>
<td>0.05M HCl</td>
<td>2.20</td>
<td>77.3</td>
</tr>
<tr>
<td>5</td>
<td>0.1M HCl</td>
<td>2.20</td>
<td>79.5</td>
</tr>
<tr>
<td>6</td>
<td>0.5M NaCl</td>
<td>2.35</td>
<td>2.1</td>
</tr>
<tr>
<td>7</td>
<td>1.0M NaCl</td>
<td>2.35</td>
<td>6.4</td>
</tr>
<tr>
<td>8</td>
<td>0.1M NaHCO₃</td>
<td>2.35</td>
<td>2.1</td>
</tr>
</tbody>
</table>
Table 4.6.  
Analysis of electroplating wastewater

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)</td>
<td>21.00</td>
</tr>
<tr>
<td>Ni (II)</td>
<td>3.20</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>0.22</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>0.97</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>390.00</td>
</tr>
<tr>
<td>pH</td>
<td>5.60</td>
</tr>
</tbody>
</table>

Table 4.7.  
Desorption of metal ions from electroplating wastewater by batch process (Eluent = 0.1N HCl).

<table>
<thead>
<tr>
<th>Metals ions</th>
<th>Amount loaded (mg/L)</th>
<th>% Adsorption</th>
<th>% Desorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)</td>
<td>21.00</td>
<td>90.0</td>
<td>89.90</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>3.20</td>
<td>81.2</td>
<td>77.00</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>0.22</td>
<td>90.9</td>
<td>80.00</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>0.97</td>
<td>67.0</td>
<td>69.20</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>390.00</td>
<td>18.0</td>
<td>n.d.</td>
</tr>
</tbody>
</table>
Fig 4.1. Adsorption of various metal ions on Pomgranata.
conditions: Amount of adsorbent = 0.5 g, pH of the solutions = 4.5

![Bar chart showing the amount of adsorbed metal ions](image)

Metal ions
Cr(VI), 0.042
Cd(II), 0.075
Zn(II), 0.073
Ni(II), 0.068
Cu(II), 0.074

Fig 4.2. Effect of contact time on the adsorption of Cu(II) at different concentrations

![Graph showing the effect of contact time on adsorption](image)

qe (mmol/g)
- 0.157 mmol/L
- 0.314 mmol/L
- 0.472 mmol/L
- 0.629 mmol/L
- 0.787 mmol/L

time (min.)
Fig 4.3. Adsorption of Cu(II) as a function of pH change

Fig 4.4. Point of zero charge
Fig. 4.5 Langmuir isotherms at different temperatures

Fig. 4.6 Langmuir isotherms (non-linear) at different temperatures
Fig. 4.7 Freundlich isotherms at different temperatures

Fig. 4.8 Freundlich isotherms (non-linear) at different temperatures
Fig. 4.9 Van’t Hoff Plot for the adsorption of Cu (II)

Fig. 4.10 D-R plots at different temperatures
Fig. 4.11 Pseudo-second order kinetics for the adsorption of Cu (II)

\[ \frac{t}{q_t} = k_2 t + \frac{1}{q_e} \]

- 0.157 mmol/L
- 0.314 mmol/L
- 0.472 mmol/L
- 0.629 mmol/L
- 0.787 mmol/L

Fig. 4.12 Desorption of Cu(II) by column operation

- Amount of Cu(II) loaded = 2.5mg
- Amount of adsorbent = 0.5g
- Flow rate = 1mL/min

Eluent 0.1N HCl
Fig. 4.13. Breakthrough capacity of Cu(II) conditions: Adsorbent = 0.5g, Flow rate = 1mL/min

Fig. 4.14  Breakthrough capacities of different metal ions. Concentration of each metal = 10mg/L, Amount of adsorbent = 0.5g, Flow rate = 1mL/min
Fig. 4.15 Breakthrough curves of metal ions in electroplating wastewater

Amount of adsorbent = 0.5g, pH of the wastewater = 4.5, Flow rate = 1mL/min
References


