Chapter-5

Glaze-An Excellent Adsorbent for the Removal of Cu(II) From Aqueous Solution
5.1. INTRODUCTION

There is a rapid increase in the use of heavy metal ions globally through various forms such as batteries, pigments, PVC stabilizers and similar other industrial applications [Gaballah et al., 1998 and Gonzalez et al., 2001]. These increases in the contamination of heavy metals are very dangerous for the environment as it shows from many serious environmental problems in the past and recent years [Pharr et al., 2007]. Specially, the heavy metal ions from the transition series are more toxic in the environment and thus posing a great threat in various forms of life. Copper is a heavy metal ion among this category, it is very toxic metal if it is taken in large quantity. The excessive amount of copper cause severe symptoms like headaches, nausea, hair loss as it can be deposited in the human brain, skin, pancreas, liver and myocardium which may cause Wilson’s disease [Chen et al., 2003] and results in brain damage, damage of liver and kidney, depression and anemia [Al-Rub et al., 2006]. Copper in the form of Cu(II) ions are soluble in water and because of this reason it is a universal toxic element in high concentrations. Due to cooking in copper-lined or copper glazed or copper designed pots and the supply of water through copper pipes [Manahan et al., 1991] there is an easy exposure of human to this toxic metal.

Various techniques have been employed for the removal of heavy metals but adsorption is the most important technique which has the advantage of being cheaper than the other techniques. This technique is easy to operate and equally effective in the removal of heavy metals at very low concentrations.

The choice of adsorbent is a key point and the literature review suggested the use of new adsorbents which have high adsorption capacity and can remove the heavy metal ions effectively. Among them Gyttja (which has multilayer coal deposits with clay and calcareous gyttja partings) [Dikici et al., 2010], natural kaolinite clay [Jiang et al., 2010], kaolinite supported zero valent iron nanoparticles [Uzum et al., 2009], natural bentonite [Korkut et al., 2010], Mg oxide coated bentonite [Eren et al., 2010], bentonite- polyacrylamide composites [Zhao et al., 2010], humic acid- immobilized bentonite composite [Anirudhan et al., 2010], Na- bentonite [Zhi-rong and Shaoqi, 2010], montmorillonite [Christianah et al., 2009], sodium dodecyl sulfate modified iron pillared montmorillonite [Li et al., 2010], sepiolite [Dogang et al., 2009], mineral soil [Vidal et al., 2009], perlite [Ghassabzadeh et al., 2010], sandy soil [Yip et al., 2010].
zeolite prepared from Egyptian Kaolin [Tarek et al., 2010], chitosan coated sand [Wan et al., 2010] have recently been reported. In this study, we have investigated and utilized the adsorption capacity of glaze. Glaze is a thin layer or coating of a vitreous substance or liquid which is fired to fuse to a ceramic object and put on a piece of pottery to color, strengthen, decorate and gives hard and shiny look [Ching et al., 1995]. Glaze is also used in building materials. The Iron Pagoda, built in 1049 CE in Kaifeng (China) is an example which was made from glazed bricks [Dai and Gao, 2002]. Many painters used glaze in the paint application to increase illusions or brightness, opaque and depth [Simon et al., 2008]. It is widely used in pottery and porcelain to give a waterproof finish. Glaze is also used in furniture, finishing and in cabinet. Glaze is a form of basically glass forming minerals (boron or silica), melting agents (such as soda) and combined with clay and fluxes to give stiffness. This material has not yet been tested for the adsorption of heavy metals from aqueous solution therefore its adsorption properties were explored. The present study deals with a series of batch adsorption experiments to explore the feasibility of glaze as an adsorbent for the removal of Cu(II) ions.

5.2. MATERIALS AND METHODS

5.2.1. Adsorbent

Glaze was purchased in the form of slurry from Asian Chemicals (INDIA). The slurry was dried in an oven at 70-80°C. The dried mass was then crushed and washed several times with double distilled water (DDW) to remove dust, dirt etc. It was again dried in an oven at 50-60°C for further study.

5.2.2. Adsorbate solution

All reagents and chemicals used were of analytical grade. Stock solution of Cu(II) was prepared (1000 mg/L) by dissolving the desired quantity of Cu(NO₃)₂·H₂O in DDW.

5.2.3. Adsorption studies

Batch process was employed for adsorption studies. The mass of 0.5 g of adsorbent was taken in a conical flask containing 50 mL Cu(II) solution of desired concentration. The solution was shaken in a shaker incubator and then filtered at the
end of the predetermined time interval. The final concentration of Cu(II) was determined in the filtrate by Atomic Absorption Spectrophotometer (AAS) (GBC-902). The adsorbed amount of Cu(II) was then calculated by subtracting the final concentration from initial concentration. The adsorption capacity at equilibrium (qe) was calculated by using the following relation.

\[
\text{Sorption Capacity (}\, q_e\, \text{)} = \left( \frac{C_0 - C_e}{W} \right) \times V \tag{1}
\]

Where \( C_0 \) is the initial concentration of adsorbate (mg/L), \( C_e \) is the final concentration of adsorbate (mg/L), \( V \) is the volume of the solution (L) and \( W \) is the mass of the adsorbent (g).

### 5.2.4. Effect of pH

The effect of hydrogen ion concentration on the adsorption of Cu(II) was studied over pH ranges 2-10. A 50 mL Cu(II) solution of 50 mg/L concentration was taken in a flask. The desired pH of the solution was adjusted by adding 0.1N HCl or 0.1 N NaOH solutions. 0.5 g adsorbent was then added in each flask and after equilibrium the final concentration of Cu(II) was determined. In order to see the effect of electrolyte on the adsorption of Cu(II) the same procedure was repeated with 50 mg/L Cu(II) prepared in 0.1N KNO₃ solution.

### 5.2.5. Determination of point of zero charge

The point of zero charge (\( \text{pHpzc} \)) of the adsorbent was determined by solid addition method using DDW, 0.01N and 0.1N KNO₃ solutions. The volume of DDW (50 mL) was transferred to a series of conical flasks and the initial pH (pHi) of these solutions were roughly adjusted between 2.0 to 10.0 by adding either 0.1N HCl or 0.1N NaOH solution. The initial pHs (pHi) of these solutions were then accurately noted with the help of pH meter. After that, 0.5 g of adsorbent was added to each flask and allowed to equilibrate for 24 h with intermittent manual shaking. The final pH (pHf) of the
supernatant liquid was then noted. The difference between the initial pH (pHi) and
final (pHf) values (ΔpH = pHi-pHf) were plotted against pHi, the point of intersection
of the resulting curve with abscissa, at which ΔpH=0, gave the pHpzc. The same
procedure was repeated using 0.01N and 0.1M KNO₃ solutions.

5.2.6. Effect of contact time and concentration

Effect of time on the adsorption of Cu(II) was determined by analyzing the residual
Cu(II) in the liquid after contact period from 5 to 300 min. Experiments were
performed using batch process at room temperature. The mass of adsorbent (0.5 g)
was added to 50 mL solution of various initial concentrations of Cu(II) (10-100
mg/L). Samples were withdrawn from each conical flask after specified time interval
and analyzed for residual metal content.

5.2.7. Effect of adsorbent doses

The effect of adsorbent dose on the adsorption of Cu(II) was studied by varying the
adsorbent doses from 0.2 to 1.0 g at fixed volume of the solution (50 mL) of Cu(II)
with initial concentration of 50 mg/L. The adsorbent was treated with the solution in
250 mL conical flasks. These flasks were kept into temperature controlled water bath
shaker at different temperatures (30-50°C) for 4 h and then filtered. The final
concentration of Cu(II) in the filtrate from each flask was then determined as
described earlier.

5.2.8 Desorption studies

Batch process was used to perform desorption studies by varying the adsorbent
amount (0.5 – 1.0 g). The desired amount of adsorbent was taken in a conical flask
and treated with 50 mL of Cu(II) solution. After the contact time of 24 h, the solution
was filtered and filtrate was analyzed for residual Cu(II) concentration. The adsorbent
was then washed several times with DDW to remove excess Cu(II) ions and then
treated with 50 mL of desorbing solution (0.1N HCl). The amount of Cu(II) desorbed
in the supernatant liquid was then determined by AAS.
5.3. RESULTS AND DISCUSSION

5.3.1. Adsorption of heavy metals

The adsorption capacities of metal ions are affected by many factors e.g. property of metal ions and solutions. This adsorption of Cu(II), Cd(II), Ni(II), Pb(II) and Cr(VI) is shown in Figure 5.1. The efficiency of adsorption was in the order of Pb(II) > Cu(II) > Ni(II) > Cd(II) > Cr(VI). Cu(II) was selected as the adsorbate in order to examine the heavy metal removal characteristics and adsorption capacity of glaze. The effect of treatment of adsorbent with a complexing agent like PAN [l-(2- Pyridylazo)-2-naphthol] was also studied and it was found that treatment did not show any increase in the adsorption. Infact, the adsorption of metal ions decreased while there was almost no change on the adsorption of Pb(II). The efficiency of adsorption on PAN-treated glaze was in order of Pb(II) > Ni(II) > Cd(II) > Cu(II) > Cr(VI).

5.3.2. Characterization of adsorbent

5.3.2. (a) Chemical composition

The chemical composition of glaze slurry (Table 5.1) shows high percentage of Al₂O₃ (as feldspar) and SiO₂ (in the form of quartz).

5.3.2. (b) Scanning electron microscopy (SEM) analysis

SEM images of native and Cu(II) adsorbed glaze are shown in Figure 5.2a and 5.2b. The surface of the glaze appeared to be heterogeneous. The morphology of the surface is slightly changed after Cu(II) adsorption. Adsorbed Cu(II) on the surface of the glaze can be seen clearly in the form of white patches (Figure 5.2b).
Table 5.1
Chemical composition of Glaze slurry

<table>
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<tr>
<th>Material</th>
<th>Chemical formula</th>
<th>(%)</th>
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<tr>
<td>Potash feldspar</td>
<td>K₂O·Al₂O₃·6SiO₂</td>
<td>52</td>
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<tr>
<td>Quartz</td>
<td>SiO₂</td>
<td>21</td>
</tr>
<tr>
<td>Calcite</td>
<td>CaCO₃</td>
<td>15</td>
</tr>
<tr>
<td>China clay</td>
<td>Al₂O₃·2SiO₂·2H₂O</td>
<td>7</td>
</tr>
<tr>
<td>Barium carbonate</td>
<td>BaCO₃</td>
<td>3</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>ZnO</td>
<td>2</td>
</tr>
</tbody>
</table>
Figure 5.2 (a) SEM micrograph of native glaze

Figure 5.2 (b) SEM micrograph of glaze after Cu(II) adsorption
5.3.2. (c) FTIR analysis

FTIR spectra of native and Cu(II) treated adsorbent are shown in Figure 5.3a and 5.3b. The peaks at 3694 and 3619 cm\(^{-1}\) are due to the presence of –OH groups while peaks between 900 -1100 cm\(^{-1}\) are due to metal oxide [Coates, 2000]. When FTIR spectra of untreated and Cu(II) treated adsorbent were compared, the wave number associated with –OH group was shifted. After treatment with Cu(II) ions, a decrease of 30% in transmittance have been observed showing that interaction of Cu(II) occurs at –OH groups. All these changes show that this shift is due to metal binding process on the surface of glaze.

5.3.3. Effect of time and concentration

The mechanism of the metal uptake generally depends on the initial concentration of heavy metal to which the adsorbent is in contact. At low concentrations the specific sites are responsible for the adsorption of metal, while with increasing metal concentrations the specific sites are saturated and the adsorption sites are filled [Lehman et al., 1984]. The effect initial concentration of Cu(II) on the extent of adsorption is shown in Figure 5.4. It has been found that adsorption increases with time and attains maximum for all the concentrations. The adsorption capacities at 20, 40, 60, 80 and 100 mg/L concentrations are found to be 1.1, 1.3, 3.2, 4.1 and 7.0 mg/g respectively. This result may be due to increased driving force with the increased initial Cu(II) concentration. The uptake of metal ions at any particular concentration also increases with contact time. The equilibrium time however remains constant (60 min) when concentration is varied between 20 – 60 mg/L showing that at lower concentrations (up to 60 mg/L) the equilibrium time is independent of concentration but when concentration is increased above 60 mg/L, the equilibrium time increases (300 min at 100 mg/L initial concentration). Therefore a higher initial Cu(II) concentration may increase the adsorption capacity but will require more contact time for maximum removal [Chen et al., 2005].
Figure 5.3 (a) FTIR of native glaze

Figure 5.3 (b) FTIR of glaze after Cu(II) adsorption
Figure 5.4 Effect of time and initial concentration
5.3.4. Effect of pH and electrolyte concentration

The effect of pH on the adsorption of Cu(II) is shown in Figure 5.5. The variation in the adsorption of Cu(II) with respect to pH can be explained by considering the surface charge of the adsorbent and the speciation of Cu(II) ions. At pH 2, the adsorbent possesses positive charge because the point of zero charge (pHpzc) of the adsorbent is 8.2 (Figure 5.6). The surface is positive if pH of the solution is less than pHpzc which is not favorable for the adsorption of Cu(II) ions due to electrostatic repulsion. The reaction may be explained as follows

\[
A-O^+ + H_2O \rightarrow H^+ + O-H + HO^-
\]

Hence adsorption at pH 2 is less (18%), also a high concentration of H\(^+\) ions in the solution compete with metal ions resulting in the least uptake of metal ions at low pH. When initial pH of the solution is increased above 2, the final pH or equilibrium pH increases very quickly (Figure 5.5) because of the simultaneous adsorption of Cu\(^{2+}\) and H\(^+\) ions since there is less competition from H\(^+\) ions to the adsorption sites. The chemical species of Cu(II) formed at different pH values [Xue et al., 2009] are Cu\(^{2+}\) (pH 2-4); Cu(OH)\(^+\) (pH 4-6); Cu(OH)\(_2\) (pH 6-10); Cu(OH)\(_3\)\(^-\) (pH 10-12). The speciation suggests that majority of Cu\(^{2+}\) ions is present as Cu(OH)\(^+\) in the pH range 4-6 therefore it can be concluded that large quantity of Cu\(^{2+}\) ions (98%) is removed in the form of Cu\(^{2+}\) ions at pH< 4 and removal of Cu(II) in the pH range 4-6 occurs in the form of Cu(OH)\(^+\). When pH of the system is increased further (pH>pHpzc), the adsorbent surface becomes negatively charged as shown below

\[
A-O + HO^- \rightarrow A-O^- + H_2O
\]

\[
A-O^- + Cu^{2+} \rightarrow AOCu
\]

Negatively charged surface therefore favors the adsorption of cations due to electrostatic attraction. The species of Cu(II) are present as Cu(OH)\(^+\) and Cu(OH)\(_2\) in the pH range 6-10 hence uptake of Cu(II) at higher pH occurs in the form of Cu(OH)\(_2\) or micro precipitation. Further a shift in pHpzc towards lower pH value (Figure 5.6) in presence of increasing concentration of electrolyte (KNO\(_3\)) indicates specific adsorption of cations on the adsorbent surface [Tripathy and Kanugo, 2010]. The effect of electrolyte concentration is also shown in Figure 5.5. The percent adsorption of Cu(II) is decreased slightly in presence of 0.1 N KNO\(_3\).
Figure 5.5 Effect of pH

Figure 5.6 Point of zero charge
5.3.5. Effect of adsorbent dose

The effect of adsorbent doses on percent adsorption and adsorption density (mg/g) is shown in Figure 5.7. The experiment was performed at fixed volume (50 mL) at different temperatures (30°, 40° and 50°C). Percent adsorption increases with increase in adsorbent dose at any fixed temperature. This may be due to increased surface area of the adsorbent and availability of more adsorption sites with increased adsorbent dose. The % adsorption was found to be 92, 98.8 and 99.6 respectively at 30°, 40° and 50°C at fixed adsorbent dose (1g) indicating that adsorption process is endothermic in nature. The adsorption density however decreases with increase in adsorbent dose. The adsorption density at 30°, 40° and 50°C was found to be 2.3, 2.47 and 2.49 mg/g respectively at 1g adsorbent dose. The decrease in adsorption density with increase in adsorbent dose may be attributed to the interaction of adsorbent particles such as aggregation that might have resulted in decrease of total surface area of the adsorbent [Xue et al., 2009]. This decrease in adsorption density is more pronounced at lower adsorbent dose but as adsorbent dose increases the decrease in adsorbent density becomes negligible.

![Figure 5.7 Effect of adsorbent dose](image-url)
5.3.6. Adsorption isotherms

In order to optimize the design of adsorption system for the removal of Cu(II) from aqueous solution, it is important to explain the good relationship between adsorbed Cu(II) ions per unit weight of adsorbent (qe) and residual concentration of Cu(II) in solution (Ce) at equilibrium. Experimental data were fitted in the well known Langmuir, Temkin, Freundlich and Dubinin-Radushkeuich models at various temperatures.

According to Langmuir model the adsorption occurs on a homogenous surface forming monolayer of adsorbate with constant heat of adsorption for all sites without interaction between adsorbed molecules [Kalavathy et al., 2010]. The linear form of Langmuir model may be given as

\[
\frac{1}{q_e} = \frac{1}{q_m \times b} \times \frac{1}{C_e} + \frac{1}{q_m}
\]

(2)

Where Ce is the equilibrium concentration of Cu(II) in the solution (mg/L), qe is the amount of Cu(II) adsorbed per unit weight of adsorbent (mg/g), qm is the amount of Cu(II) required to form monolayer (mg/g) and b (mg/L) is a constant related to energy of adsorption. A plot of 1/qe versus 1/Ce gives straight line. The values of b and qm can be calculated from the slope and intercept.

The Freundlich model is an empirical equation based on adsorption on a heterogeneous surface. The linear form of Freundlich model can be represented as

\[
\log q_e = \log K_f + \frac{1}{n} \log C_e
\]

(3)

Where, K_f and n are Freundlich constants related to multilayer adsorption and adsorption intensity. A plot of log qe versus log Ce will generate straight line and values of 1/n and K_f can be calculated form the slope and intercept.

Temkin isotherm assumes that the decrease in the heat of adsorption is linear rather logarithmic, as implied in the Freundlich isotherm [Nemr, 2009]. It assumes that heat of adsorption on the surface of the adsorbent decreases linearly with coverage due to adsorbent-adsorbate interactions [Nemr, 2009]. The linear form of Temkin equation can be represented as
\[ q_e = \left( \frac{RT}{b} \right) \times \ln A + \left( \frac{RT}{b} \right) \times \ln C_e. \]  

(4)

Where \((RT/b) = B\), \(R\) is universal gas constant, \(T\) is absolute temperature and \(b\) is another constant. \(A\) (g/L) and \(B\) are Temkin constants related to adsorption potential and heat of adsorption. The values of \(A\) and \(B\) can be calculated from the slope and intercept of the plot of \(q_e\) versus \(\ln C_e\).

Dubinin-Redushkeuich (D-R) isotherm does not assume a homogenous surface or a constant sorption potential [Gonzalez et al., 2006]. The linear form of this equation is represented as

\[ \ln q_e = \ln q_m - \beta \varepsilon^2 \]  

(5)

Where, \(\varepsilon\) is the Polyanyi potential, \(q_m\) is the monolayer capacity (mol/g), \(q_e\) is the equilibrium concentration (mol/L), \(K\) is a constant related to adsorption energy \(m^2/(kT)^2\). The parameters \(q_m\) and \(k\) can be obtained from the intercept and slope of the plot of \(\ln q_e\) versus \(\varepsilon^2\). The Polyanyi potential \(\varepsilon\) and mean free energy of adsorption \((E, Kj/mol)\) can be calculated from the equations

\[ \varepsilon = RT \ln \left( 1 + \frac{1}{Ce} \right) \]  

(6)

\[ E = \frac{1}{\sqrt{-2\beta}} \]  

(7)

The fitting procedure was performed using R software version 2.10.1 (2009-12-14). To evaluate the fitness of the data, correlation coefficients \((R^2)\), error analysis (residual standard error (RSE) and P-values were calculated. The values of constants obtained from different models were fitted and corresponding \(q_e\) values (\(q_e\) cal) were calculated from each model. The values found experimentally were compared with \(q_e\) (cal) using chi-square test \((\chi^2)\). Chi-square test values were calculated from the following relation.
The data obtained from Langmuir, Freundlich and Temkin models were well fitted as indicated by low values of RSE and chi-square ($\chi^2$) test (Table 5.2) at 30°C. Freundlich model showed better applicability as compared to Langmuir and Temkin model since Freundlich model showed high correlation coefficient ($R^2$) and least $\chi^2$ test values in the temperature ranges 30°C to 50°C. The p-values for all the models at 30°C, 40°C and 50°C were less than 0.05 (p<0.05).
Table 5.2
Adsorption isotherm parameters at different temperatures

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<td>R²</td>
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<td>χ²</td>
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<td>R_L</td>
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<td>Raw rubber wood sawdust (RSD)</td>
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<td>Pottery glaze</td>
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<td>Present study</td>
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5.3.7. Thermodynamic study

The effect of temperature on the adsorption of Cu(II) was studied at temperature ranging from 30-50°C. Thermodynamic parameters such as standard free energy change (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°) were calculated using the following relations [Narmasivayam et al., 1995].

\[ K_c = \frac{C_{AC}}{C_e} \]  
\[ ΔG° = -RT \ln K_c \]  
\[ \ln K_c = -\frac{ΔH°}{RT} + \frac{ΔS°}{R} \]

Where, Kc is the adsorption equilibrium constant, CAC and Ce are equilibrium concentrations of Cu(II) on the adsorbent and in the solution, respectively.

A plot of ln Kc verses 1/T gives straight line and ΔH° and ΔS° were calculated from the slope and intercept (Figure 5.8). The thermodynamic parameters are reported in Table 5.4. Values of free energy change ΔG° are negative confirming that adsorption of Cu(II) is spontaneous and thermodynamically favorable since ΔG° becomes more negative with increase in temperature, indicating high driving force and hence resulting in higher adsorption capacity at higher temperature. The value of ΔH° is positive showing that adsorption process is endothermic in nature. A little but positive value of ΔS° in the temperature range 30-50°C suggests increased in randomness at the solid-solution interface during adsorption [Namasivayam et al., 1995] since adsorption of Cu(II) dislodge some water molecules from the surface of the adsorbent that results an increased randomness.

The D-R isotherm data (Table 5.2) indicate that mean free energy (E) remains almost constant (11.00 - 11.20 kj/mol) in the temperature ranges 30°-50°C. These values of indicate that chemisorption’s process is involved in the adsorption of Cu(II) onto glaze.
Figure 5.8 Van't Hoff Plot

\[ y = -9785.7x + 34.509 \]

\[ R^2 = 0.9979 \]

Table 5.4
Thermodynamic parameters at different temperature for the adsorption of Cu(II) on glaze

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>( \Delta G^0 ) (kJ/mol)</th>
<th>( \Delta H^0 ) (kJ/mol)</th>
<th>( \Delta S^0 ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>-5.50</td>
<td>8.12</td>
<td>0.28</td>
</tr>
<tr>
<td>313</td>
<td>-11.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>323</td>
<td>-13.67</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
5.3.8. Kinetics studies

The rate constants were calculated by using pseudo-first order and pseudo-second order kinetic models. The first order rate expression is given below [Lagergren, 1898].

\[
\log(q_e - q_t) = - \left( \frac{K_1}{2.323} \right) t + \log q_e 
\]

(13)

Where, \( q_e \) is the amount of metal ions adsorbed per unit weight of adsorbent at equilibrium or adsorption capacity (mg/g), \( q_t \) is the amount of Cu(II) adsorbed per unit weight of adsorbent at any given time \( t \), \( K_1 \) is the rate constant for pseudo-first order model. The values of \( K_1 \) and \( q_e \) (calculated) were calculated from slope and intercept of the linear plot of \( \log (q_e - q_t) \) verses \( t \) at various concentrations. The values of regression coefficient (\( R^2 \)) and rate constants at various concentrations are reported in Table 5.5.

The pseudo-second order kinetic rate equation is given as [Ho et al, 2000].

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

(14)

Where, \( h \) is the initial rate of adsorption (\( h = K_2 q_e^2 \)) and \( K_2 \) is the rate constant of pseudo-second order adsorption (g/mg/min). The values of \( K_2 \) and \( q_e \) (calculated) were calculated from the slope and intercept of the linear plots of \( t/q_t \) verses \( t \) at various initial Cu(II) concentrations. Table 5.5 provides data of pseudo-first order rate constants \( K_1 \), pseudo-second order rate constants \( K_2 \), \( h \), calculated equilibrium sorption capacity \( q_e \) (cal) and experimental equilibrium sorption capacity \( q_e \) (exp) at different initial Cu(II) concentrations. The \( q_e \) (cal) values from pseudo-first order kinetic model differed appreciably from the experimental value showing that system did not follow pseudo-first order model. In pseudo-second order kinetic model the \( q_e \) (cal) are however very close to \( q_e \) (exp) values at various initial Cu(II) concentrations as compared to pseudo-first order model. The values of correlation coefficient (\( R^2 \)) of pseudo-first order also confirmed it which was lower in comparison of pseudo-second order model indicating that pseudo-second order model is better obeyed.
Table 5.5
Pseudo-first-order and second-order parameters for adsorption of Cu(II) on glaze

<table>
<thead>
<tr>
<th>Concentration (mg/L)</th>
<th>Pseudo-first-order kinetics</th>
<th>Pseudo-second-order kinetics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_1$ (min$^{-1}$)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>10</td>
<td>0.0092</td>
<td>0.9043</td>
</tr>
<tr>
<td>20</td>
<td>0.3700</td>
<td>0.9463</td>
</tr>
<tr>
<td>40</td>
<td>0.0420</td>
<td>0.9389</td>
</tr>
<tr>
<td>60</td>
<td>0.0500</td>
<td>0.7403</td>
</tr>
<tr>
<td>80</td>
<td>0.0027</td>
<td>0.8084</td>
</tr>
<tr>
<td>100</td>
<td>0.0071</td>
<td>0.7531</td>
</tr>
</tbody>
</table>
5.3.9. Desorption study

The adsorption and desorption studies were performed with different adsorbent doses at room temperature and the results are depicted in Figure 5.9. The percent adsorption increases with increasing adsorbent dose. The desorption of Cu(II) also increases with adsorbent dose and shows 100 % desorption at 1.0 g adsorbent dose when 0.1 N HCl was used as desorbing solution. It can therefore be concluded that 1.0 g adsorbent is sufficient to achieve maximum efficiency of the adsorbent.

![Figure 5.9 Adsorption/Desorption of Cu(II) by batch process](image-url)
5.4. CONCLUSIONS

Pottery glaze slurry, the important material of pottery industry shows potential for the removal of Cu(II) from aqueous solution. Adsorption is fast and equilibrium is reached within 60 min. over a wide range of Cu(II) concentration. The maximum amount of Cu(II) can be removed from aqueous solution in the pH ranges 4-6. High concentration of electrolyte in the solution has negligible effect on the adsorption of Cu(II) therefore it can be concluded that maximum amount of Cu(II) can be removed from aqueous solution even in presence of large quantity of other salts. Langmuir and Temkin and are best obeyed at 30°C while Freundlich isotherm is obeyed at all the studied temperatures as indicated by their correlation coefficient ($R^2$, $\chi^2$, RSE values). Thermodynamic parameters indicate endothermic adsorption of Cu(II). Kinetic data show the applicability of pseudo-second order model which also confirms that chemisorption process is involved. Desorption studies show 100 % recovery of Cu(II) ions when 0.1 N HCl was used as desorbing solution.
REFERENCES


