ABSTRACT

Prosopis Juliflora Leaf Powder (PJLP) treated with nitric acid and used as a low cost adsorbent for the removal of copper ions from aqueous solution and industrial waste water. The effect of temperature, pH, contact time, adsorbent dose and initial concentration of adsorbate were studied for the removal of copper (II) by PJLP. Batch experiments were carried for adsorption kinetics and isotherms. Adsorption capacity found to be enhanced by increasing temperature and adsorbent dose. Equilibrium data were well represented by the Freundlich and Langmuir isotherm model for all tested adsorption systems. Beside these the Thermodynamic study has showed that the Cu (II) adsorption phenomenon onto PJLP was favorable and spontaneous. Applicability of adsorbent was tested for the removal of Cu (II) from industrial waste water and the results obtained were encouraging.

Keywords: Adsorption, Low cost material, Freundlich and Langmuir isotherm.

1. INTRODUCTION

Industries use chemicals like metals and dyes etc. for different purposes. Now a day metals found in industrial effluent are beyond permissible limit which may be attributed to improper treatment process, non-degradable and creates disposal problems. Hence it has become an alarming environmental problem and systematic investigation has to be carried to remove heavy metals from waste water. The discharge effluents from chemical industries, electroplating, tanning industries etc. contains heavy metals like Zinc, Copper, Chromium, Nickel, Iron, Lead, Mercury, Arsenic etc. [1]-[3]. Copper the metal considered in the present study, may be found as contaminant in food, especially shellfish, liver, mushroom, nuts, chocolate etc.[3].

Copper has three common oxidation states Cu (0) (metal), Cu (I) (cuprous) and Cu (II) (cupric). The main species of concern in aqueous solution is Cu (II) [4], but beyond permissible limit it is carcinogenic, causes gastrointestinal problems also it can cause headaches, fatigue, and depression, skin rashes, learning disorders and even lead to accumulation in the kidneys, brain, skin, pancreas and heart [5], therefore, they must be removed from industrial waste water. Toxic metals can be removed by ion exchange, precipitation, reverse osmosis, evaporation, and electrodialysis etc. These methods were found unaffordable in India for removal of heavy metals due to operational difficulties and high treatment expenditure. Activated carbon is the most widely used adsorbent but commercially available activated carbons are very expensive.

Adsorption using low cost adsorbents is one of the effective and economic methods [6], [7]. Various low cost adsorbents like brick kiln ash, tea waste, Ravi river sand and egg shells have been used for the removal of heavy metals [8]. Literature survey reveals that the use of PJLP as a low cost adsorbent for the removal of heavy metals from aqueous solutions and industrial waste water has not been reported. Thus in the present study the systematic work was carried to investigate the adsorption properties of PJLP for the removal of Cu (II).
2. MATERIALS AND METHODS

2.1 Preparation of adsorbent
Adsorbent used for the present study was Prosopis Juliflora which is locally available plant and was collected in Ahmednagar District of Maharashtra. The sample leaves were dried in shadow, avoiding direct sunlight on them. The dried plant leaves of PJ were grinded into powder and washed with distilled water and filtered. The residue left was treated with very dilute solution of nitric acid (0.1 N). It was then stirred for half an hour vigorously using mechanical stirrer at room temperature and filtered, washed with distilled water repeatedly to remove free acid. After chemical treatment the residue was dried first in air and finally in oven at 90-100°C for 8-10 hours and powdered using electric grinder. The homogeneous powder was passed through mesh for desired particle size. The adsorbent once prepared was used throughout the experimental work.

2.2 Preparation of Cu (II) metal ion solution
Cu (II) prepared by dissolving cupric sulphate in double distilled water. The chemicals used were of analytical grade and used without further purifications. The solutions were prepared in doubly distilled water. A distilled water prepared by using first metal distillation unit and then all quick fit glass assembly in permanganatic condition, wherever necessary the prepared solutions were standardized as per literature [9].

Industriel waste water samples were collected from MIDC area of Ahmednagar.

2.3 Adsorption experiments
Adsorption study was carried out by using nitric acid treated PJLP and Copper ion solution under different conditions at maximum time 60 minutes. Copper was determined using spectrophotometer [10], [11] (SL-159 ELICO UV-VISIBLE SPECTROPHOTOMETER). Copper from Industrial waste water was determined using AAS (LABINDIA AA 7000, Atomic Absorption Spectrophotometer) before adsorption experiments and using spectrophotometer [10],[11] (SL-159 ELICO UV-VISIBLE SPECTROPHOTOMETER) after the adsorption experiments.

After batch experiments percentage adsorption of Cu (II) from aqueous solution and industrial waste water were computed,

\[ \% \text{ Adsorption} = \frac{(C_I - C_F)}{C_I} \times 100 \]

Where, CI and CF are the initial and final Cu (II) concentrations respectively.

3. RESULTS AND DISCUSSION
The experimental data obtained from the different batch experiments, in the present investigation was analyzed and interpreted based on the adsorption of Cu (II) onto the surface of PJLP.

3.1 Effect of contact time
The effect of contact time was studied at 1 g of adsorbent, room temperature (303 K) and different time. The adsorption percentage increases with increase in time. (Fig.1). Time taken for the completion of adsorption was 60 minutes. It was in good agreement with the reported work of Rao et.al. [12]. The equilibrium contact time was 60 minutes. Ions diffuse to surface and in to the pores of PJLP which have very large number of surface area. When the time increased more than 60 minute remaining ions adsorbed or diffused into the pore could be saturated, the affinity of metals adsorbed will decrease. Thus, the affinity of metal adsorbed is depending upon appropriate time. Therefore the contact time 60 minutes was selected in all experiments which were in good agreement with the reported work of Tangiuank et.al. [13]

The first and second order equations were used to test the experimental data.

In pseudo –first order kinetic model a simple kinetics of adsorption given by Lagergren rate equations [14] were as,

\[ \frac{d q}{d t} = k_1 (q_e - q_t) \]

The integrated form is,

\[ \log (q_e - q_t) = \log q_e - k_1/2.303 \times t \]

Where \( q_e \) and \( q_t \) represent the amount of Cu adsorbed (mg/g) at equilibrium time and at time \( t \) (min) respectively, \( k_1 \) represents the first order rate constant \( (\text{min}^{-1}) \). Plot of \( \log (q_e - q_t) \) versus \( t \) is linear with \( R^2 = 0.951 \) (Fig.1.a)

In second order adsorption kinetics, the plot of \( t/q_t \) versus \( t \) was also found to be linear with \( R^2 = 0.979 \) (Fig.1.b) .The present studies reveal that adsorption of Cu (II) onto the surface of PJLP followed second order kinetic model.

![Figure.1 Effect of contact time on removal of Cu (II)](image-url)
3.2 Effect of temperature
Adsorption as the effect of temperature was carried out in different temperature range (293-333 K) and remaining parameters were kept constant and found that adsorption increases with increase in temperature (Fig.2). Adsorption equilibrium is a thermo-dependent process it may be attributed increased temperature which increases the kinetic energy of the metal ions and thus weakening the forces of attraction between the metal ions and the adsorbent (PJLP) [15].

Temperature plays a major role in the adsorption of heavy metals on the surface of adsorbent and has two major effects on the adsorption process, increase in the temperature increases the rate of adsorbate diffusion across the external boundary layer and in the internal pores of the adsorbate particles as the liquid viscosity decreases with increase in temperature and other affects the equilibrium capacity of the adsorbate [16], [17].

The increase in adsorption at higher temperature during the present investigation may be attributed to acceleration of some originally slow steps, creation of new activation sites on adsorbent surface, decrease in the size of adsorbing species, this could well occur due to progressive dissolution of the metal ions as the solution temperature increases. Our findings are in good agreement with the findings of different researchers [18], [19].

3.3 Effect of adsorbent dose
Effect of adsorbent dose plays an important role in standardizing the adsorption process with quantification of adsorbate solution and the adsorbent. In our present investigation with increase in the amount of adsorbent the removal efficiency increased rapidly (Fig.3) which may be attributed to the greater availability of the exchangeable sites or surface areas at higher concentration of the adsorbent. Our findings are in good support with Srinivas et.al.[20] and Hussein.et.al.[21]
3.4 Effect of pH

pH is one of the most important factors in controlling the uptake of heavy metals from wastewater and aqueous solutions [22]. In order to establish the effect of pH on the adsorption of copper ions, the batch equilibrium was studied at different pH values. According to Fig.4, the amount of metal adsorbed increases with increasing pH. At a low pH adsorption of copper was less; the H⁺ ions are much larger than ions of copper on the surface of the powder which limits the access of copper ions on the surface of grains of the adsorbent. When the pH increases, the effect of competition from H⁺ ions decreases and the positive charged ions take their place on the surface [23]-[25].

3.5 Effect of initial concentration of adsorbate

The adsorption of copper onto the surface of PJLP was rapid initially, slows down later on and finally reached towards equilibrium indicating saturated adsorption. The increased in adsorption may be attributed to increase in surface activity and due to micelle formation or the aggregation of copper ions in the concentration range studied. The percentage removal of Copper has shown significant decrease with the increase in the initial concentration of adsorbate (Fig.5). Our findings are in good agreement with the reported work of Jambulingam et.al. [26]

3.6 Adsorption isotherms
The adsorption isotherm is a graphical representation of amount of substance adsorbed against the residual concentration of the adsorbate and adsorbent doses were analyzed using Langmuir and Freundlich isotherm in order to find the adsorption capacity of PJLP.

### 3.6.1 Freundlich Adsorption isotherm

The Freundlich equation was applied to describe the analytical results on adsorption. It was an empirical result agrees quite well with Langmuir equation and experimental data over a moderate range of adsorbate concentration. It is represented by the equation [27],

\[
\log \frac{x}{m} = \log k + \frac{1}{n} \log C_{eq}
\]

Where, \(C_{eq}\) is the equilibrium concentration (mg/L) and \(x/m\) is the amount adsorbed per unit mass of adsorbent (mg/g). Plotting \(\log x/m\) vs. \(\log C_{eq}\) a straight line was obtained with a slope of \(1/n\), and \(\log k\) is the intercept. The \(k\) value was found to be 4.027. The value of ‘\(n\)’ was calculated to be 1.1745. As the value of ‘\(n\)’ is \(1<n<10\), shows favorable adsorption of Cu (II) on PJLP.

### 3.6.2 Langmuir Adsorption isotherm

Langmuir equation was also applied for adsorption equilibrium. The Langmuir treatment is based on the assumption that maximum adsorption corresponds to monolayer of adsorbate 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 [27].

\[
\frac{C_e}{q_e} = \frac{1}{Q_0}b + \frac{C_e}{Q_0}
\]

Where, \(q_e\) is the amount of solute adsorbed per unit weight of adsorbent (mg/g), \(C_e\) is the equilibrium concentration of solute in the bulk solution (mg/L), \(Q_0\) is the monolayer adsorption capacity (mg/g) and \(b\) is a constant related to the free energy of adsorption.

The linear plot of \(C_e/q_e\) vs. \(C_e\) shows that the adsorption obeys Langmuir adsorption model. \(Q_0\) and \(b\) respectively were determined from the Langmuir plots and found to be 201.08 mg/g and 0.3022 mg/L. The essential characteristic of Langmuir isotherm were expressed in terms of a dimensionless constant separation factor or equilibrium factor \(R_L\), which is defined by

\[
R_L = \frac{1}{1 + bC_0}
\]

Where \(b\) is the Langmuir constant and \(C_0\) is the initial concentration of Cu (II).

\(R_L\) is indicative of the nature of the isotherm and is enlisted below as [28], [29].

<table>
<thead>
<tr>
<th>(R_L) Value</th>
<th>Type of Isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R_L &gt; 1)</td>
<td>Unfavorable</td>
</tr>
<tr>
<td>(R_L = 1)</td>
<td>Linear</td>
</tr>
<tr>
<td>(0 &lt; R_L &lt; 1)</td>
<td>Favorable</td>
</tr>
<tr>
<td>(R_L = 0)</td>
<td>Irreversible</td>
</tr>
</tbody>
</table>

\(R_L\) value observed between 0 and 1 indicate favorable adsorption of Cu (II) on PJLP. \(R_L\) value in the present study was 0.0008.

### 3.7 Thermodynamic Parameters
Thermodynamic parameters such as free energy, enthalpy and entropy of adsorption were calculated and found that $\Delta G$ was negative and showed spontaneous nature of adsorption process, $\Delta H$ was positive and showed endothermic nature of adsorption process, $\Delta S$ was positive and showed the increasing randomness at solid/liquid interface during the adsorption of copper. The values demonstrate a spontaneous and favorable adsorption process.

3.8 Application to industrial waste water

The suitability of the PJLP adsorbent for the removal of Cu (II) with respect to Industrial waste water was evaluated. Adsorption experiments were conducted with Industrial waste water samples $S_1$, $S_2$ and $S_3$ containing Cu (II). Table-1 and 2 gives the details of the Industrial waste water samples applied for this study before and after adsorption experiments. The concentration of Cu (II) in $S_1$, $S_2$ and $S_3$ were determined by AAS. The percentage of Cu (II) removal in each sample was determined by usual procedure. The results are shown in Table-2. From which it is evident that Cu (II) removals were 79.48, 78.68 and 88.90 from $S_1$, $S_2$ and $S_3$ respectively. It has been observed that 88.90 % removal of Cu (II) could be achieved with a adsorbent dose of 1gm/100ml.

<table>
<thead>
<tr>
<th>Name of sample/Name of metal ion</th>
<th>$S_1$ Co(ppm)</th>
<th>$S_2$ Co (ppm)</th>
<th>$S_3$ Co (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>6.008</td>
<td>4.335</td>
<td>12.489</td>
</tr>
</tbody>
</table>

Table 1: Concentration of copper in industrial waste water before adsorption

<table>
<thead>
<tr>
<th>Name of sample</th>
<th>Industri al waste water (ml)</th>
<th>Amount of adsorbent (gm.)</th>
<th>Time (min)</th>
<th>O.D.</th>
<th>Conc.(Ce)</th>
<th>Co-Ce</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_1$</td>
<td>100</td>
<td>1</td>
<td>60</td>
<td>0.016</td>
<td>1.230</td>
<td>4.769</td>
<td>79.48</td>
</tr>
<tr>
<td>$S_2$</td>
<td>100</td>
<td>1</td>
<td>60</td>
<td>0.012</td>
<td>0.923</td>
<td>3.406</td>
<td>78.68</td>
</tr>
<tr>
<td>$S_3$</td>
<td>100</td>
<td>1</td>
<td>60</td>
<td>0.018</td>
<td>1.384</td>
<td>11.095</td>
<td>88.90</td>
</tr>
</tbody>
</table>

Table 2: Concentration of copper in industrial waste water after adsorption

4. CONCLUSIONS

The present study shows that the nitric acid treated Prosopis Juliflora Leaf Powder (PJLP) is an efficient low-cost adsorbent for the removal of toxic Cu (II) from aqueous solution and industrial waste water. The adsorption of Cu (II) was found to be dependent on contact time, adsorbent dose, initial concentration of adsorbate, temperature and pH. The equilibrium adsorption data showed significant correlation to Langmuir and Freundlich adsorption isotherms and the adsorption was followed second order kinetics. Value of RL indicates this adsorption process is favorable. Adsorption with low cost adsorbent is not only cheaper but requires less maintenance and supervision. With the application of very small dose of adsorbent (1gm/100ml), it is possible to remove about 89 % Cu (II) from industrial waste water. It is suggested that the use of this adsorbent for removal of Cu (II) from industrial waste water is an effective and low cost process.

REFERENCES