Adsorption of Pb(II) Ions on Teak Leaves Activated Carbon-
A Kinetic and Equilibrium Study

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ABSTRACT

In the present study, attempts have been made to use teak leaves (Tectona grandis) for the preparation of activated carbon with a view to use it in the treatment of wastewater and industrial effluent. The air-dried powders of teak leaves are carbonized using sulphuric acid and characterized by the methods suggested by the Bureau of Indian Standards. It has been planned to study about the nature of the surface of the adsorbent using Scanning Electron Microscope and FTIR. A comparative study of the experimental adsorbent material with commercial activated carbon, lignite and some other activated carbons procured from waste materials has revealed that the experimental adsorbent material is economically feasible and easily available one. In the present investigation, the activated carbon prepared from Teak Leaves (TLAC), has been used as the adsorbent and carried out batch mode experiments to study the effect of contact time on the removal of lead with the variation of the dose of the adsorbent. Models such as Lagergren, Bhattacharya-Venkobachar, Langmuir and Freundlich were tested and the results are interpreted.

Key words: Pb(II) ions, Teak Leaves, Activated Carbon, Lagergren, Bhattacharya-Venkobachar, Langmuir, Freundlich, Low-Cost Adsorbent

INTRODUCTION

The present investigation describes the preparation of activated carbon (TLAC) from teak leaves and its characterization. The study is aimed at to remove Pb(II) ions from wastewaters by adsorption technique using TLAC as the adsorbent. Batch mode experiments were conducted to determine the effect of contact time on various doses of the adsorbent. Kinetics of the experiments was arrived at by employing Lagergren, Bhattacharya-Venkobachar equations.
Langmuir and Freundlich adsorption isotherms were also employed to determine the adsorption capacity of the adsorbent for the removal of Pb(II) ions.

MATERIALS AND METHODS

Adsorbent
Preparation: The teak leaves were collected which are then air dried to remove maximum moisture content. Initially the crushed teak leaves were impregnated with H$_2$SO$_4$ for 24 h, separated, washed with distilled water and then kept in a muffle furnace at 110 °C for drying. Then it is carbonized at 400 °C and activated at 750 °C for a period of 30 min. The activated carbon thus obtained (Here after TLAC) was ground well, sieved and the adsorbent of the size 75-125 µm has been used for the present study.

Characterization: IR spectrum of TLAC was recorded (Thermo Nicolet, Nexus 670) in the range of 4000 – 450 cm$^{-1}$ with a resolution of 4 cm$^{-1}$. SEM images of the surface of the TLAC were obtained using LEO 1445 VP Scanning microscope. The physico-chemical characterization of TLAC, such as moisture content, ash content, matter soluble in water, matter soluble in acid, pH, apparent density have been determined by the methods suggested by the Bureau of Indian Standards [1]. The surface area and pore specific volume were determined by BET method.

Batch Studies
About 200 mg of the adsorbent was accurately weighed and transferred in to a stoppered bottle. 50 ml of the experimental lead solution (~500 mg / L) was pipetted out in to the stoppered bottle containing the adsorbent. It was then kept in a mechanical shaker and agitated for 30 min. It was taken out from the shaker and filtered through an ordinary filter paper. The filtrate was analyzed for residual lead concentration. From this, the amount of lead adsorbed was calculated. Similarly a number of sets of experiments were conducted for 60, 90,120,150,180 and 210 min to find out the equilibrium time for the adsorption of lead on to the surface of the selected adsorbent. Batch mode adsorption experiments were conducted to study the effect of contact time on the removal of lead with the variation of dose of the adsorbent.

RESULTS AND DISCUSSION

Table.1 presents the comparative values [2-4] of characteristics of commercial activated carbon (CAC) with TLAC. It is found from table.1 that the bulk density values for TLAC (0.39 g /cc) is comparable with that of CAC. The other physicochemical characteristics like ash content, matter soluble in water and acid are also comparable with those of CAC. The pH value suggested that the carbon chosen may be considered to have the characteristics of CAC.
Table 1 - Characteristics Of TLAC

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Characteristics</th>
<th>CAC</th>
<th>TLAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bulk Density, g/cc</td>
<td>0.68</td>
<td>0.39</td>
</tr>
<tr>
<td>2</td>
<td>Moisture Content, %</td>
<td>12.57</td>
<td>0.86</td>
</tr>
<tr>
<td>3</td>
<td>Ash Content, %</td>
<td>2.91</td>
<td>2.24</td>
</tr>
<tr>
<td>4</td>
<td>Matter Soluble in Water, %</td>
<td>1.55</td>
<td>1.85</td>
</tr>
<tr>
<td>5</td>
<td>Matter Soluble in Acid, %</td>
<td>4.58</td>
<td>4.79</td>
</tr>
<tr>
<td>6</td>
<td>pH</td>
<td>9.2</td>
<td>6.7</td>
</tr>
<tr>
<td>7</td>
<td>Surface Area, m²/g</td>
<td>296</td>
<td>234</td>
</tr>
</tbody>
</table>

The figure 1 shows the SEM Photographs of the selected adsorbent at different magnifications 100, 500 and 1000.

Fig.1 SEM images of TLAC at 100 (a), 500 (b) and 1000 (c) magnifications

Though TLAC has a low surface area and porosity, it has a wide pore size distribution giving a wide distribution of surface area [5] as can be seen from figure a, b and c. The size analysis shows the dominance of micro pores with the pore surface area being $13.1247 \text{ m}^2 / \text{g}$. The BJH pore area is found to be $6.5447 \text{ m}^2 / \text{g}$. The BET average pore size is $4.7233 \text{ m}^2 / \text{g}$, and the BJH average pore size is $107.6 \text{ Å}$. SEM images of TLAC shows that the adsorbent has a rough surface with almost non-compact structure. It is obvious that the sorbent has considerable number of pore spaces, where appropriate conditions exist for Pb(II) ions to be trapped and adsorbed into these pores. The SEM photos also illustrate that the metals can be homogeneously adsorbed on the surface of adsorbent. It is revealed from the SEM figures that the surface of TLAC is found to be not so random but rough in such a way to adhere the solute species on to the surface of the adsorbent. Therefore the adsorptive characteristics of teak leaves are expected to be highly effective.

Analysis of the IR spectrum has been used to explore the complete surface characteristics of the adsorbent (Fig.2).
Fig. 2. IR spectrum of TLAC

The band at 3420.20 cm\(^{-1}\) is due to the stretching of O-H group. The band at 2924.21 cm\(^{-1}\) and 2853.96 cm\(^{-1}\) indicates the position of asymmetrical and symmetrical stretching of methylene groups in the aliphatic and cyclic hydrocarbons. The bands in region between 2363.18 and 2131.53 cm\(^{-1}\) shows the presence of carboxylate ion. The band at 1637.27 cm\(^{-1}\) represents the aromatic ring vibration assigned to aromatic carbonyl and carbonyl motion in carboxylic acid with intermolecular hydrogen bonding. The band at 1562.88 cm\(^{-1}\) is assigned to \(\text{C} = \text{C}\) stretching vibration of cycloalkenes. The (S=O) symmetric stretching frequency of organic sulphates occurs in the region of 1415.61 cm\(^{-1}\). The band at 1112.31 cm\(^{-1}\) shows the alcoholic C-O stretching vibration. The bands between 777.93 and 619.76 cm\(^{-1}\) likely results from \(\text{NO}_2\) bending vibrations. The band at 514.42 cm\(^{-1}\) represents the S-S stretching vibration of disulphide. The C-C bending vibrations of normal alkenes occur in the region of 474.38 cm\(^{-1}\). Thus the IR results have confirmed the presence of functional groups such as OH\(^{-}\), COO\(^{-}\), CO, \(\text{NO}_2\), S\(_2\) on the surface of TLAC that could be the potential adsorption sites for interaction with the Pb(II) ions [6].

It has been reported [7] that pH of wastewater is a significant controlling factor in the adsorption process. Literature survey [8,9] has revealed that the Pb(II) ions were adsorbed only at less acidic medium (i.e.) at the pH range of 4-5. Hence, experiments were conducted using a lead nitrate solution of concentration around 500 mg/L with the pH of 5.0 at different doses viz., 2.0, 4.0, 6.0, 8.0, 10.0 g/L. The percent removal of Pb(II) and the corresponding doses are given in table 2.

During the process of adsorption, the rate of removal of Pb\(^{2+}\) ions increases with increasing time, up to a certain period and thereafter the rate of removal of solute becomes constant. At one stage, it may even become insignificant and such a trend is observed in the plot of % of solute removed against contact time (Fig. 3) in which the curve becomes asymptotic to the axis of contact time after a certain period. Such a curve represents nearly an equilibrium pattern.
It is understood from the figure that the residual concentration of Pb(II) ions in the adsorbate solution drops steeply in the first 180 min and then gradually decreases to a constant value. The initial steep drop of the residual concentration of Pb(II) ions is due to the rapid removal of Pb(II) ions which occurs as a result of the presence of large number of active adsorption sites available on the surface of the adsorbent, compared to the number of adsorbate species in the solution. Hence for all practical purposes, 210 min is presumed to represent equilibrium time which means that 210 min appears to be sufficient for the maximum adsorption of Pb(II) ions by the chosen adsorbent, under a given set of experimental conditions. The maximum amount of Pb(II) ions adsorbed corresponding to the equilibrium is found to be 32.6 % for a weight of 2.0 g/L of the adsorbent. The nature of the curve indicates the uptake of Pb(II) ions per unit mass of adsorbent increases with the increasing dose of the adsorbent.

Table 2 presents the values of the amount of Pb(II) adsorbed at the 30th min as 25.8, 46.4, 59.5, 71.2, 81.6 %, when the concentration of the adsorbent is 2.0, 4.0, 6.0, 8.0 and 10.0 g/L respectively, and at the 210th min the corresponding Pb(II) removal is 32.6, 59.8, 80.8, 87.2 and 87.2.
87.2 %. This shows that as the dose of the adsorbent increases, the adsorption of lead also increases. The minimum time required to achieve maximum adsorption decreases with the increase in the dose of the adsorbent which may be attributed to the increase of the surface area. In other words, the number of available active sites may be more compared to the number of adsorbate species.

The experimental data obtained for the adsorption of Pb(II) on to the surface of TLAC under the given set of conditions, were analyzed in the light of Lagergren model with the view to evaluating the mechanistic parameters associated with the process of adsorption.

Lagergren equation [10] is

$$\log_{10}(q_e - q) = - \frac{k_{Lager} t}{2.303} + \log_{10} q_e \quad \ldots \ldots (1)$$

where, $q_e$ is the amount of metal ions adsorbed at equilibrium, mg g$^{-1}$; $q$ is the amount of metal ions adsorbed at time, t, mg g$^{-1}$; $k_{Lager}$ is the overall rate constant for the adsorption process, s$^{-1}$ and t is time, s.

![FIG.4-LAGERGREN PLOT-DOSE VARIATION](image)

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Adsorbent Dose, mg/L</th>
<th>$k \times 10^4$, s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$k_{Lager}$</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>2.48</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>2.18</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>2.12</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>1.97</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>1.97</td>
</tr>
</tbody>
</table>

The Lagergren equation suggests linearity for the plot of $\log_{10}(q_e - q)$ against time, t. The fig.4 represents the relation between $\log_{10}(q_e - q)$ and t under a given set of experimental conditions.
From the slope of each line, the rate constants were determined. The values of \( k_{\text{Lager}} \) obtained for different doses of the adsorbents are presented in Table -3.

The results obtained in the light of Lagergren were further confirmed by Bhattacharya-Venkobachar equation \([11]\).

\[
\log_{10} [1-u(t)] = - k_{\text{Bhatt}} t / 2.303 \quad \ldots \ldots (2)
\]

where, \( u(t) \) is \( \left( \frac{(C_0-C_t)}{(C_0-C_{eq})} \right) \); \( k_{\text{Bhatt}} \) is the overall rate constant, \( s^{-1} \); \( C_0 \) is the initial metal ion concentration, mg/L ; \( C_t \) is the concentration of metal ion at time, \( t \), mg/L and \( C_{eq} \) is the concentration of metal ion at equilibrium, mg/L.

The values of \( k_{\text{Bhatt}} \) obtained by using different doses of the adsorbent at pH 5.0, are presented in the Table-3. It is found that the \( k_{\text{Bhatt}} \) values agree well with those of \( k_{\text{Lager}} \).

These values reveal the trend of decreasing rate constant with the increase of the dose of the adsorbent. Furthermore, the applicability of the Bhattacharya and Venkobachar equation confirms the formation of a monomolecular layer of Pb(II) ions on to the surface of adsorbent, as well as the first order kinetic nature of the process.

Langmuir isotherm has been extensively used by many authors for the sorption of heavy metals on clays, metal oxides, soils etc. The model assumes uniform energies of adsorption on to the surface and no transmigration of adsorbate in the plane of the surface. The linear form of Langmuir isotherm equation is:

\[
\frac{1}{q_e} = \frac{1}{\theta_0} b + \frac{1}{b \theta_0 C_e} \quad \ldots \ldots (3)
\]

where, \( q_e \) is the amount of metal ion adsorbed (mg / L) ; \( C_e \) is the equilibrium concentration of the adsorbate ions (mg / L); \( \theta_0 \) & \( b \) are Langmuir constants related to adsorption capacity and energy of adsorption respectively.

When \( 1/q_e \) is plotted against \( 1/C_e \), a straight line with the slope \( 1/ \theta_0 b \) and intercept \( 1/ \theta_0 \) is obtained had shown that the adsorption of Pb(II) ions follows the Langmuir isotherm model. The Langmuir parameters \( \theta_0 \) and \( b \) are calculated from the slope and intercept of the graphs and are given in the table .4. These values are used for comparison and correlation of the sorptive properties of the adsorbent.

The adsorption data for Pb(II) ions has also been analyzed using the logarithmic form of Freundlich isotherm:

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e \quad \ldots \ldots (4)
\]

where, \( q_e \) is the amount of metal ions adsorbed (mg/L) ; \( C_e \) is the equilibrium concentration of the adsorbate species (mg/L) ; \( K_F \) and \( n \) are Freundlich constants related to adsorption capacity and adsorption intensity respectively.

When \( \log q_e \) is plotted against \( \log C_e \), a straight line with slope \( 1/n \) and intercept \( \log K_F \) is obtained. This reflects the satisfaction of Freundlich isotherm model for the adsorption of Pb(II) ions.
The Freundlich parameters for the adsorption of Pb(II) ions are given in table 4. The intercept of the line, log $K_F$ is roughly an indicator of the adsorption capacity and the slope $1/n$ is an indication of adsorption intensity [12].

Table 4: Effect of dose on Langmuir and Freundlich constants

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Adsorbent Dose, mg/L</th>
<th>$\theta_0$, mg/g</th>
<th>$b \times 10^5$, /L</th>
<th>$1/n$</th>
<th>$K_F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>128.53</td>
<td>1.17</td>
<td>0.62</td>
<td>7.92</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>181.81</td>
<td>1.43</td>
<td>0.68</td>
<td>4.73</td>
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<tr>
<td>3</td>
<td>6</td>
<td>86.02</td>
<td>5.97</td>
<td>1.39</td>
<td>3.14</td>
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<tr>
<td>4</td>
<td>8</td>
<td>8.77</td>
<td>171</td>
<td>3.44</td>
<td>2.78</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>7.19</td>
<td>247.88</td>
<td>3.83</td>
<td>1.28</td>
</tr>
</tbody>
</table>

CONCLUSION

It is found from the characterisation study that the selected adsorbent, TLAC, is expected to have more adsorptive capacity, and hence it acts as a suitable adsorbent for the removal of Pb(II) ions from aqueous solution of lead nitrate. The adsorption data suggest that the pH of the solution is the most important parameter in the control of metal ion adsorption on to the TLAC. This study has shown the ability of the adsorbent to adsorb metal ions only in less acidic medium. Hence the batch mode studies were carried out at pH 5.0.

The equilibrium time 210 min appears to be sufficient for the maximum adsorption of Pb(II) species by TLAC, and under the given set of experimental conditions, the maximum amount of Pb(II) adsorbed is found to be 32.6%. The percent removal of Pb(II) from wastewaters increases with the increasing dose of the adsorbent that the minimum time required to achieve maximum adsorption decreases with the increase of the dose of the adsorbent.

The conclusions derived from the study of applicability of Lagergren, Bhattacharya-Venkobachar, Langmuir and Freundlich isotherms to the present system revealed the first order kinetic nature of the adsorptive process.

Detailed literature survey has revealed the applicability of only little work on record concerning the use of TLAC as the adsorbent for the removal of lead. All the above informations revealed that the chosen adsorbent namely TLAC, may be used as a suitable adsorbent for the removal of not only Pb(II) ions but also any heavy metal ions from wastewaters.

Acknowledgement

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REFERENCES

[10] S.Lagergren, K.Bill,