Removal of mercury(II) ions by adsorption onto dates nut and commercial activated carbons: A comparative study

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Received 28 June 2004; revised received 17 May 2005; accepted 14 June 2005

Studies on the removal of mercury(II) ions by adsorption onto indigenously prepared dates nut (DC) and commercial activated carbons (CAC) have been carried out with an aim to obtain data for treating effluents from metal processing and chloralkali industries. The effect of various process parameters has been investigated by following the batch adsorption technique at 30±1 ºC. The percentage removal of mercury(II) ions increased with the decrease in initial concentration and increase in contact time and dose of adsorbent. As initial pH of the slurry increased, the percentage removal increased and reached a maximum value. The process parameters were optimised. Adsorption data were modeled with the Freundlich and Langmuir isotherms, the first order kinetic equations proposed by Lagergren and Bhatacharya and Venkobachar and Weber-Morri’s intra-particle diffusion model and the equations models were found to be applicable. The kinetics of adsorption is observed to be first order with intra-particle diffusion as one of the rate determining steps. Removal of mercury(II) ions by DC and CAC is found to be favourable and hence DC could be employed as an alternative low-cost adsorbent for effluent treatment, especially for the removal of mercury(II) and other metal ions.

Keywords: Mercury(II), activated carbon, dates nut carbon, adsorption, kinetic equations, intra-particle diffusion

IPC Code: C02F3/00; C01B31/00; C02F101:30

Although some attempts have already been made to economise the activated carbon(AC), the scope for minimizing its cost and development of alternative adsorbent materials to commercial AC(CAC) by obtaining indigenously prepared ACs(IPACs) from agricultural wastes is still open. Heavy metals are generally present as pollutants in a variety of industrial effluents. Industries such as metal plating, metal finishing, rubber processing, paint, chloralkali, oil refining, fertilizer, chemical etc., are well known sources of heavy metal discharge. The behaviour of mercury in natural water system is highly complicated by numerous inter-relations including precipitation, complexation, chelation, oxidation-reduction and sorption. The tolerance limit prescribed by Bureau of Indian Standards (BIS), India for discharge of Hg(II) ions into inland surface water is 10 ppm and for drinking water is 1 ppm. The effluent from chloralkali industry is the major source of Hg(II) contamination, other than the natural discharge and degradation. Mercury(II) ions are highly toxic, harmful to living beings when they exceed the tolerance limit. This necessitates the removal of Hg ions from wastewater before its discharge, transport and cycling into the environment.

Conventional methods for the removal of Hg(II) ions from wastewater include sulphide precipitation, ion exchange, coagulation and adsorption. The use of fly ash, iron oxide, waste tyre, peanut hull carbon, polymerized onion skin, AC prepared from flax sheive, and fertilizer waste, low rank Turkish coal and Fe(III)/Cr(III) hydroxide as adsorbents for the removal of Hg(II) ions from wastewater has been attempted. Mention may also be made on the removal of mercury(II) ions by using clay and clay minerals by Blinski et al., granular AC (GAC) by Bhattacharya and Sharma, exhausted coffee grounds, granulated slag of steel plants by Loomba and Panday, bicarbonate treated coconut husk carbon by Anirudhan and Sreedhar, fly ash by Srinivastava et al., and ACs obtained from wood and cashew nut shell by Kannan and Raja Kumar. The reported results revealed that carbons prepared from agricultural wastes exhibited a high adsorption capacity, obeyed Langmuir and Freundlich isotherms and first order kinetic equations, and were sensitive to pH. IPACs are found to be porous in nature with high surface area and hence suitable for the removal of metal ions. The present work is an attempt to

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obtain IPAC from a locally available agricultural waste viz., dates nut (DC), to study its suitability for the removal of mercury(II) ions by determining the effect of various process parameters on the extent of removal of mercury(II) ions, to model the adsorption data with various isotherms and to compare the results with that of CAC.

**Experimental Procedure**

**Materials**
Raw materials for the preparation of DC viz., dates nut were collected locally, cleaned, dried and cut into small pieces before carbonisation. All the other chemicals used were of analytical grade reagent obtained from either SD fine chemicals or Fischer (India). Double distilled water was used throughout the experiment. Mercuric chloride (BDH, AR) was used as a source of mercury(II) ions.

**Method**
The raw material was carbonised at 300-400 °C and kept at 600 °C in a muffle furnace (Neolab, India) to get DC. DC and CAC were sieved (90 micron; using Jayanth sieve shaker); activated by digesting it with 4 N nitric acid solution for 2 h at 80 °C and finally activated in an air-oven for 5 h at 120 °C. DC and CAC were stored in an air-tight wide mouth reagent bottles and used for adsorption studies.

Adsorption experiments were carried out at room temperature (30±1 °C) under batch mode. Stock solution of mercuric chloride (2000 ppm) was prepared, suitably diluted and estimated by EDTA method using xylenol orange as indicator. Exactly 50 mL of mercury(II) ion solution of known initial concentration (range: 25 – 175 mg L^{-1}) was shaken with a required dose of adsorbent (1.0 – 7.0 g L^{-1} for CAC and 4.0–16.0 g L^{-1} for DC) of a fixed particle size (90 micron) in a thermostatic orbital incubator shaker (Neolab, India) at 200 rpm after noting down the initial pH of the solution (pH = 6.0 for DC and 6.7 for CAC) for a specified period of time (Table 1). The initial pH was varied to the required value (range: 4.0 –10). After equilibration, the final concentrations (C_e) were also measured complexometrically. The value of percentage removal and amount adsorbed (q in mg g^{-1}) were calculated using the following relationships:

\[
\text{Percentage removal} = 100 \left( \frac{C_i - C_e}{C_i} \right) \quad \text{(1)}
\]

\[
\text{Amount adsorbed (q)} = \frac{\text{Vol.}(C_i - C_e)}{m} \quad \text{(2)}
\]

where, \(C_i\) and \(C_e\) are initial and equilibrium (final) concentrations of mercury (in mg L^{-1}), respectively and \(m\) is the mass of adsorbent used.

**Results and Discussion**

**Effect of process parameters**
The results on the extent of removal of mercury ions by CAC and DC under various experimental conditions are given in Table 2. The percentage removal of mercury(II) ions increased with the decrease in initial concentration and increase in contact time, and dose of adsorbent. The amount adsorbed (q) increased with increase in initial concentration and contact time but decreased with increase in dose of adsorbent. The plots of q_e versus c_e – for initial concentration variation and log c_t versus t – for contact time variation are found to be

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Variation / Adsorbent</th>
<th>Agitation speed: 200 rpm</th>
<th>Temperature: 30±1 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>For CAC</td>
<td>Initial concentration (ppm)</td>
<td>Contact time (min)</td>
</tr>
<tr>
<td>a) Initial concentration (ppm)</td>
<td>25–175</td>
<td>60</td>
<td>4.0</td>
</tr>
<tr>
<td>b) Contact time (min)</td>
<td>75</td>
<td>15-105</td>
<td>4.0</td>
</tr>
<tr>
<td>c) Dose (gL^{-1})</td>
<td>Optimum</td>
<td>60</td>
<td>1.0 – 7.0</td>
</tr>
<tr>
<td>d) Initial pH</td>
<td>Optimum</td>
<td>Optimum</td>
<td>4.0</td>
</tr>
<tr>
<td>II</td>
<td>Optimum conditions</td>
<td>75</td>
<td>60</td>
</tr>
<tr>
<td>III</td>
<td>For DC</td>
<td>a) Initial concentration (ppm)</td>
<td>25-175</td>
</tr>
<tr>
<td>b) Contact time (min)</td>
<td>100</td>
<td>15 – 105</td>
<td>10.0</td>
</tr>
<tr>
<td>c) Dose (gL^{-1})</td>
<td>Optimum</td>
<td>60</td>
<td>4.0 – 16.0</td>
</tr>
<tr>
<td>d) Initial pH</td>
<td>Optimum</td>
<td>Optimum</td>
<td>10.0</td>
</tr>
<tr>
<td>IV</td>
<td>Optimum conditions</td>
<td>100</td>
<td>60</td>
</tr>
</tbody>
</table>
exponential. The correlations of log $q_e$ versus $c_e$ ($r = 0.982$ for CAC and $0.994$ for DC) and log $c_i$ versus $t$ ($r = 0.992$ for CAC and $0.987$ for DC) are found to be linear with $r$-values. The values of log $q_i$ were correlated ($r = 0.991$ for CAC and $0.989$ for DC) and found to be linear with $r$ values close to unity. These observations are as expected. Similar results have been reported in literature for the removal of dyes, organic acids, and metal ions. The optimum conditions are initial concentration ($C_i$) = 75 ppm and 100 ppm, dose $= 4$ g L$^{-1}$ and $10$ g L$^{-1}$ for CAC and DC, respectively; contact time $= 60$ min. for both the adsorbents. The values of log ($%$ removal) are also found to be linearly correlated with log (dose) values ($r = 0.996$ for CAC and $0.994$ for DC). The values of log $q$ are found to be linearly correlated to log (dose) with correlation coefficients, which are almost unity ($r$-values: CAC = 0.998 and DC = 0.995). This is in accordance with the fractional power term of the dose as:

$$q = [\text{dose}]^n + c \quad \ldots (3)$$

where, $n = 0.664$ and 0.759 and intercept, $c = 1.49$ and 1.56, respectively for CAC and DC. This suggests that the adsorbed Hg(II) ions may either block the access to the internal pores of carbon or may cause particles to aggregate and thereby minimising the availability of active sites for adsorption.

The effect of initial pH on the extent of removal of mercury ions by adsorption on CAC and DC is found to be highly pH dependent (Table 2). As pH increases, the extent of removal increases, and reaches a maximum value. The optimum pH for removal of Hg$^{2+}$ ions is fixed as 6.0 for the CAC and DC. Slightly acidic pH is found to be favourable. The change in pH (ΔpH = initial pH – final pH) values slightly decreases in the order of 0.3 – 0.5 pH units. This suggests that during the adsorption of mercury species, protons are released from the surface functional groups present on the carbon (surface area: CAC = 604 m$^2$g$^{-1}$ and DC $= 580$ m$^2$g$^{-1}$). The surface functional groups like –C = O, -OH (phenolic), δ-lactone, etc. are found to be present on the surface of adsorbent. As pH of the solution varies the charge on the surface functional group also varies. This is responsible for the change in the extent of removal. Above pH 9.0, the Hg$^{2+}$ ions are precipitated as hydroxide, and maximum removal occurred due to precipitation and therefore adsorption is not studied. These results suggest that DC could be used as a low-cost adsorbent alternative to CAC for the removal of mercury ions.

**Adsorption isotherms**

Adsorption data were modeled with the help of Freundlich and Langmuir isotherms. The adsorption data were fitted with these isotherms (a) by plotting the values of log $q$ versus log $C_e$ and ($C_e/q_e$) versus $C_e$ and (b) by carrying out correction analysis between the values of (i) log $q_e$ and log $C_e$, and (ii) ($C_e/q_e$) and $C_e$ (Table 3).

**Freundlich isotherm:** $log \, q = log \, K + (1/n) \log \, C_e \quad \ldots (4)$

**Langmuir isotherm:** $(C_e/q_e) = (1/Q_o b) + (C_e/Q_o) \quad \ldots (5)$
where, \( K \) and \( 1/n \) are the measures of adsorption capacity and intensity of adsorption, respectively; \( q_e \) is the amount adsorbed per unit mass of adsorbent (in mg g\(^{-1}\)) at equilibrium; \( Q_0 \) and \( b \) are Langmuir constants, which are the measures of monolayer adsorption capacity (in mg g\(^{-1}\)) and surface energy (in L mg\(^{-1}\)), respectively. The results of correlation analysis along with the isotherm parameters are given in Table 3. The observed linear relationships are statistically significant at 95% confidence level as evidenced from the correlation co-efficient (\( r \)-value) close to unity, which indicate the applicability of these two adsorption isotherms and the monolayer coverage of mercury species on the carbon surface.

Further, the essential characteristics of the Langmuir isotherm can be described by a separation factor, \( R_L \), which is defined by the following equation:\(^\text{28}\)

\[
R_L = \frac{1}{1 + b C_i}
\]

\( \text{...}(6) \)

The separation factor, \( R_L \), indicates the shape of the isotherm and the nature of the adsorption process as given below:

- \( R_L > 1 \) Unfavourable
- \( 0 < R_L < 1 \) Favourable
- \( R_L < 0 \) Irreversible

In the present study, the computed values of \( R_L \) (Table 3) are found to be fraction in the range of 0-1, indicating that the adsorption process is favourable for these two adsorbents viz., CAC and DC, for the removal of Hg\(^{2+}\) ions.

### Kinetics of adsorption

The kinetics of adsorption of mercury ions by CAC and DC has been studied by testing the applicability of the first order kinetic equation proposed by Lagergren– as cited by Pandey et al.\(^\text{29}\), and Bhattacharya and Venkobachar.\(^\text{30}\).

#### Lagergren equation

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

\( \text{...}(7) \)

#### Bhattacharya & Venkobachar equation

\[ \log [1 - U(T)] = -(k / 2.303) t \]

\( \text{...}(8) \)

where, \( U(T) = [(C_i - C_t) / (C_e - C_t)] \); \( C_e \), \( C_t \), and \( C_i \) are the concentrations of mercury (II) ions (in mg L\(^{-1}\)) at time zero, \( t \), and at equilibrium (60 min.); \( q_e \) and \( q_t \) are the amounts adsorbed per unit mass of adsorbent (in mg g\(^{-1}\)) at 60 min and at time \( t \), respectively, and \( k \) is the first order rate constant for adsorption of mercury ions on CAC and DC. Different \( q_t \) versus \( t \) one curves (which were exponential plots) were obtained; one curve for each kinetic run was obtained. The values of \( \log q_t \) were found to be linearly correlated with \( t \) as shown by \( r \)-values close to unity. The values of first order rate constant are given in Table 4. All the linear correlations are found to be statistically significant at 95% confidence level as evidenced by \( r \)-values close to unity. The results (Table 4) indicate the first order nature of adsorption process and applicability of these first order kinetic equation. The \( k \) values calculated from Bhattacharya and Venkobachar equation are noted to be close to those of the \( k \) values computed from Lagergren equation, for any given adsorbent. This concludes that, in future any one of these two kinetic equations can be employed to calculate the \( k \) values.

### Table 4—Kinetics and dynamics of adsorption of Hg(II) ions by adsorption on CAC and DC at 30 °C

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>Parameter</th>
<th>Parameter</th>
<th>CAC</th>
<th>Hg(II) ion</th>
<th>DC</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>Lagergren equation</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>I a)</td>
<td>Correlation coefficient (( r ))</td>
<td></td>
<td>0.993</td>
<td>0.887</td>
<td></td>
</tr>
<tr>
<td>I b)</td>
<td>( k ) (min(^{-1}))</td>
<td></td>
<td>0.039</td>
<td>0.063</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>Bhattacharya and Venkobachar equation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>II c)</td>
<td>Correlation coefficient (( r ))</td>
<td></td>
<td>0.993</td>
<td>0.887</td>
<td></td>
</tr>
<tr>
<td>II d)</td>
<td>( k ) (min(^{-1}))</td>
<td></td>
<td>0.039</td>
<td>0.063</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>Intra-particle diffusion equation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>III e)</td>
<td>Correlation coefficient (( r ))</td>
<td></td>
<td>0.964</td>
<td>0.968</td>
<td></td>
</tr>
<tr>
<td>III f)</td>
<td>( k_p ) (mg g(^{-1}), min(^{1/2}))</td>
<td></td>
<td>0.251</td>
<td>0.235</td>
<td></td>
</tr>
<tr>
<td>III g)</td>
<td>Intercept (( c ))</td>
<td></td>
<td>10.35</td>
<td>3.294</td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>Log (% removal) versus log (time)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IV h)</td>
<td>Correlation coefficient (( r ))</td>
<td></td>
<td>0.984</td>
<td>0.962</td>
<td></td>
</tr>
<tr>
<td>IV i)</td>
<td>Slope (( m ))</td>
<td></td>
<td>13.71</td>
<td>5.82</td>
<td></td>
</tr>
</tbody>
</table>
values in adsorption process of metal ions. The first order rate constant of adsorption is found to be high in DC (0.063 min\(^{-1}\)) and low in CAC (0.039 min\(^{-1}\)). This indicates that the adsorption process of Hg(II) by DC is fast compared to that in CAC.

The adsorbate (mercury) species are most probably transported from the bulk of the solution to the solid phase through intra-particle diffusion/transport process, which is often the rate limiting step in many adsorption processes, especially in a rapidly stirred batch reactor\(^{31}\). The possibility of the presence of intra-particle diffusion as the rate limiting step was explored by using the intra-particle diffusion model as suggested by Weber and Morris\(^{32}\).

\[ q_t = k_p t^{1/2} + c \]  \hspace{1cm}  \text{... (9)}

where, \( q_t \) = amount adsorbed in time \( t \), \( c = \) intercept and \( k_p \) = intra-particle diffusion rate constant (in mg g\(^{-1}\) min\(^{1/2}\)). The values of \( q_t \) are found to be linearly correlated with values of \( t^{1/2} \). The computed \( k_p \) values are also given in Table 4. The results indicate that CAC is more porous than DC, as evidenced by high values of \( k_p \) (Table 4). The values of intercept \( (c) \) given an idea about the boundary layer thickness, \textit{i.e.}, the larger the intercept, greater is the boundary layer effect\(^{35}\) \([c \text{ is greater in CAC (10.35) than in DC (3.294)}\].

The correlation of the values of log (\% removal) and log (time) also resulted in linear relationship, as evidenced by \( r \)-values close to unity (CAC = 0.984 and DC = 0.962). The divergence in the value of slope from 0.5 (slope: CAC = 13.71 and DC = 5.82) indicate the presence of intra-particle diffusion as one of the rate limiting steps\(^{30,31}\), in the adsorption of mercury species besides many other processes controlling the rate of adsorption, all of which may be operating simultaneously\(^{32,35}\).

**Conclusion**

The results of the present study conclude that, DC could be used as low-cost adsorbent alternative to CAC in effluent treatment, especially for the removal of metal/mercury ions. The results will be highly useful in designing cost-effective effluent treatment plant. Thus, this study results in the development of strategy for the production of low-cost adsorbent (DC), which could be indigenously prepared from the locally available agricultural waste/by-product (dates nut).

**Acknowledgement**

The authors thank the Management and Principal of ANJA College, Sivakasi for providing facilities and encouragement. The authors also gratefully acknowledge the UGC-SERO, Hyderabad for financial support to one of them (N.K.).

**References**
