Adsorption characteristics of chloramine-T on activated carbon

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The adsorption behaviour of chloramine-T (CAT) from aqueous solutions on activated carbon is studied at 298, 303, 310 and 315.5K. The obedience to Langmuir (LAI) and Freundlich (FAI) adsorption isotherms is good while the obedience to Harkins Jura (HJAI) and Temkin (TAI) adsorption isotherms is poor. The specific adsorption is found to decrease with increase in temperature. From kinetic studies, kinetic parameters such as rate constant at each of the above temperatures, energy of activation for the adsorption process, half life period and Elovich constants have been evaluated. Calorimetric enthalpy of adsorption is determined and other enthalpies of adsorption have been evaluated. The specific surface area of AC determined by BET method is lower than that determined by Langmuir method. A probable mechanism of adsorption is suggested.

Chloramine-T (CAT) is a strong electrolyte stable in aqueous solution and has been extensively used as an oxidant and synthetic reagent. Kinetics of oxidation of organic substrates by CAT has received much attention. Extensive reports are available on CAT as an analytical reagent. Since work on adsorption of CAT is scanty and since such work will be useful in pollution control, in waste water treatment, in synthesis of compounds and in seed protection, the present work is undertaken.

Experimental
All chemicals used were of AR grade. Activated carbon (Sarabhai M) and CAT(Fluka) were used. Batch Studies were conducted with aqueous solutions of CAT(0.001 to 0.1 mol dm⁻³) at 298, 303, 310 and 315.5K with one g of activated carbon (AC) and 100 ml of CAT. Elico digital pH meter was used and temperature was controlled within ± 0.01°C. Filtration was done with G₃ sinters. The adsorption was optimised with an adsorbent close of 1g/100 ml, at pH 7 with equilibration time of 2 hours. The concentrations of CAT before and after adsorption were estimated iodometrically.

Sodium thiosulphate solutions were prepared afresh and standardised. As per ISI Specifications the activated carbon was characterised. Surface area of AC was determined by acetic acid adsorption on AC (Langmuir method) and Nitrogen gas adsorption on AC at liquid air temperature (BET method).

Results and discussion
The characteristics of the active carbon are as follows: Particle size = passes through 100-150 ASTM; water soluble substance 0.08%; hydrochloric acid soluble substance 0.5%; chloride 0.01%; heavy metals 0.002%; iron 0.05%; loss on drying 8%; decolourising power 180 mg g⁻¹; phenol number 200 mg; ash content 2.5%, pH 7.04 and bulk density 0.34 g cm⁻³.

Effects of temperature
The data from batch studies at different temperatures reveal that LAI and FAI are perfectly obeyed while HJAI and TAI are poorly obeyed. The reason is that the latter two are obeyed by gaseous adsorbates. TAI is based on the gaseous adsorbates and on the supposition that the adsorption enthalpy changes linearly with the pressure of the gaseous adsorbates. The constants from adsorption isotherms are presented in Table I. The constant of FAI = x/m (the specific adsorption) when equilibrium concentration c = 0. The increase in thermal motion with increase in temperature opposes adsorption, the more ordering process. Hence specific adsorption decreases with increase in temperature and so do k and n of FAI. The constant n in FAI is actually a correction factor for the mutual interaction among the adsorbed species. If the forces within the surface layers are attractive then n is greater than unity and if repulsive n is less than unity.

The fractional values of n suggest repulsive interaction among the adsorbed layers. It is evident from the data in Table 1 that excluding the abnormality at 310K, there is a regular trend of these slopes and intercepts. Adsorption studies were carried out with different ini-
ential concentrations of CAT at 298,303,308,310, 310.5,311,312,313,315 and 315.5. The very low values of specific adsorption around 310 ( Table 2 ) suggest a charge in molecular nature of CAT around this temperature as proposed by Rao 7 and that these agglomeration is poorly adsorbed. Conductance studies of CAT in aqueous solutions showed abnormal decline in conductance at these temperature range confirming the possibility of dimerisation as suggested by Rao.

Kinetic studies
Since a single solute is generally involved in the adsorption process, a simple first order reaction kinetic model 8 was used to establish the rate of attainment of adsorption equilibria. It can be shown

\[ c_n - c_t / c_n = x / x_r \]  \hspace{1cm} (1)

\[ 2.303 / t \log (1 - x / x_r) = k_n + k_d = k \]  \hspace{1cm} (2)

where \( c_n \) = concentration of CAT before adsorption; \( c_t \) = concentration of CAT at any time 't'; \( c_e \) = equilibrium concentration of CAT; \( k_n \) = rate constant for the adsorption process; \( k_d \) = rate constant for the description process; and \( k \) = overall rate constant.

From Eq. (2) it follows that

\[ k = k_n + (k_n / k_r) \]  \hspace{1cm} (3)

\[ = k_n (1 + 1 / k_r) \]  \hspace{1cm} (4)

where \( k_n \) is the adsorption equilibrium constant.

The overall rate constant \( k \) from the experimental data the adsorption desorption rate constants \( k_n \) and \( k_d \) and the equilibrium constants are presented in Table 3. In addition the other kinetic parameters such as log A, graphically determined energy of activation for chemisorption of CAT on AC and equilibrium constant calculated from Langmuir plots are presented. The overall rate constants decrease with increase in temperatures except at 310K. While \( k_n \) are high \( k_d \) are comparatively low. Hence adsorption is favoured at these temperatures. The decrease in equilibrium constant \( k_n \) and rate constant \( k \), the increase in \( t_{1/2} \) and the decrease in log A with increase in temperature show that the exothermic adsorption of CAT on AC is favoured more at lower temperatures than at higher temperatures. All these parameters are abnormal at 310K due to agglomeration. The high value of energy of activation proves that chemisorption is activated adsorption. The decrease in equilibrium con-
Table 3 - CAT - AC system - Kinetic and Elovich parameters

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>$k$ (s$^{-1}$)</th>
<th>$k_a$ (mol dm$^{-3}$ s$^{-1}$)</th>
<th>$k_b$ x 10$^{-4}$ (mol dm$^{-3}$ s$^{-1}$)</th>
<th>$k_c$ x 10$^{1}$ (s$^{-1}$)</th>
<th>$t_{1/2}$ x 10$^2$ (s)</th>
<th>Energy of activation (kJ mol$^{-1}$)</th>
<th>log A</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.0</td>
<td>3.4 x 10$^3$</td>
<td>3.3 x 10$^3$</td>
<td>0.8</td>
<td>4.3</td>
<td>2.1</td>
<td>16.7</td>
<td></td>
</tr>
<tr>
<td>303.0</td>
<td>(3.4 x 10$^4$)*</td>
<td>1.7 x 10$^3$</td>
<td>0.7</td>
<td>2.4</td>
<td>4.1</td>
<td>16.1</td>
<td></td>
</tr>
<tr>
<td>308.0</td>
<td>7.9 x 10$^4$</td>
<td>(4.2 x 10$^5$)</td>
<td>0.6</td>
<td>1.1</td>
<td>8.7</td>
<td>109.4</td>
<td>15.5</td>
</tr>
<tr>
<td>315.5</td>
<td>3.6 x 10$^4$</td>
<td>(1.0 x 10$^6$)</td>
<td>0.9</td>
<td>0.3</td>
<td>20</td>
<td>15.5</td>
<td></td>
</tr>
<tr>
<td>310.0</td>
<td>7.7 x 10$^4$</td>
<td>(1.3 x 10$^6$)</td>
<td>0.9</td>
<td>8.4</td>
<td>0.9</td>
<td>*Standard deviation</td>
<td></td>
</tr>
</tbody>
</table>

*Standard deviation

Elovich Parameters

<table>
<thead>
<tr>
<th>T in K</th>
<th>Slope</th>
<th>$\alpha$ (mol dm$^{-3}$ g$^{-1}$)</th>
<th>$a$ (mol dm$^{-3}$ s$^{-1}$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.0</td>
<td>1.8</td>
<td>1.3</td>
<td>1.5 x 10$^{-1}$</td>
</tr>
<tr>
<td>303.0</td>
<td>6.3 x 10$^{-3}$</td>
<td>3.7 x 10$^2$</td>
<td>5.4 x 10$^{-4}$</td>
</tr>
<tr>
<td>308.0</td>
<td>5.0 x 10$^{-3}$</td>
<td>4.6 x 10$^2$</td>
<td>4.3 x 10$^{-4}$</td>
</tr>
<tr>
<td>315.5</td>
<td>3.8 x 10$^{-3}$</td>
<td>6.0 x 10$^2$</td>
<td>3.3 x 10$^{-4}$</td>
</tr>
<tr>
<td>310.0</td>
<td>2.0 x 10$^{-3}$</td>
<td>12.0 x 10$^2$</td>
<td>1.7 x 10$^{-4}$</td>
</tr>
</tbody>
</table>

Elovich parameters

For a wide variety of activated adsorption, the variation of velocity with the amount adsorbed obeys Elovich equation the integrated form of which is

$$q = \frac{2.303}{\alpha} \{ \log (t + t_o) \} - 2.303 \{ \alpha( \log t_o + q_o) \}$$

where $\alpha =$ deceleration constant for the process; $t_o =$ an arbitrary constant chosen for the linearisation of $q$ versus $\log (t + t_o)$ plots and $t_o = 1/\alpha a$; $a =$ initial rate of uptake at $t = 0$; $q_o =$ volume of adsorbate gas adsorbed at $t = 0$; and $q =$ volume of gas adsorbed at any time $t$.

The Elovich constant $a$ shows a roughly exponential dependence on temperature. As adsorption is exothermic the deceleration constant increases with increase in temperature.

From Eyring plot the activation parameters have been calculated for the activated chemisorption process represented by the simple scheme

$$A + S \leftrightarrow AS^t + AS$$

($A =$ adsorbate, $S =$ adsorbent solid and $AS^t =$ transition state complex ). The values obtained are $\Delta H^t$ is -108.1 kJ/mol, $\Delta S^t$ is -620.7 J K$^{-1}$ mol$^{-1}$ and $\Delta G^t$ at 298 is 7.7 J mol$^{-1}$.

Enthalpies of adsorption

Heat of adsorption determined using Clausius Clapeyron equation is the isosteric enthalpy (enthalpy at constant specific adsorption ) which is the isothermal or differential heat of adsorption.

The calorimetric heat of adsorption is the integral heat of adsorption, aslo called as adiabatic enthalpy.
The isochoric enthalpy is the standard enthalpy of adsorption.

The Semenov Shilov enthalpy is based on the assumption that a part of the exothermic heat is used in activating the reactants. The different enthalpies in kJmol⁻¹ are as follows.

\[ \Delta H_{\text{calorimetric}} = 209.3, \quad \Delta H_{\text{Semenov Shilov}} = 483.7, \quad \Delta H_{\text{isochoric}} = 478.7 \text{ and } \Delta H_{\text{isotropic}} = -119.7. \]

The specific surface area of AC obtained by BET method is 868.9 m² g⁻¹ while that obtained by Langmuir method is 1946 m² g⁻¹. This difference in the methods is due to the fact that while the former involves nitrogen adsorption on solid, the latter involves adsorption of acetic acid from solution at room temperature on solid.

**Mechanism of adsorption**

On the positively charged surface sites of AC the anion \( \text{CH}_3\text{CH}_2\text{SO}_2\text{NCl} \) is adsorbed through nitrogen. The evidences in favour of such a conclusion are:

(i) Activated carbons have both acidic (L carbon) and basic (H carbon) sites and which type predominates decides the carbon to be L type or H type; (ii) the predominant species at the working pH 7 is \( \text{CH}_3\text{CH}_2\text{SO}_2\text{NCl} \); (iii) in aqueous solution the equilibrium given below exists;

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{SO}_2\text{NCl} & \rightleftharpoons \text{CH}_3\text{CH}_2\text{SO}_2^- + \text{N}^+ \\
& \rightleftharpoons \text{CH}_3\text{CH}_2\text{SO}_2^- + \text{H}^+ \\
& \rightleftharpoons \text{CH}_3\text{CH}_2\text{SO}_2^- + \text{H}_2\text{O}
\end{align*}
\]

(iv) though the negative charge may be preferred to stay on oxygen rather than nitrogen, when more and more of the species II is chemisorbed on AC the equilibrium will shift to the right; and (v) the likelyhood of adsorption of anion through nitrogen is further confirmed by the fact that when =N-Cl moiety is replaced by =N-Br moiety the cross section of the species adsorbed is increased. If species I is adsorbed through oxygen the cross section of the species adsorbed will be unaffected by change form =N-Cl to =N-Br.

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**References**