Kinetic Study of sorption of Manganese on chitosan

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Abstract: Manganese is one of the major heavy metal pollutant found in water and wastewater. It is commonly used in non-ferrous alloys, steel making and chemical industries. It causes retardation in growth, eye blindness, fever, muscular fatigue etc. Chitosan was used as a sorbent for the present investigation. The sorption of Manganese (II) on chitosan has been found to be dependent on contact time, concentration, temperature, and pH of the solution. The adsorbents were evaluated for the adsorption capacity using Langmuir and Freundlich adsorption model. The process of removal follows first order kinetics and absorption of heat. The study indicated that due to chemical composition, structure, more adsorption sites, cheap, availability in plenty etc. this substance proves to be efficient adsorbent.

Keywords: Adsorption, Manganese Removal, Metal Oxide, Nanoparticles

I. Introduction

The effluent treatment in developing countries is expensive and major cost is associated with the dependence on imported technologies and chemicals. The indigenous production of treatment techniques and chemicals locally, or using locally available non-conventional materials to treat pollutants seems to be the increasing problem for treatment of effluents. In this regard, there has been a focus on the use of appropriate low cost technology for the treatment of wastewater in developing countries in recent years. Technically feasible and economically viable pretreatment procedures with suitable biomaterials based on better understanding of the metal bio sorbent mechanism(s) are gaining importance. Activated carbon of agricultural waste products as low cost adsorbents has been reported till now. However, there is an additional cost involved in the processing of the agricultural wastes to convert the same to activated carbon, which is posing economic difficulties necessitating research on alternate adsorbents with equivalent potential of activated carbon. In this paper, attempt has been made to remove Mn (II) from aqueous system by sorption method utilizing treated and untreated low grade chitosan which is commonly a bio sorbent. This investigation deals with the source and characterization of chitosan through IR method, preparation of stocks solution, experimental procedures at different conditions of temperature, PH, particle size and concentration.

II. Sorbent

Low grade chitosan has been used as a sorbent for the removal of heavy metals at different concentrations, temperatures, pH and particle sizes. The structure of chitosan is presented schematically in Figure 1.

![Fig. 1: structure of chitosan](image-url)
sorption of Manganese on chitosan from aqueous solution increase with time (fig. 2) till equilibrium is attained in 140 min. The fig. show that time of saturation is independent of concentration. It is further noted that the amount of Mn (II) sorbed increases from 2.190 mg.g^{-1}(87.60%) to 5.680 mg.g^{-1}(89.54%) by increasing Mn (II) concentration from 100 mg/l to 250 mg/l. The time-amount sorbed curve is single, smooth and continuous indicating monolayer coverage of Mn (II) on the outer surface of chitosan.

**Sorption Kinetics**

The kinetics of sorption of Mn (II) on chitosan was studied using Lagergren equation (yadav et. al. 1987)

\[
\log (q_e - q) = \log q_e - \frac{kt}{2.3} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (1)
\]

Where \( q_e \) and \( q \) are the amount sorbed (mg.g^{-1}) of Mn (II) at equilibrium and at time ‘t’ respectively and \( k \) is sorption constant. The straight lines obtained from the plots of \( \log (q_e - q) \) against time (fig. 4) and different concentrations indicate that the sorption process follows first order kinetics.

**Effect Of Temperature:**

The amount of Mn (II) sorbed on chitosan increases from 2.190 mg.g^{-1}(87.60%) to 2.3336 mg.g^{-1} (96.13%) by increasing temperature from 30oc to 40oc indicating the process to be endothermic (fig. 5).

**Langmuir Isotherm**

The equilibrium data at the different temperatures follow Langmuir equation.

\[
\frac{C_e}{q_e} = \frac{1}{\phi b} + \frac{C_e}{\phi} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (2)
\]

Where \( C_e \) mg.L^{-1} is equilibrium concentration of Mn (II) and \( \phi \) and \( b \) are Langmuir constants related to sorption capacity and sorption energy respectively. The value of \( \phi \) and \( b \) (table 4) were determined from the slope and intercept of linear plots Fig. 6. The sorption capacity also increases with temperature suggesting that the active centres available for sorption have increased with temperature.
The change in free energy ($\Delta G^\circ$), enthalpy ($\Delta H^\circ$), and entropy ($\Delta S^\circ$) of sorption have been calculated using following equations.

\[
\Delta G^\circ = -RT \ln K \quad \cdots \quad (3)
\]
\[
\Delta H^\circ = RT \frac{T_1-T_2}{T_1} \ln \frac{k_2}{k_1} \quad \cdots \quad (4)
\]
\[
\Delta S^\circ = \Delta H^\circ - \Delta G^\circ / T_1 \quad \cdots \quad (5)
\]

Where $K_1$ and $K_2$ are equilibrium constants at temperature $T_1$ and $T_2$ respectively.

The negative values of $\Delta G^\circ$ (Table 2) indicate the spontaneous nature of the sorption process. The positive values of $\Delta H^\circ$ at different temperature support the endothermic nature of the process.

![Fig 4: Effect of temperature on the sorption of Mn (II) on Chitosan • 30°C, ▪ 40°C, ◄ 50°C](image)

**Table 1:** $\Phi$ values at different temp. and $p^H$

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$\Phi$ mg.g$^{-1}$</th>
<th>$p^H$</th>
<th>$\Phi$ mg.g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.7543</td>
<td>2</td>
<td>0.3891</td>
</tr>
<tr>
<td>40</td>
<td>1.1865</td>
<td>4</td>
<td>0.6880</td>
</tr>
<tr>
<td>50</td>
<td>1.3656</td>
<td>6.5</td>
<td>0.7543</td>
</tr>
</tbody>
</table>

![Fig 5: Langmuir isotherm for the sorption of Mn (II) on chitosan; • 30°C, ▪ 40°C, ◄ 50°C.](image)

**Table 2:** Thermodynamic parameters at different temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$\Delta G^\circ$ (kcal.mol$^{-1}$)</th>
<th>$\Delta H^\circ$ (kcal.mol$^{-1}$)</th>
<th>$\Delta S^\circ$ (kcal.mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>-4.96</td>
<td>13.01</td>
<td>19.36</td>
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<tr>
<td>40</td>
<td>-5.12</td>
<td>25.90</td>
<td>34.28</td>
</tr>
<tr>
<td>50</td>
<td>-7.26</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Effect of pH The amount of Mn (II) sorbed on chitosan increases from 1.640mg.g$^{-1}$ (65.60 %) to 2.190 mg.g$^{-1}$ (87.60 %) by increasing pH of the solution from 2.0 to 6.5 (Fig.6). The Sorption capacity $\Phi$, also increase with the increase of pH.

![Fig 6: Effect of pH on the sorption of Mn (II) on chitosan; • 2.0, ▪ 4.0, ◄ 6.5; temp: 30 °c, conc. 100 mg/l.](image)

**Table 2:** Thermodynamic parameters at different temperatures

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<tr>
<th>Temperature (°C)</th>
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IV. Conclusion

From the above observations it is clear that low grade chitosan can be effectively used for the removal of heavy metal ions under investigation from wastewater as it shows significantly high adsorption capacity for removal of Manganese from water as compared to other adsorbents.

References


