BATCH ADSORPTION STUDIES FOR THE REMOVAL OF Mn$^{2+}$ IONS FROM AQUEOUS SOLUTION

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ABSTRACT

Adsorption studies for removal of Mn$^{2+}$ ions from aqueous solution using Granular Activated Carbon fitrasorb 300 (GAC-F-300) and filtrasorb 100 (GAC-F-100) containing adsorbed 3,5-Dinitrobenzoic acid were carried out at temperature 25 ± 1°C. The adsorption isotherms of Mn$^{2+}$ions on different GAC have been determined and the data fitted reasonably well to Langmuir and Freundlich isotherm for activated carbon. The adsorption parameters were determined using both Langmuir and Freundlich isotherm models.

Key Word: Adsorption, Manganese, Granular Activated Carbon (GAC), GAC-F-100, GAC-F-300, 3,5-Dinitrobenzoic acid (DNBA)

INTRODUCTION

Pollution due to toxic metals is a major environmental issue concerning the industries handling metal process across the world. The main sources of toxic metals are industrial wastes from processes such as electroplating, battery manufacturing, chemical manufacturing, tannery, metallurgical, ceramic, fertilizer industries which contaminated the surface and ground water to large extent. It is well known that some metals can have toxic and harmful effect on many form of life. The inorganic micro pollutants are of considerable concern because they are non-biodegradable and highly toxic.$^1$ On the other hand, the ground water contain an appreciable amount of Fe$^{2+}$and Mn$^{2+}$or both is always devoid of dissolved O$_2$ and high in CO$_2$ content. Chronic manganese poisoning has been reported to affect the central nervous system, lungs and liver. The United state environmental protection agency recommends a concentration not more than 0.05 mg/L of manganese.$^2$ Hence, it becomes necessary to remove toxic metals from wastewater by an appropriate treatment before releasing them into the fresh bodies of water. In this study we focus on the adsorption process because it is inexpensive, efficient and creates relatively little sludge. Granular activated carbon widely accepted because of its low cost and high affinity towards the removal of metal ions. The capacity and rate of adsorption vary significantly for different potentially hazardous compound and different commercial carbons. The technique of complex formation between the metal ions and ligand was used in this study to enhance the adsorptive capacity of GAC. A number of adsorbents have been used by several workers for adsorbing toxic metals from their aqueous solution.$^3$-$^11$ It is therefore proposed to carry out adsorption of Mn$^{2+}$ from aqueous solution by using granular activated carbon whose surface is chemically modified with 3,5-Dinitrobenzoic acid.

MATERIAL AND METHODS

Experimental

All the chemicals were analytical reagent grade. Water was purified and distilled. Granular activated carbons namely filtrasorb 300 (GAC-F-300) and filtrasorb 100(GAC-F-100) gifted by Calgon Carbon Corporation Ltd. Pittsburgh, PA USA were used in present study. Both the grades were first...
subjected to size fractionation by sieving them using a sieve shaker (M/s Jayant Test Siever Mumbai) to obtain particles of mesh size 840 u to 1400 u. The sieved GAC particles were washed several times with boiled distilled water until clear lechate was obtained and collected in petridish. Finally the samples were dried in an oven at a temperature of 100-110°C, cooled at room temperature and stored in desiccators until use.

Initial stock solution of Mn²⁺ ion was prepared by dissolving requisite MnSO₄ in distilled water. A series of standard solution of Mn²⁺ ions were prepared from main stock solution by diluting with distilled water. Each solution was treated with potassium periodate and phosphoric acid and then absorbance was measured at wavelength of 525 nm using spectrophotometrically (Chemito-spectrosan UV 2700, double beam UV-Vis Spectrophotometer). The Beer’s law calibration curve was constructed by plotting the graph between absorbance versus concentration.

RESULTS AND DISCUSSION

Adsorption of Mn²⁺ ions on ligand loaded GAC was studied by batch technique. The concentration of Mn²⁺ on the loaded GAC was determined from equation

\[ q_e = \left( C_0 - C_e \right) \times \frac{V}{W} \]

Where

- \( q_e \) = Concentration of Mn²⁺ on the ligand loaded GAC in mg/mmol of ligand,
- \( C_0 \) = Initial concentration of Mn²⁺ in solution in mg/L,
- \( C_e \) = Final concentration of Mn²⁺ in solution in mg/L,
- \( V \) = Volume of solution in Lit
- \( W \) = Weight of the carbon taken

The adsorption isotherms of ligand loaded GAC obtained by plotting \( q_e \) and \( C_e \) are shown in Fig.1 and Fig.2.
Fig. 2: Adsorption isotherm system: GAC-F-100-DNBA-Mn^{2+}

Data of equilibrium isotherm was tested for adherence to both Langmuir and Freundlich models. As per Langmuir theory, the saturated value is that beyond which no further sorption can take place. The saturated monolayer can be represented by:

$$q_e = Q^0 b \times \frac{C_e}{1 + b C_e}$$

The linearised form of Langmuir isotherm can be represented by:

$$\frac{1}{q_e} = \frac{1}{b Q^0} \times \frac{1}{C_e} + \frac{1}{Q^0}$$

Where,

- $Q^0$ = amount adsorbed per unit weight of the carbon forming a complex monolayer on the adsorbent surface,
- $b$ = Langmuir constant,
- $C_e$ = Final concentration of manganese in solution in mg/L

Freundlich equation on the other hand represented as

$$q_e = k \cdot C_e^{\frac{1}{n}}$$

Above equation may be linearised as

$$\log q_e = \log k + \frac{1}{n} \log C_e$$

A plot of log $q_e$ versus log $C_e$ was fairly showing validity of Freundlich equation over a range of concentration. Fig. 3 to Fig. 6 illustrate the plot of Langmuir and Freundlich isotherm GAC-F-300-DNBA-Mn^{2+} and GAC-F-100-DNBA-Mn^{2+}. The plot of $1/q_e$ versus $1/C_e$ found to be linear indicating applicability of Langmuir model. The parameter $Q^0$ and $b$ are Langmuir constant relating to the adsorption capacity and adsorption energy respectively. The intercept and slope of the linear plot of $\log q_e$ versus $\log C_e$ and $1/q_e$ versus $1/C_e$ under given set of experimental condition provide values of $k_f$, $1/n$ and $Q^0$ and $b$ respectively. The corresponding Freundlich and Langmuir constant obtained are reported below in Table 1.

Fig. 3: Langmuir adsorption isotherm system: GAC-F-300-DNBA-Mn^{2+}
Table 1: Isotherm constants

<table>
<thead>
<tr>
<th>System</th>
<th>Langmuir constant</th>
<th>Freundlich constant</th>
<th>$q_e$ max (mg/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GAC-300-DNBA - Mn$^{2+}$</td>
<td>1.3755</td>
<td>0.1855</td>
<td>0.4960 0.5470</td>
</tr>
<tr>
<td>GAC-100-DNBA - Mn$^{2+}$</td>
<td>1.2771</td>
<td>0.2119</td>
<td>0.3830 0.3565</td>
</tr>
</tbody>
</table>
The Kf value of the Freundlich model and the Q0 value of the Langmuir model both indicate that the capacity of GAC to adsorb Mn2+ follows the order, GAC-F-300-DNBA-Mn 2+ > GAC-F-100-DNBA-Mn2+. The value of Kf and Q0 for GAC-F-100 DNBA-Mn2+ and GAC- F-300-DNBA-Mn2+ systems indicating the superiority of the later for this adsorption process & also supported from the regression coefficient (R²). The linear equations and regression coefficients are reported in Table 2.

**Table 2 : Equations and regression analysis data**

<table>
<thead>
<tr>
<th>System</th>
<th>Langmuir equation</th>
<th>Regression coefficient</th>
<th>Freundlich equation</th>
<th>Regression coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>GAC- F-300-DNBA-Mn2+</td>
<td>y=0.3919x+0.727</td>
<td>R²=0.934</td>
<td>y=0.4960x-0.547</td>
<td>R²=0.926</td>
</tr>
<tr>
<td>GAC- F-100-DNBA-Mn2+</td>
<td>y=3.6940x+0.783</td>
<td>R²=0.971</td>
<td>y=0.3830x-0.448</td>
<td>R²=0.934</td>
</tr>
</tbody>
</table>

**CONCLUSION**

The granular activated carbon works as a very efficient and economical adsorbent for effective removal of manganese ions from aqueous phase. The metal ion binding capacity of GAC-F-300 is found to be appreciably high as compared to GAC-F-100. This can be probably due to high surface area of GAC-F-300 and more coordinating sites available for approaching metal ion during adsorption. On the basis of regression coefficient R², it was clear that the Langmuir and Freundlich isotherm were best fitted for the sorption of manganese onto granular activated carbon. These experimental studies on coal based adsorbents would be quite useful in developing on appropriate technology for the removal of heavy metal ions from contaminated industrial effluent.

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**REFERENCES**


