Utilization of Granular Activated Carbon for Sustainable Environmental Contaminants Remediation

YOGITA K. MESHRAM1*, RAM U. KHOPE2 and RESHAL A. DESHMUKH3

1,2,3Department of Chemistry, S.S.E.S Amt's Science College, Congressnagar, Nagpur, (M.S), India.
*Corresponding author E-mail: meshramyogita249@gmail.com

http://dx.doi.org/10.13005/ojc/390631

(Received: November 21, 2023; Accepted: December 25, 2023)

ABSTRACT

An environment eco-friendly adsorbents such as filtrasorb-816 and filtrasorb-820 were used in this work. For the evaluation of the adsorption of manganese from the aqueous phase, granular activated carbons were used in conjunction with organic ligands such as 3,5-Dinitrobenzoic acid. The phenomenon of adsorption characteristics of manganese in an aqueous phase was studied at a constant temperature of 25 ±1°C and pH 5. Granular activated carbons were characterized by SEM analysis. Experimental data were tested by using Pseudo-first and Pseudo-second-order kinetic models. From the results, it was investigated that Pesudo-second-order data is more favorable than the pseudo-first-order for this system. The Langmuir, Freundlich, and Temkin isotherms models were used to describe the equilibrium characteristics of adsorption of Mn²⁺ onto activated carbon but the R² value of the Langmuir isotherm model was higher than other isotherms and hence it is the best fit. From this study, it was found that F-820 has more adsorption capacity to scavenge Mn²⁺ than F-816 from aqueous phase.

Keywords: Granular activated carbon, Manganese, Isotherm, Adsorption, Heavy metals.

INTRODUCTION

Water is a crucial advent for human beings and is used in many sectors. Rapid and unorganized urban and industrial developments have contributed to various environmental issues. The water resources continue to be contaminated with run-off water from agriculture fields containing pesticides, fertilizers, the industrial effluents, raising serious health and environmental concerns. The improper disposal and management of industrial and municipal wastewater are major sources of water pollution. Polluted water contains toxic metals, inorganic chemicals, and colored reagents creating a significant threat to public health.

Industries such as electroplating, leather, and textiles release substantial amounts of heavy metals, including arsenic, manganese, chromium, cobalt, lead, and nickel, contributing significantly to water pollution. Heavy metals highly reactive and non-degradable which may be deposited on the surface and water...
resources, posing immense dangers to all forms of life and the environment. The excess level of manganese in the water causes several detrimental consequences and can damage multiple organ of human. As well as manganese deficiencies causes wide range of clinical complications, including migraines, fibromyalgia, arrhythmia. Consequently, the removal of heavy metals from wastewater is a challenging task that demands continuous monitoring and attention. Heavy metals, accumulate in the environment, emphasizing the urgency of their removal from wastewater before discharge. Several treatment methods, such as chemical reduction, electro-coagulation, membrane adsorption, ion exchange, precipitation, membrane separation, and adsorption are available to lower the Mn(II) ion concentration from industrial wastewater. To prevent future adverse consequences on both human beings and the environment, these hazardous metals must be effectively removed from wastewater. However, the effective method for the treatment of heavy metals is the adsorption technique and the specific properties of adsorbents elevate the adsorption process. The appropriate selection of adsorbents is crucial, focusing on functional groups, high surface area, porosity, and polarity of adsorbents. Adsorption has proven to be more efficient and cost-effective for heavy metal removal compared to other methods. Its fundamental advantage lies in its economic viability, making it a low-cost approach for heavy metal removal. Another significant benefit of the adsorption process is its ability to be regenerated, allowing for the repeated use of adsorbents. Both commercial and conventional adsorbents have applications in scavenging heavy metals from aqueous phases.

MATERIAL AND METHOD

All chemicals of analytical grade were utilized. Initially, a requisite amount of MnSO₄ was dissolved in 1 liter of distilled water to prepare a stock solution of Mn²⁺ ions. Different grades of carbon were initially sized using a siever, resulting in particles ranging from 840μ to 1400μ mesh size. Subsequently, activated carbon particles F-816 and F-820 were thoroughly washed with boiled distilled water repeatedly, till a clear leachate was obtained. The washed carbon particles were collected and dried at a temperature of 100-110°C in an oven and then stored in desiccator till further use.

3,5-Dintrobenzoic acid was chosen as the ligand and then it is recrystallized by conventional method. The purity of 3,5-Dinitrobenzoic acid an essential component of the experiment, was confirmed by determining its melting point using Thiele's apparatus. The experimental melting point of 206°C was in close agreement with the literature value of 207°C, indicating its purity.

For determining adsorption isotherm, 200 mL solution containing a specific concentration of 3,5-Dinitrobenzoic acid and 0.5 g dried granular activated carbon were taken in a shaking bottle. The mixture was shaken for 5 h using a mechanical shaker (Remi Model, No. R.S.24). After that, the solution was filtered out, and the carbon was properly washed with distilled water multiple times. Then, 200 ml Mn²⁺ ion solution of pH 5 and washed carbon were transferred into the shaking bottle. The resulting mixture was shaken at a constant temperature of 25±1°C for 5 hours. The Mn²⁺ ions concentration, both before and after adsorption, was determined in mg/L by measuring absorbances using a spectrophotometer. The experimental data were analyzed using a calibration curve, ensuring accurate quantification. The graph was drawn by using the values of absorbance and concentrations of different standard solutions of Mn²⁺. To guarantee the reliability of the results, the experiments were repeatedly done to ensure consistency and reproducibility.
RESULT AND DISCUSSION

grams, respectively. The equilibrium isotherms for the ligand-loaded granular activated carbon were obtained by plotting the graph of $q_e$ (the amount of adsorbed Mn$^{2+}$ per millimole of ligand) against $C_e$ (the equilibrium concentration of Mn$^{2+}$ ions). The results of these plots are illustrated in Fig. 3 and Fig. 4.

Fig. 3. Equilibrium Isotherm, System- F-816_3,5-Dinitrobenzoic acid_Mn$^{2+}$

Fig. 4. Equilibrium Isotherm, System-F-820_3,5-Dinitrobenzoic acid_Mn$^{2+}$

Scanning electron micrographs were taken at various magnifications, displayed in Fig. 1a and 2a, revealing large cracks and uneven cavities on the surface of both Granular Activated Carbon (GAC) i.e. F-816 and F-820. These irregularities provide a substantial surface area, enhancing the metal adsorption capacity for Mn$^{2+}$ ions. Changes in the adsorbent's surface morphology after adsorption are illustrated in Fig. 1b and Fig. 2b. It was noted that the previously uniform porosity of the adsorbent was disrupted due to the accumulation of Mn$^{2+}$ ions on the carbon surface.

The Adsorption of Mn$^{2+}$ ions on ligand-loaded GAC was investigated using batch adsorption studies. The concentration of Mn$^{2+}$ ions was calculated by the following equation,

$$q_e = \frac{(C_0 - C_e) \times V}{W}$$

Where $q_e$ = The concentration of Mn$^{2+}$ on the ligand-loaded granular activated carbon, expressed in milligrams per millimole of ligand, the initial and equilibrium concentrations of Mn$^{2+}$ ions i.e. $C_0$ and $C_e$, in milligrams per liter respectively. The variables $V$ and $W$ represent the volume of the solution in liters and the weight of the adsorbent in grams, respectively.

Langmuir, Freundlich, and Temkin models were used in an attempt to fit the equilibrium isotherm data on both systems i.e. F-816-3,5-Dinitrobenzoic acid+Mn$^{2+}$ and F-820-3,5-Dinitrobenzoic acid+Mn$^{2+}$.

In the first, the linearized form of the Langmuir equation is expressed by the following equation,$^{22}$

$$\frac{1}{q_e} = \frac{1}{bQ^0} + \frac{1}{Q^0}$$

The Langmuir constant, denoted as $b$, $Q^0$
represents the amount adsorbed per unit weight of activated carbon forming a complex monolayer on the activated carbon.

The linear graphs of \( 1/q_e \) verses \( 1/C_e \) in Fig. 5 and 7 demonstrate the applicability of the Langmuir model. All the constants i.e. the Langmuir constant \( b \) and \( Q^0 \) were determined from the slope and intercept of the Langmuir isotherm, respectively given in Table 1. The Langmuir equation and corresponding regression coefficients are shown in Table 2.

The second one is the Freundlich model and equation\(^ {23} \) is represented as

\[
q_e = K_f C_e^{1/n}
\]

Above equation may be linearized as

\[
\log q_e = \log K_f + 1/n \log C_e
\]

Figure 6 and Fig. 8 show consistent linear plots of \( \log C_e \) versus \( \log q_e \) which demonstrate the validity of the Freundlich equation across a range of concentrations. The Freundlich constants, \( 1/n \) and \( K_f \), were calculated from the slope and intercept of the Freundlich equation, respectively. These Freundlich constants have been reported in Table 1, and the corresponding equation along with the regression coefficients are presented in Table 2.

Third one is the Temkin model\(^ {24} \) which is represented by the following equation

\[
q_e = \frac{RT}{b} \times \ln(K_T C_e)
\]

The linearized form of the above equation can be expressed as

\[
q_e = B_1 \ln K_T + B_2 \ln C_e
\]

\[
B_2 = R/T
\]

Where \( B_1 \) is the Temkin constant associated with the heat of adsorption (in kJ/mol), The variation of adsorption energy \( b \) (kJ/mol), \( R \) is the Universal gas constant (8.314 J/mol K), \( T \) is the absolute temperature (in K), and \( K_T \) is the Temkin isotherm constant (in L/mg). The Temkin isotherm posits that the heat of adsorption decreases linearly due to interactions between the adsorbent and adsorbate molecules. It provides insight into the adsorption potential of the adsorbent for the adsorbate. The Temkin constants, \( B_1 \) and \( K_T \) for Mn\(^ {2+} \) ions were determined by plotting \( \ln(C_e) \) against \( q_e \). The resulting linear plots over a concentration range allowed the calculation of Temkin constants, which are presented in Table 1. The R\(^2 \) values indicated a partial fit of the data to the Temkin adsorption isotherm for both systems: F-816-3,5-Dinitrobenzoic acid+Mn\(^ {2+} \) and F-820-3,5-Dinitrobenzoic acid+Mn\(^ {2+} \). The adsorption equilibrium data in this study were assessed using Langmuir, Freundlich, and Temkin isotherms. Fig. 5 to 10 depict the plots for the Langmuir, Freundlich, and Temkin isotherms, respectively. The correlation factor R\(^2 \)=1 suggests that the Langmuir model provides a more accurate depiction of the adsorption process compared to the Freundlich and Temkin models.
Kinetics studies

To investigate the adsorption kinetics of Mn²⁺ on granular activated carbon (GAC), kinetic analyses employing Lagergren’s pseudo-first-order and pseudo-second-order models were conducted. These analyses aid in understanding the rate of adsorption and identifying the rate-limiting step in the transport mechanism, essential for the design and modeling of the adsorption process.

The Lagergren pseudo-first-order model is described by the following linear equation:

\[ \ln \left( q_e - q_t \right) = \ln q_e - k_1 t \]

Here, \( q_t \) is the amount of Manganese on the ligand absorbed on GAC (mg/mmol) at any time \( t \), \( q_e \) is the amount of Manganese on the ligand absorbed on GAC at equilibrium (mg/mmol), and \( k_1 \) is the rate constant of the pseudo-first-order adsorption process (h⁻¹). The values of \( k_1 \) and \( q_e \) are determined by plotting \( t \) versus \( \ln(q_e - q_t) \). The metal uptake capacity at equilibrium and the rate constant for the pseudo-first-order model can be obtained from the slope and intercept of the plot. Table 3 presents the metal uptake capacity and rate constants for the pseudo-first-order model for different granular activated carbons. The experimental data for the F-816_3,5-Dinitrobenzoic acid_Mn²⁺ system and the F-820_3,5-Dinitrobenzoic acid_Mn²⁺ system are illustrated in Fig. 11 and Fig. 13, respectively.

The pseudo-second-order kinetics can be expressed in a linear form as follows:

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \frac{t}{q_t} \]

Here, \( k_2 \) is the rate constant of the pseudo-
second-order adsorption process. This equation allows for the determination of \( k_2 \) and \( q_e \) by plotting \( t/q \) against \( t \).

The results of the pseudo-second-order kinetics analysis provide further insights into the adsorption process i.e. chemisorption and rate limiting step which contribute to a comprehensive understanding of system.

### Table 1: Constants for Langmuir, Freundlich and Temkin adsorption isotherm

<table>
<thead>
<tr>
<th>S. No</th>
<th>System</th>
<th>Langmuir constant</th>
<th>Freundlich constant</th>
<th>Temkin constant</th>
<th>( q_{max} ) (mg/m.mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>GAC-F-816-3,5-Dinitrobenzoic acid+Mn(^{2+})</td>
<td>1.5151</td>
<td>0.4091</td>
<td>0.310</td>
<td>0.5956</td>
</tr>
<tr>
<td>2</td>
<td>GAC-F-820-3,5-Dinitrobenzoic acid+Mn(^{2+})</td>
<td>1.5337</td>
<td>0.4298</td>
<td>0.256</td>
<td>0.6886</td>
</tr>
</tbody>
</table>

### Table 2: Isotherm equation and regression coefficient

<table>
<thead>
<tr>
<th>S. No</th>
<th>Adsorption system</th>
<th>Equation</th>
<th>Reg. Coefficient</th>
<th>Types of isotherms</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>GAC-F-816-3,5-Dinitrobenzoic acid+Mn(^{2+})</td>
<td>( y=1.6133x+0.6602 )</td>
<td>( R^2=0.9853 )</td>
<td>Langmuir adsorption isotherm</td>
</tr>
<tr>
<td>2</td>
<td>GAC-F-820-3,5-Dinitrobenzoic acid+Mn(^{2+})</td>
<td>( y=1.5176x+0.6526 )</td>
<td>( R^2=0.9925 )</td>
<td>Langmuir adsorption isotherm</td>
</tr>
<tr>
<td>3</td>
<td>GAC-F-816-3,5-Dinitrobenzoic acid+Mn(^{2+})</td>
<td>( y=0.3105x-0.2251 )</td>
<td>( R^2=0.9660 )</td>
<td>Freundlich adsorption isotherm</td>
</tr>
<tr>
<td>4</td>
<td>GAC-F-820-3,5-Dinitrobenzoic acid+Mn(^{2+})</td>
<td>( y=0.2567x-0.1623 )</td>
<td>( R^2=0.9780 )</td>
<td>Freundlich adsorption isotherm</td>
</tr>
<tr>
<td>5</td>
<td>GAC-F-816-3,5-Dinitrobenzoic acid+Mn(^{2+})</td>
<td>( y=0.331x+0.452 )</td>
<td>( R^2=0.9610 )</td>
<td>Temkin adsorption isotherm</td>
</tr>
<tr>
<td>6</td>
<td>GAC-F-820-3,5-Dinitrobenzoic acid+Mn(^{2+})</td>
<td>( y=0.288x+0.579 )</td>
<td>( R^2=0.9830 )</td>
<td>Temkin adsorption isotherm</td>
</tr>
</tbody>
</table>
The authors declare no conflict of interest.

CONCLUSION

The study underscores the importance of considering cost-effectiveness and technical applicability when selecting adsorbents for crucial applications.

ACKNOWLEDGMENT

Authors expressed sincere gratitude towards Prof R.U. Khope, Head, Department of Chemistry, SSES Am'ts Science College, Congressnagar, Nagpur (M.S.) India, for their support and encouragement.

Conflict of interest

The authors declare no conflict of interest.

REFERENCES