INTERNATIONAL JOURNAL OF RESEARCHES IN BIOSCIENCES, AGRICULTURE & TECHNOLOGY
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www.vmsindia.org

# Verification of Langmuir, Freundlich and Temkin Isotherm Models in Adsorption Study of Cobalt onto Chemically Modified Activated Carbon

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**Abstract:**
The potential to remove cobalt ions from aqueous solution using Granular Activated Carbon such as filtrasorb 400 (F-400) and filtrasorb 200 (F-200) was investigated. Batch mode experiments were carried out to obtain adsorption isotherms of Cobalt ions onto Granular Activated Carbon. F-200 and F-400 loaded by 5-Sulphosalicylic acid at constant temperature 25 ± 0.5 °C and pH 5. The isothermal data could be well described by the Langmuir, Freundlich and Temkinequations. The experimental study revealed that 300 min of stirring time was enough to achieve equilibrium. The aim of present work was to explore the usage of activated carbon as a promising precursor for the removal of cobalt from waste water.
**Keywords**: Adsorption, Cobalt, Granular Activated Carbon, 5-Sulphosalicylic acid.

**Introduction**

The inappropriate disposal of pollutants in waste water constituents an environmental problem and can affect the ecosystem to large extent. Many industries such as electroplating tannery, chemical manufacturing, mining, battery manufacturing industries release toxic heavy metals [1-2] .It is well known that some metals can have hazardous effects on many forms of life. Metals, which are significantly toxic to human beings and ecological environments, include chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), manganese (Mn), cadmium (Cd), nickel (Ni), zinc (Zn),coblat (Co) and iron (Fe), etc. Cobalt is naturally found in most rocks, soil, water, plants, and animals, typically in small amounts. A biochemically important cobalt compound is vitamin B12 or cyanocobalamin. Vitamin B12 is essential for good health in animals and humans. Cobalt released from power plants and other combustion processes is usually attached to very small particles. In most drinking water, cobalt levels are less than 1–2 ppb. Sources of cobalt in water are metal mining, smelting, and refining, in industries that make or use cutting or grinding tools, or in other industries that produce or use cobalt metal and cobalt compounds Serious effects on the lungs, including asthma, pneumonia, and wheezing have been found in people exposed to 0.005 mg cobalt/m$^3$.

Conventionalmethods for treatment of metal ions include chemical precipitation [3], electrochemical oxidation [4], reverse osmosis [5], ozone [6] andoxidative/reductive chemical processes [7]. However these methods can be expensive and most times do not work well for low concentration of metal ions. Therefore it becomes imperative to search some alternatives. Currently sorption process is proving to be one of the effective and attractive processes for the treatment of these metal-bearing wastewater [8-13].

**Materials And Methods:**

In the present work commercially available Granular Activated Carbons namely F-400 and F-200 supplied by Calgon Corporation, Pittsburgh, USA were used as adsorbents. These were first subjected to the size fractionation and sieved through siever (M/S Jayant Test Sievers, Mumbai) to get the particles of desired size range between 1400 micron to 1600 micron. The GAC was then washed with boiled distilled water to remove the surface adhered particles and then dried in an oven at a temperature of 100-110°C for one hour and stored in $CaCl_2$ desiccator for further use. All chemical used were of AR grade. A stock solution of cobalt ions was obtained by appropriate quantity of cobalt sulphate (E. Merck). Stock solution was further diluted with distilled water to desired concentration for obtaining the test solution. Beer's law calibration curve was established for $Co^{2+}$spectophotometrically [14]. A sample of 5-Sulphosalicylic acid was recrystallised by the routine method. The experimental melting point of 5-Sulphosalicylic acid (121°C )was compared with the literature value ( 120 °C)[15]. All experiments were carried out in batches of five units at a time. For determining the adsorption isotherm of cobalt ion on the carbon containing adsorbed ligand such as 5-Sulphosalicylic acid , 0.5 gm of the GAC were taken in clean shaking bottles of capacity 300 ml and 200 ml of 0.001M. 5-Sulphosalicylic acid solution was agitated for about five hours using Remi Stirrers (Type L-157 M/s RemiUdyog, Mumbai, India) in constant temperature bath at around 500 rpm. The solution was then filtered off and the carbon was washed thoroughly with distilled water. This carbon was then transferred to a clean shaking bottle and then 200 ml of cobalt solution pH of solutions was adjusted to 5 using $HNO_3$, NaOH and buffer solutions. The system was then stirred for five hours completely with same speed maintaining the temperature at 25 ± 0.5 °C. The initial and final concentration of the cobalt ion was then determined spectrophotometrically (Type 166 Systronics India Ltd.).

**Results And Discussion**

The evaluation of adsorptive capacity was studied using the two popular models, namely Freundlich and Langmuir. The adsorption isotherms for different grades of granular activated carbon are shown in Fig.1. The slope of the isotherms indicates the high affinity between sorbent surface and adsorbate molecules. The amount of cobalt on the ligand loaded GAC was determined using the equation

$$q_e = (C_o - C_e) \times \frac{V}{W} \qquad \text{--(1)}$$

where,

$q_e$ = Concentration of Cobalt ion on the acid loaded GAC in mg/millimoles of ligand

$C_o$= Initial concentration of Cobalt ion in solution in mg/L.

$C_e$= Final concentration of the Cobalt ion in solution in mg/L.

V = Volume of solution in liters

W= Millimoles of the acid actually present on GAC.

The correlation of the experimental adsorption data with Langmuir and Freundlich model was behavior and the heterogeneity of the adsorbent surface.

**Langmuir Model:**

This model describes the maximum adsorption capacity consists of a monolayer adsorption and adsorption energy is distributed homogeneously over the adsorbent surface and that there is no interaction between adsorbed molecules. The mathematical expression for the Langmuir model in terms of Cobalt ion concentration in solution Ce(mg/L) in equilibrium with that on ligand loaded GAC $q_e$ (mg/millimoles ) is given by

$$q_e = \frac{Q^o b C e}{1 + b C_e} \qquad \text{--(2)}$$

The linear form of Langmuir isotherm can be represented by following equation.

$$\frac{1}{q_e} = \frac{1}{Q^o\ b} \times \frac{1}{Ce} + \frac{1}{Q^o} \qquad \text{..(3)}$$

Where Q° and b are Langmuir constants.

Q° - Maximum monolayer coverage capacity (mg/g)

b - Langmuir isotherm constant (L/mg).

The values of $q_{e\ max}$ and b were computed from the slope and intercept of the Langmuir plot of 1/Ce versus 1/qe [16]

**Freundlich Model:**

The Freundlichmodel assumes a heterogeneous surface with non-uniform distribution of adsorption over the surface of adsorbent. Freundlich equation can be represented by

$$q_e = K_f . C_e^{1/n} \text{--(4)}$$

The equation may be linearised as

$$Log\, q_e = Log\ K_f + \frac{1}{n} Log\ C_e \qquad \text{--(5)}$$

Where $k_f$ and 1/n are Freundlich constants.

The constant $K_f$ is an approximate indication of adsorption capacity, while 1/n is a function of the strength of adsorption in the adsorption process.Fig.2 to 4 illustrate the plot of Langmuir and Frendlich isotherms for GAC F-200. The plots of $1/q_e$ versus $1/C_e$ were found to be linear indicating the applicability of Langmuir model. The parameters Q° and b are Langmuir constants relating to the sorption capacity and adsorption energy respectively.

**Temkin Model**

This model assumes on assumption that the heat of adsorption of all the molecules in layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the bonding energies, up to some maximum binding energy [35]. The Temkin isotherm is represented as,

$$q_e = \frac{RT}{b} \times \ln(K_T C_e) \qquad \text{.....(6)}$$

Equation (6) can be literalized as:

$$q_e = B_T \ln K_T + B_T \ln C_e \qquad \text{.....(7)}$$

Where,

$$B_T = \frac{RT}{b}$$

T = Absolute temperature (K),

R = Universal gas constant (8.314J/mol.K),

$K_T$= The equilibrium binding constant (L/mg),

b = Variation of adsorption energy (kJ/mol).

$B_T$= Temkin constant related to the heat of adsorption (kJ/mol).

The Temkin adsorption isotherm model was chosen to evaluate the adsorption potentials of the adsorbent for adsorbates. The Temkin isotherm plot for the cobalt ion are presented in figure 4. The Temkin constant, b related to heat of sorption for $Co^{2+}$ ions was calculated and reported in Table 2. The low values of Temkin constant indicate a weak interaction between sorbate and sorbent, supporting the adsorption mechanism for the present study [36].

The values for the Temkin constants, binding energies (b) and regression coefficients are given Table 2.

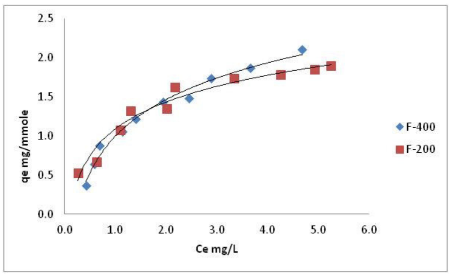


Figure :1. Adsorption Isotherm
System : GAC_5-Sulphosalicylic acid_$Co^{2+}$ at 298 K

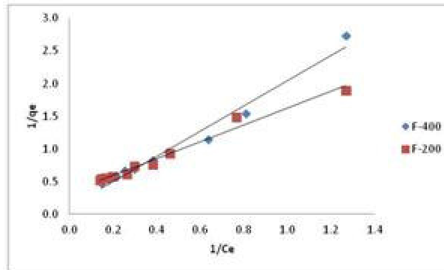


Figure :2. Langmuir Adsorption Isotherm
System : GAC_5-Sulphosalicylic acid_$Co^{2+}$ at 298 K

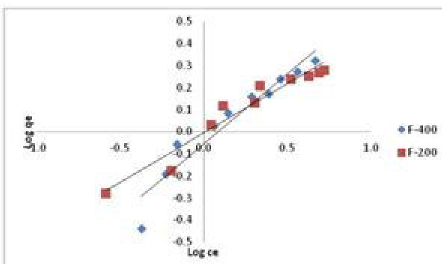


Figure :3. Freundlich Adsorption Isotherm
System : GAC_5-Sulphosalicylic acid_$Co^{2+}$ at 298 K

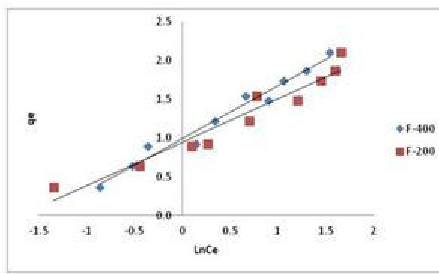


Figure :4.Temkin Adsorption Isotherm
System : GAC_5-Sulphosalicylic acid_$Co^{2+}$ at 298 K

**Table 1:** Values of Langmuir and Freundlich constants $q_e$ max (mg/m.mole) and $R^2$ for adsorption of Cobalt ion containing adsorbed acids.

| Sr. No. | Adsorption System | qemax | Langmuir Constant | | | Freundlich Constant | | |
|---|---|---|---|---|---|---|---|---|
| | | | $Q^o$ | b | $R^2$ | $K_f$ | n | $R^2$ |
| 1 | F-400_5-Sulphosalicylic acid_$Co^{2+}$ | 2.1045 | 2.5484 | 0.2861 | 0.9902 | 0.8784 | 1.5723 | 0.9199 |
| 2 | F-200_5-Sulphosalicylic acid_$Co^{2+}$ | 1.9017 | 2.1997 | 0.2479 | 0.9494 | 0.4448 | 1.0147 | 0.9411 |

The comparative adsorption capacities $q_e$ max of cobalt ion on different grades of GAC used in the present work can be assessed from Fig. 1. The Langmuir model exhibit a better fit to the adsorption data than the Freundlich model. All n values were greater than unity, indicate that Cobalt adsorption was favorably adsorbed by the GAC.

**Table 2 :** Equilibrium Isotherm Parameters for Temkin model

| Sr. No. | Adsorption System | $K_T$ | $B_T$ | b | $R^2$ |
|---|---|---|---|---|---|
| 1 | F-400_5-Sulphosalicylic acid_$Co^{2+}$ | 5.7742 | 0.6837 | 3625.5947 | 0.9723 |
| 2 | F-200_5-Sulphosalicylic acid_$Co^{2+}$ | 5.3725 | 0.5421 | 4409.9254 | 0.9362 |

**Conclusions :**

The experimental data were very well correlated with Langmuir, Freundlich and

Temkin Adsorption Isotherm and isotherm parameters were reported. In this investigation adsorption was carried out at 25$\pm$0.5$^0$ C and pH 5. Isotherm parameters were determined and three adsorption isotherm models were studied. The removal of Cobalt ions from aqueous solution using F-400 and F-200 was found to be economical and effective process. In present study F-400 modified with 5-Sulphosalicylic acid as a potential and active adsorbent for removal of cobalt ions from aqueous solution as compared to F-200. The adsorption data fitted into Langmuir and Freundlich isotherms out of which Langmuir adsorption model was found to have the highest regression value and hence the best fit.

**Acknowledgement**

The authors are thankful to The Director, Laxminarayan Institute of Technology, Nagpur and The Principal, Science College, Congress Nagar, Nagpur for providing necessary laboratory facilities to carry out the work.

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