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Adsorption of Cobalt on Granular Activated Carbon by Complexation with Surface Functional Group

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ABSTRACT

The present study is carried out for the removal of cobalt from aqueous solution using different commercial grades of Granular Activated Carbon namely F-816, and F-200 with 3, 5-Dinitrobenzoic acid at temperature $25 \pm 1^\circ\text{C}$. The adsorption isotherm of cobalt on Granular Activated Carbon has been determined and the data fitted reasonably well to the Langmuir and Freundlich isotherm for activated carbon.

Key words: Adsorption, Cobalt, Granular Activated Carbon (GAC), 3, 5-Dinitrobenzoic acid.

INTRODUCTION

The excessive release of heavy metals into the environment is a major concern worldwide. Heavy metal contamination exists in aqueous wastes of many industries, such as plating, mining operations, tanneries, smelting alloy industries and storage batteries industries etc. [1] and these metal ions do not degrade into harmless end products [2].

Cobalt is beneficial for humans because it is a part of vitamin B₁₂, which is essential for human health. However, too high concentrations of cobalt may damage human health. When we breathe in too high concentrations of cobalt through air we experience lung effects, such as asthma and pneumonia. When plants grow on contaminated soils they will accumulate very small particles of cobalt, especially in the parts of the plant we eat, such as fruits and seeds. Soil near mining may contain very high amounts of cobalt, so that the uptake by humans through eating plants can cause health effects [3].

Granular Activated Carbon is widely used for the removal and recovery of toxic metals because of its low cost and high affinity towards the metal ions. Activated carbon is the collective name for a group of porous carbons manufactured by the treatment of a char with oxidizing gases or by carbonization of carbonaceous materials impregnated with dehydrating chemicals. All these carbons exhibit a high degree of porosity and an extended internal surface area. The use of porous carbon in the form of carbonized wood (charcoal) has been described as early as 1550BC in an ancient Egyptian papyrus [4].

A number of adsorbents have been used by several workers for adsorbing toxic metals from their aqueous solutions. [5-17]. It is therefore proposed to carry out adsorption of cobalt metal form aqueous solution using Granular

Activated Carbon in the presence of 3, 5-Dinitrobenzoic acid. The work was also extended to study the kinetics of Cobalt.

MATERIALS AND METHODS

Apparatus

Systronics Digital Spectrophotometer, Type 166 was used for all absorbance measurements. A pH meter (ELICO Pvt. Ltd. Hyderabad, India. Model NO LI-120) was used in the laboratory for maintaining the pH of the solutions. It was standardized every time using a phthalate buffer of pH 4.01 at 25^oC. Five mechanical stirrers were employed for stirring the solutions for about 5 hours at around 500 rpm. All glasswares obtained were from M/s Borosil, Bombay and used in all experimental processes.

Reagents and Chemicals

All the reagents and chemicals used for the entire work were of A. R. Grade

GENERAL PROCEDURE

Standardization and Characterization of grades of carbon.

In the present work two grades of carbon namely F-200D and F-816D gifted by M/s Calgon Corporation Ltd. Pittsburgh USA. were selected for comparative studies. The selected grades of carbon were first sieved in appropriate size corresponding to mesh size (16x25). After size fractionation the selected carbon was washed with boiled distilled water until a clear leachate was obtained. Then water was decanted and GAC was transferred to a petri dish. Carbon was then air dried properly to remove all the moisture on the surface of carbon and from pores of carbon. Then it was kept in an oven at temperature range 100-110^oC for two hours and cooled in desiccator containing moisture absorbent CaCl₂. To ensure that the carbon sample was in equilibrium with the surroundings, 0.5 gm of the carbon sample was kept in a weighing bottle in the same desiccator and its weight was monitored over a period of one week until it shows dry and constant weight.

Preparation of the solution of Cobalt ion and its estimation.

A Standard solution of Cobalt Sulphate (Loba make) was prepared by dissolving 1.4055 gm in distilled water with a drop of sulphuric acid to prevent hydrolysis and the solution was diluted to 500 ml. It was then standardized with EDTA. A standard aliquot of the cobalt solution was taken for the estimation. To 10 ml of the solution, 2-3 drops of Xylenol Orange indicator followed by very dilute sulphuric acid was added. The colour changed from red to yellow. Then powdered Hexamine was added with continuous shaking until the deep red colour was restored (pH=6). The solution was then warmed to 40^oC and 0.5 ml of 0.001 M phenanthroline was added. Such an addition improved the end point. The solution was titrated with standard EDTA solution until the colour changed from red to yellow orange at the end point.

Spectrophotometrically, Beer's law calibration curve was established for Co²⁺ [18].

Experimental set up for the study of adsorption isotherm on GAC.

To get appropriate results of adsorption isotherm proper arrangement of experimental set up was essential. All the adsorption isotherms were carried out at a fixed temperature of 25^oC ± 1^oC. For this a water bath was used to maintain constant temperature of solution. Mechanical shaker (Eltek Motor, Type M 56. Elektrocrats India, Pvt. Ltd. Mumbai) was used as a stirrer. An acrylic rod with paddle was attached to the stirrer to agitate the experimental solution. 10 cm long acrylic rods having 2 cm × 1cm thick paddle was used for stirring the solution. Reagent bottles of 300 ml capacity were used as the flask. All reagent bottles were kept in the water bath to maintain constant temperature.

To get an adsorption isotherm 0.5g of GAC was weighed carefully and transferred to each of five reagent bottles. 200 ml of 0.001M, 3, 5-Dinitrobenzoic acid solution was transferred to each reagent bottle. All the five reagent bottles and stirrer were adjusted in the water bath to maintain 25^oC ± 1^oC temperature. This was done for the loading of 3, 5-Dinitrobenzoic acid on GAC for six hours.

Residual 3, 5-Dinitrobenzoic acid solution was then drained off from the reagent bottle and the carbon washed several time with distilled water. Any water drops in the bottle were completely eliminated by inverting the bottle draining the water and keeping carbons at the side inside the bottle. Without drying the carbon particle it was used

for further adsorption process. 200 ml of cobalt solution of pH 5 was introduced carefully. The system was then stirred for five hours at around 500 rpm at constant temperature of $25^{\circ}\text{C} \pm 1^{\circ}\text{C}$. After the equilibrium was achieved the concentration of the solution was estimated. Ten such systems of different concentration were arranged. The equilibrium concentration of cobalt was estimated using the standard calibration curve.

Experimental procedure for studying the kinetics of adsorption of the cobalt ions on ligand loaded GAC.

To study the kinetics of cobalt ion on GAC loaded by 3,5-Dinitrobenzoic acid, 1 gm of GAC was shaken with 400 ml of 0.001 M ligand solution for about four hours. The weight of GAC and concentration of Co^{2+} was fixed throughout the kinetic study. The solution was filtered off and solution was removed by decanting and inverting the flask, keeping carbon particles at side. This loaded carbon was then shaken with 400 ml of cobalt ion solution at pH 5 at around 500 rpm. The time of addition of carbon was noted as $t = 0$. Thereafter aliquots of 5 ml samples of experimental solution were withdrawn from the flask by momentarily interrupting the stirrer. The first four readings were taken at 15 minute time intervals, the next two readings were taken at 30 minute intervals and the final two readings were taken at a time interval of one hour. The concentrations of cobalt ion C_0 and C_t in mg/L in the sample were estimated using standard calibration curve.

RESULTS AND DISCUSSION

Adsorption Isotherm of Cobalt.

A set of ten consistent points of equilibrium concentration of cobalt which was obtained as per the procedure outlined earlier permitted calculation of equilibrium concentration of cobalt on loaded GAC using the following expression.

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

Where,

q_e = Concentration of cobalt on the ligand loaded GAC in mg/millimoles of ligand;

C_o = Initial concentration of cobalt in solution in mg /L,

C_e = Final concentration of cobalt in solution in mg/L;

V = Volume of solution in liters;

W = Millimoles of the ligand actually present on GAC.

A plot of q_e versus C_e represented an adsorption isotherm with different grades of loaded Granular Activated Carbon, namely, F-816D and F-200D is given in Figs. 1& 2. The comparative adsorption capacities (saturation values of q_e) of cobalt on different grades of loaded GAC used in the present work can be assumed from Figs. 1&2. The trend in the q_e values at the saturation level are in the order.

F-816D > F-200D.

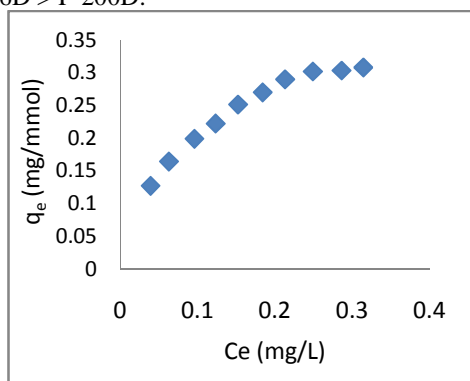


Fig. No. 1- Adsorption Isotherm
System: F 816 D - 3,5-Dinitrobenzoic acid Co^{2+}

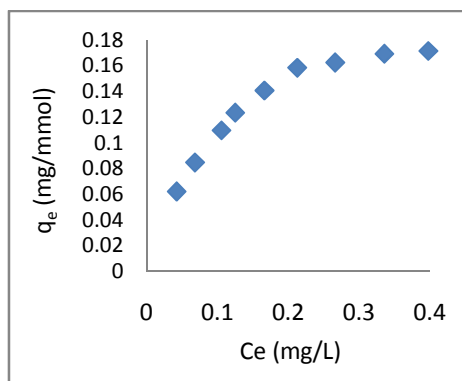


Fig. No. 2- Adsorption Isotherm
System: F 200 D - 3,5-Dinitrobenzoic acid Co^{2+}

On plotting $\log q_e$ versus $\log C_e$ linear plots were obtained. The plot of $1/q_e$ versus $1/C_e$ was also linear. It can be concluded from these plots that the Freundlich equation as well as Langmuir equations are applicable in almost the entire range of concentrations used in this work. A few representative plots justifying the adherence to the Langmuir and Freundlich equations are given in Figs. 3&4.

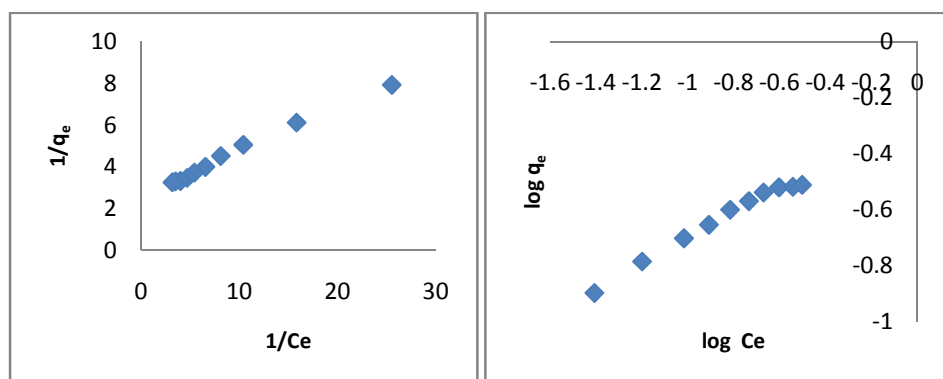


Fig. No. 3 Langmuir Adsorption Isotherm

System: F 816 D-3,5Dinitrobenzoic acid - Co^{2+}

Fig. No. 4 Freundlich Adsorption Isotherm

System: F 816 D-3,5Dinitrobenzoic acid - Co^{2+}

The Langmuir equation is useful in determining the surface area of the adsorbent under the present experimental conditions. Estimations of the specific surface areas of loaded GAC are based upon measurement of the capacity of the adsorbent for a selected solute having a well accepted molecular cross sectional area. This is done by using Q^0 obtained from Langmuir plot and related to surface area of the adsorbent by relation,

$$S = N_a Q^0 A$$

Where,

S = Surface area of the adsorbent, m^2/gm

N_a = Avogadro number

A = Cross sectional area of the adsorbate molecule, m^2

The values of Q^0 , A and S are given in the following Table.

Surface area of grades of GAC

| Sr. No. | Grades of GAC | Q^0 | A | S |
|---------|---------------|--------|--------------------------|-------------------------|
| 1 | F-816 | 0.3867 | 5.4225×10^{-16} | 85.725×10^{-3} |
| 2 | F-200 | 0.2295 | 5.4225×10^{-16} | 50.868×10^{-3} |

The above Table clearly shows the fact that Cobalt is inaccessible to the inner pores of the GAC and it adsorbed superficially. However the values being close enough when one proceeds from F-816 to F-200 is suggestive of the same amount of surface groups available to Cobalt.

The Rate of Exchange of Cobalt with GAC

From the initial concentration of Cobalt C_0 and the concentration of Cobalt at different time intervals C_t values of q were estimated by the procedure given in the experimental. The plots of approach to equilibrium, i.e. of both q versus t and q^* versus t, are given in Figs, 5 & 6.

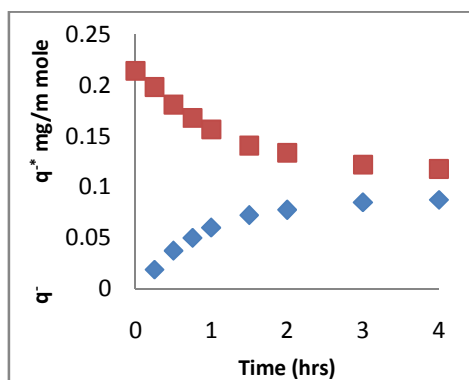


Fig. No. 5- Approach to Equilibrium plots of q and q^* versus time

System: F 816 D-3,5Dinitrobenzoic acid - Co^{2+}

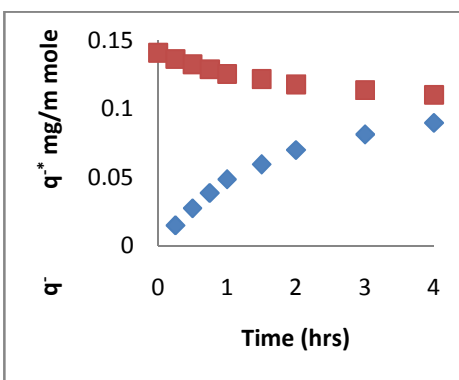


Fig. No. 6- Approach to Equilibrium plots of q and q^* versus time

System: F 200 D-3,5Dinitrobenzoic acid - Co^{2+}

In adsorption it is essential to study the rate controlling factors in diffusional process. Diffusion arises from a concentration gradient either in the fluid phase or on the solid phase. When diffusion involves separation of solute from the fluid phase to the sorbent phase it is called particle phase diffusion or homogeneous diffusion described by an effective diffusion coefficient D . The driving force for pore diffusion, which usually occurs within the pores of the adsorbent, is due to the concentration gradient of the adsorbate in the pore space, and characterized by pore diffusion coefficient D_p . Alternatively surface diffusion which occurs after adsorption due to migration of the adsorbed molecules along the pore walls may be represented in terms of the gradient of the amount of the adsorbate on the pore walls. This is characterized by the surface diffusion coefficient D_s .

It is oftenly observed that one of the two types of the above mentioned diffusional processes could be treated under certain specified conditions, which are specific to the cases. Several investigators have estimated pore diffusivities in the agitated tank, [19] while some have proposed a method where surface diffusion [20] is rate controlling. This method has been subsequently modified subject to certain limitations and reasonable conclusions have been drawn from it [21].

Glueckauf and Coates [22] first suggested the linear driving force (LDF) method in which the rate of adsorption by a spherical particle is considered to be the product of surface area, an effective mass transfer coefficient and a driving force consisting of difference between the bulk average concentration in the spherical particle q and the surface concentration q^* . Glueckauf made certain approximation and suggested the most common form of linear driving force (LDF) equation which is as follows

$$\frac{dq^-}{dt} = \frac{15D}{a^2} (q^{-*} - q^-) \quad \dots (1)$$

Where,

D = Diffusion coefficient in solid phase

a = Radius of the spherical particle

A representative of the LDF plot is given in Fig. 11

The LDF method is inadequate to distinguish between surface and pore diffusion. It leads to an estimation of gross diffusion coefficient. Further it is useful method to know the adsorption process and helps considerably in designing adsorption columns. It might be worthwhile assessing the equation for initial time periods dt , when $t = 0$. In such situation the equation (1) suggests that dq^-/dt approaches the large infinite value while the right hand side stands numerically finite [23].

Vermuelen [24] proposed the following Quadratic Driving Force (QDF) expression to overcome the above mentioned anomaly.

$$\frac{dq^-}{dt} = \pi^2 \cdot \frac{D}{a^2} \cdot \frac{(q^{*-2} - q^{-2})}{2q^-} \quad \dots (2)$$

This expression was compared by Glueckauf who concluded that while for most cases this LDF approximation was adequate. The above relation approximated the solution of solid diffusion model. In both cases it was necessary to simplify assumptions before comparisons could be made. A representative of the LDF and QDF plots are given in Fig. 7&8. In the present work, the QDF equation has been used to obtain the values of D, the diffusion coefficient, and is given below.

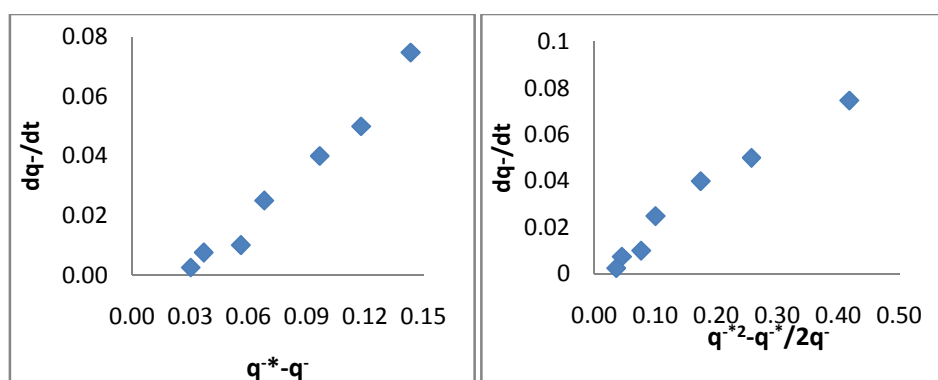


Fig. No. 11- Linear driving force plot.

System: F 816 D-3,5Dinitrobenzoic acid - Co²⁺

Fig. No. 11- Quadratic driving force plot.

System: F 816 D-3,5Dinitrobenzoic acid - Co²⁺

| System | D Values (cm ² /sec) |
|---|---------------------------------|
| F 816 D-3,5Dinitrobenzoic acid - Co ²⁺ | 1.07256 x 10 ⁻⁴ |
| F 200 D-3,5Dinitrobenzoic acid - Co ²⁺ | 1.15243 x 10 ⁻⁴ |

From this Table, it is seen that all the D values are in the range of that encountered for surface diffusion phenomena.

CONCLUSION

The present study demonstrated that Granular Activated Carbon can be used efficiently in the removal of Cobalt from aqueous solution. In the present study the uptake of Cobalt on to F-816 was found to be good. The adsorption isotherms obtained from the present work may be helpful in designing industrial adsorption columns. Kinetic study revealed that the process of adsorption is surface diffusion controlled.

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