Study of Cobalt Adsorption from Aqueous Solution on Granular Activated Carbon

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Studies on removal of cobalt from aqueous solution by adsorption on granular activated carbon (GAC) containing adsorbed 3,5-dinitrosalicylic acid (DNSA) have been carried out at temperature 25 ± 0.5°C. The adsorption isotherm of Co on GAC have been determined and the data fitted reasonably well to the Langmuir and Freundlich isotherm for activated carbon.

Key Words: Adsorption, Cobalt, Granular activated carbon.

INTRODUCTION

Industrial activities have been releasing a large proportion of metals into the environment. As a result of this men and animals are constantly exposed to heavy metals at an alarming rate. Cobalt is one of several commonly occurring toxic metals. It is an animal carcinogen producing cancer in various sites. It is believed to be a human carcinogen as well, but since the most common ores of cobalt are the arsenides, it is very difficult to separate or isolate cobalt's carcinogenicity from the other substances with which it is frequently found, *e.g.*, nickel, copper, etc. Exposure to cobalt is extremely irritating to the skin both on contact and by provoking an allergic reaction which sensitises the skin to further contact. Cobalt is also irritating to the eyes and mucous membrane, causing severe discomfort in the nose, often leading to perforation of the nasal septum. The dust causes irritation of the lungs, pneumoconiosis, fibrosis and granulomas. Ingestion of excessive amounts of cobalt causes intercellular hypoxia and polycythemia. The threshold limit value for cobalt fume and dust exposures is 0.1 mg/m^3 in the U.S. Cobalt as a metal is becoming increasingly important and getting scarce owing to large number of industries which utilize the metal in the manufacture of various alloys, permanent magnets and steels; as a catalyst in agriculture, pigments and enamels etc. Cobalt salts are used in the treatment of anemia and cyanide poisoning[1, 2]. Treatable amounts of cobalt wastes are growing fast and there is a growing need in the industrial sector to try and find ways to recover this precious metal conveniently. Several workers carried out cobalt adsorption from aqueous

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solution using granular activated carbon[3–7]. In this connection work was initiated to scavenge this metal using GAC containing adsorbed ligands which are capable of forming a chelate with the metal cobalt and thus help in its recovery. For this purpose 3,5-dinitrosalicylic acid (DNSA) has been chosen.

EXPERIMENTAL

Different grades of granular activated carbon Filtrasorb 400 and 200 (M/s Calgon Corporation, Pittusberg, USA) were first subjected to size fractionation by sieving them using a sieve shaker to obtain particles of mesh size 16×25 (M/s Jayant Test Sieves, Mumbai). The sieved granular activated carbon (GAC) was washed with boiled distilled water and then dried in an oven at a temperature of 100–110°C and stored in $CaCl_2$ desiccator until use. A stock solution of cobalt ions was obtained by using a solution of cobalt sulphate (Loba make). Spectrophometrically, Beer's law calibration curve was established[8] for Co^{2+}. For this purpose standardized 0.01 M cobalt solution was first prepared. 10 mL of this solution was diluted to 1000 mL in a volumetric flask. All the chemicals used were of AR grade. A sample of 3,5-dinitrosalicylic acid (E. Merck) was recrystallized by the standard method. The experimental melting point of 3,5-dinitrosalicylic acid (m.p. 168°C) was checked against the literature[9] value (m.p. 169°C). The sample was also characterized through determination of the molecular weight by the technique of pH titration against standard alkali. For determining the adsorption isotherm of cobalt ion on the different grades of carbon containing adsorbed ligand such as 3,5- dinitrosalicylic acid, it was first essential to fix the amount of the ligand on GAC. This process of fixing of ligand on GAC was denoted as "loading of GAC". For this purpose 0.5 g of GAC was taken in clean shaking bottles and 200 mL of the ligand solution of a specified concentration was shaken for about 12 h on a mechanical shaker (Remi, Model No. RS 24, Remi Instrument Ltd., Mumbai). The solution was then filtered off and the carbon was washed thoroughly with distilled water. This carbon was then transferred to a one litre round bottom flask and then 200 mL of cobalt solution at pH = 5 was added to it. The contents were stirred for 6 h at 25 ± 0.5°C. The initial and final concentrations of the cobalt ion in mg/L were then determined spectrophotometrically. The experiments were repeated to ensure reproducible results.

The amount of cobalt on the ligand adsorbed on the GAC was determined from the equation

$$q_e = (C_0 - C_e)\, V/W \qquad (1)$$

where q_e = concentration of cobalt on the ligand loaded GAC in mg/millimoles of ligand

C_0 = initial concentration of cobalt in solution in mg/L

C_e = final concentration of cobalt in solution in mg/L

C_0 = volume of solution in litres

W = millimoles of the ligand actually present on GAC (0.5 mg)

RESULTS AND DISCUSSION

The adsorption isotherms of ligand loaded F-400 and F-200 GAC obtained by plotting q_e versus C_e are shown in Figs. 1 and 2. It is seen that as C_e increases, q_e also increases, but at the saturation level q_e tends to be constant with increasing value of C_e which indicates formation of a monolayer of adsorbate on the surface of adsorbent. All isotherms are seen to be of the favourable type and were then subjected for adherance to both Langmuir and Freundlich adsorption isotherms.

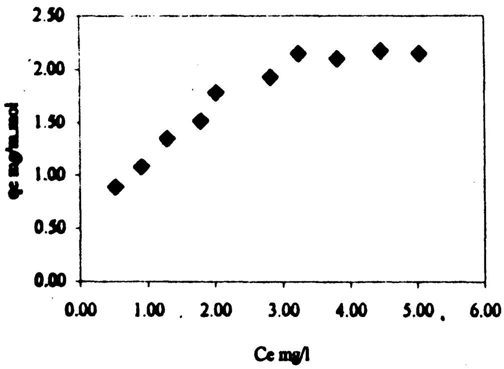

Fig. 1. Adsorption isotherm (system GAC-F-200-3,5-dinitrosalicylic acid-Co^{2+})

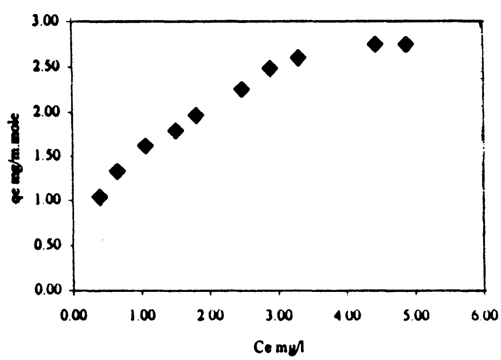

Fig. 2. Adsorption isotherm (system GAC-F-400-3,5-dinitrosalicylic acid-Co^{2+})

Using values of q_e and C_e, the Langmuir equation could be expressed as follows:

$$q_e = \frac{Q^\circ b C_e}{1 + bC_e} \tag{2}$$

where Q° = amount adsorbed per unit weight of the adsorbent forming a complex monolayer on the adosrbent surface

b = Langmuir constant.

Rearranging expression (2),

$$\frac{1}{q_e} = \frac{1}{Q^\circ b C_e} + \frac{1}{Q^\circ} \tag{3}$$

A plot of $1/q_e$ *vs.* $1/C_e$ was found to be fairly linear. Similarly, the Freundlich equation used was

$$q_e = \acute{K} \cdot C_e^{\beta} \tag{4}$$

where K and β are constants determined experimentally using equation (4).

$$\log q_e = \log K + \beta \log C_e \tag{5}$$

A plot of $\log q_e$ *vs.* $\log C_e$ was fairly showing validity of Freundlich equation also over a range of concentrations.

The saturation monolayer q_e values were used for determination of surface area of the adsorbent. For this purpose a plot of $1/q_e$ *vs.* $1/C_e$ helped in the determination of $1/Q°$ and hence $Q°$. The surface area of the carbon through such cobalt adsorptiion can then be represented as:

$$S = Na \cdot Q° \cdot A$$

where S = surface area of adsorbent, m^2/g,

Na = Avogadro number

and A = cross-sectional area of the adsorbate molecule m^2

Table-1 shows that it is possible to determine the surface area of the adsorbent using the technique of adsorbing cobalt on ligand loaded GAC at the saturation level when a monolayer of the cobalt would cover the entire surface of the adsorbent. Determination of value of S needs the determination of A, the surface area occupied by a single cobalt ion. The values of A were calculated using the expression given by Brunauer and Emmet[10].

$$A = 4 \times 0.866 \left[\frac{M}{4\sqrt{2}} Na \cdot d \right]^{2/3}$$

where M = atomic weight of cobalt, Na = Avogadro number and d = density of cobalt.

Using $M = 58.93$, $Na = 6.023 \times 10^{23}$ and $d = 8.83$ as given in ref. 11, the values of A and S were calculated and are reported in Table-1.

TABLE-1
VALUES OF Q°, A, S FOR A SYSTEM GAC-3,5-DINITROSALICYLIC ACID-Co^{2+}

Sr.No.	Grades of GAC	Q°	A ($\times 10^{16}$ cm^2)	S ($\times 10^{-3}$ cm^2/g)	qe_{max} (mg/mmol)
1.	F-200	2.4390	5.4225	5.4067	2.1353
2.	F-400	2.8571	5.4225	6.3336	2.7484

The present work brings out clearly the fact that ligand-loaded GAC could function very effectively in scavenging cobalt ions from aqueous solution. The adsorption isotherms of the cobalt on different grades of carbon loaded with 3,5-dinitrosalicylic acid clearly shows that F-400 adsorbs cobalt to a greater extent as compared to F-200.

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