Removal of Cobalt from Aqueous Solution Using Granular Activated Carbon

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Studies on removal of cobalt from aqueous solution by adsorption on granular activated carbon in combination with 3,5-dinitrosalicylic acid have been carried out at temperature 25 ± 0.5°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.

INTRODUCTION

Cobalt is one of several commonly occurring toxic metals. It is an animal carcinogen producing cancer at various sites. Exposure to cobalt is extremely irritating to the skin both on contact and by provoking an allergic reaction which sensitizes 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 threshold limit value for cobalt fume and dust exposures is 0.1 mg/m^3 in the U.S.[1] Treatable amount of cobalt wastes are 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 solutions using granular activated carbon[2–7]. In this work, cobalt was scavenged using granular activated carbon (GAC) containing adsorbed ligands. For this purpose 3,5-dinitrosalicylic acid (DNSA) has been chosen.

EXPERIMENTAL

Different grades of granular carbon Filtrasorb 400 and 200 (M/s Calgon Corp., 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 GAC was washed with boiled distilled water and then dried in an oven at a temperature of 100–110°C and stored in a $CaCl_2$ desiccator until use. A stock solution of cobalt ions was obtained by using a solution of cobalt sulphate (Loba make). Spectrophotometrically, Beer's law calibration curve[8] was established 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 (168°C) was checked from the literature value (m.p. 169°C)[9]. The sample was also characterized through determination of molecular weight by the technique of pH titration against standard alkali. For

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determining the adsorption isotherm of cobalt ion on 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 the GAC. This process of fixing of ligand on GAC was denoted as "loading of GAC". For this purpose 0.5 g of the 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 1 L round-bottom flask and then 200 mL of cobalt solution at pH = 5 was added at a desired concentration and 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. While studying the scavenging of cobalt ions from aqueous solution it was also thought worth while to investigate in a few cases the scavenging process in the presence of co-metal ions such as Zn^{2+} also.

RESULTS AND DISCUSSION

Equilibrium adsorption isotherms for q_e *vs.* C_e was plotted for different grades of granular activated carbon and are shown in Figs. 1 and 2. The amount of cobalt on

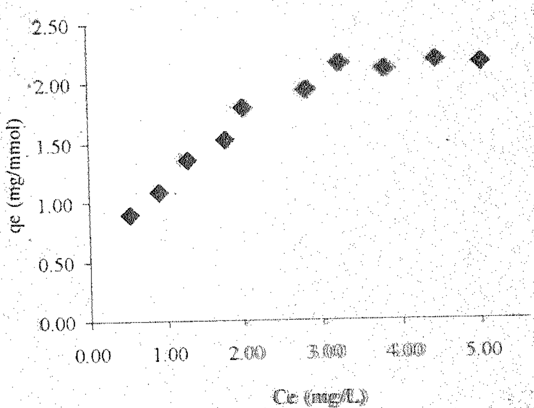

Fig. 1. Adsorption isotherm (system: GAC-F-200-3,5-dinitrosalicylic acid-Co^{2+})

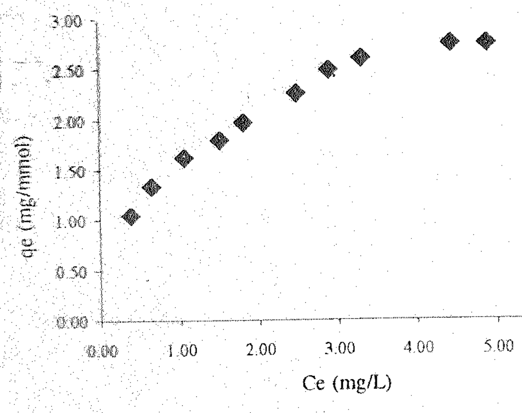

Fig. 2. Adsorption isotherm (system: GAC-F-400-3,5-dinitrosalicylic acid-Co^{2+})

the ligand adsorbed on the GAC was determined using the equation

$$q_e = (C_o - C_e) \times V/W$$

where

q_e = concentration of cobalt on the ligand loaded GAC in mg/millimol 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 litres,
W = millimoles of the ligand actually present on GAC (0.5 g).

It is observed from the results in Table-1 that cobalt adsorption follows the trend F-400 > F-200.

Data of equilibrium isotherms 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 then be represented by

$$q_e = Q^o bC_e/(1 + bC_e)$$

The linearised form of Langmuir isotherm is

$$1/qe = 1/Q^{o}b \times 1/Ce + 1/Q^{o}$$

where Q^{o} and b are Langmuir constants. Freundlich equation is on the other hand represented by

$$q_e = k_f \cdot C_e^{1/n}$$

The above equation may be linearised as

$$\log q_e = \log k_f + 1/n \log C_e$$

where k_f and 1/n are Freundlich constants.

Figs. 3 to 6 illustrate the plot of Langmuir and Frendlich isotherms for GAC F-200 and F-400. The plots of $1/q_e$ *vs.* $1/C_e$ were found to be linear indicating the applicability of Langmuir model. The parameters Q^{o} and b are Langmuir constants relating to the sorption capacity and adsorption energy respectively. The intercept and slope of the linear plots of log q_e *vs.* log C_e and of $1/q_e$ *vs.* $1/C_e$ under given set of experimental conditions provide values of k_f, 1/n, Q^{o} and b respectively. The corresponding Freundlich and Langmuir constants obtained are listed in Table-2. The values of k_f and Q^{o} for F-400-3,5-dinitrosalicylic acid-Co^{2+} system were

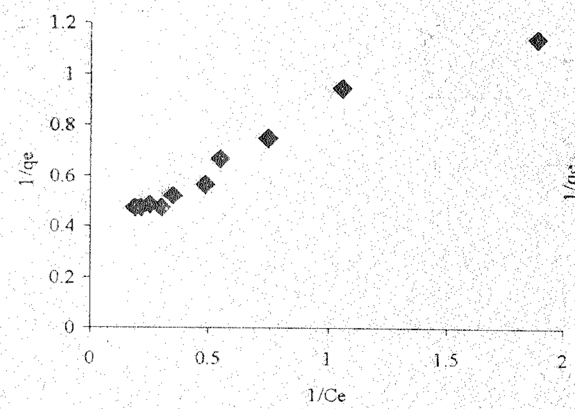

Fig. 3. Langmuir adsorption isotherm (system: GAC-F-200-3,5-dinitrosalicylic acid-Co^{2+})

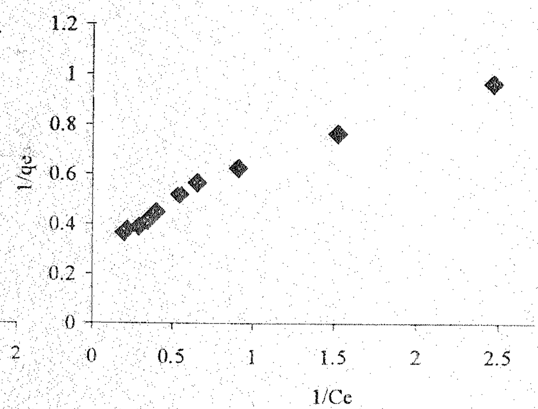

Fig. 4. Langmuir adsorption isotherm (system: GAC-F-400-3,5-dinitrosalicylic acid-Co^{2+})

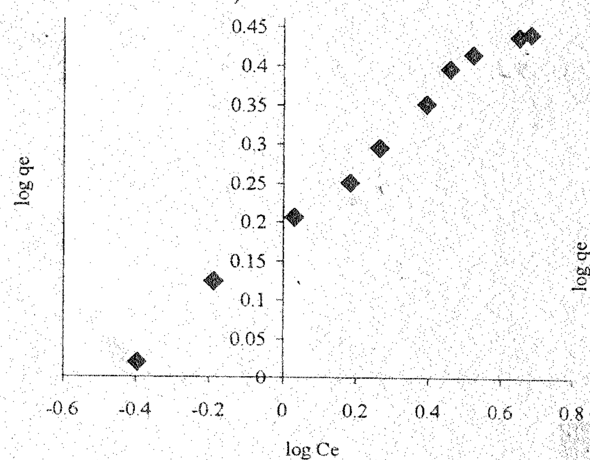

Fig. 5. Freundlich adsorption isotherm (system: GAC-F-400-3,5-dinitrosalicylic acid-Co^{2+})

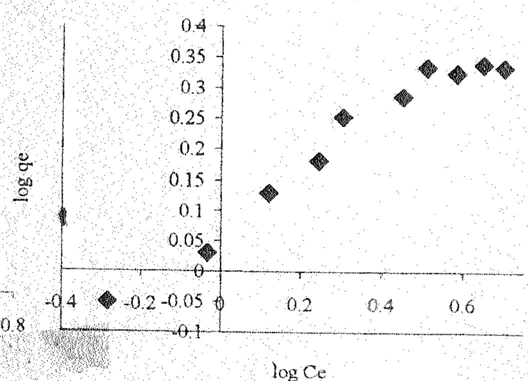

Fig. 6. Freundlich adsorption isotherm (system: GAC-F-200-3,5-dinitrosalicylic acid-Co^{2+})

greater than those for F-200-3,5-dinitrosalicylic acid Co^{2+} system, indicating the superiority of the former for this sorption process.

Effect of co-metal ions: In almost all cases the presence of co-metal ions results in the lowering of cobalt ion recovery due to hindrance caused by the presence of the co-metal ions while cobalt diffuses into the pores. The values of q_e in presence of Zn^{2+} follows the trend

F-400 (Co) > F-400 (Co + Zn) and F-200 (Co) > F-200 (Co + Zn)

TABLE-1

VALUES OF $q_{e\ max}$ (mg/mmol) FOR ADSORPTION OF COBALT ION FROM SOLUTION BY GAC CONTAINING ADSORBED LIGAND (3,5-DINITROSALICYLIC ACID)

S. No.	System	q_e max (mg/mmol)
1.	F-400-3,5-Dinitrosalicylic acid-Co^{2+}	2.7484
2.	F-400-3,5-Dinitrosalicylic acid-Co^{2+}-Zn^{2+}	1.9726
3.	F-200-3,5-Dinitrosalicylic acid-Co^{2+}	2.1353
4.	F-200-3,5-Dinitrosalicylic acid-Co^{2+}-Zn^{2+}	1.6933

TABLE-2

ISOTHERM CONSTANTS

S. No.	System	Langmuir Q^o	Constants b	Freundlich K_f	Constants 1/n
1.	F-400-3,5-Dinitrosalicylic acid-Co^{2+}	2.5610	1.5001	1.5850	0.4210
2.	F-200-3,5-Dinitrosalicylic acid-Co^{2+}	2.5316	0.6583	1.1220	0.6000

Conclusions

The present work brings out clearly the fact that ligand loaded GAC could function very effectively in scavenging metal ions from aqueous solution. The adsorption isotherms of the cobalt on different grades of carbon loaded with DNSA clearly shows that F-400 adsorbs cobalt to a greater extent as compared to F-200. Adsorption was found to be in good aggrement with Langmuir isotherm which indicates mono layer adsorption. The addition of Zn^{2+} co-metal ion caused a decrease in the sorption of cobalt by both ligand loaded F-400 and F-200. Application of the Freundich and Langumuir isotherm models gave good representations of the experimental data for cobalt sorption by GAC.

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