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Removal of Co^{2+} ions from aqueous solution by adsorption onto modified granular activated carbon

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ABSTRACT

The adsorption of Cobalt ion on Granular Activated Carbon in combination with of 2-hydroxy-5-methoxy benzoic acid at temperature 25 ± 1 ^{0}C was studied. The adsorption isotherm of Cobalt on Granular Activated Carbon has been determined and the data fitted reasonably well to the Langmuir and Freundlich isotherm model indicating favourable and monolayer adsorption. The present work brings clearly the fact that ligand loaded GAC could function very effectively in the removal of the Cobalt ions from aqueous solution.

Key words: Cobalt, Granular Activated Carbon (GAC), 2-hydroxy-5-methoxy benzoic acid, Filtrasorb 100 (F-100), Filtrasorb 820 (F-820)

INTRODUCTION

With the scientific and industrial revolution in recent past, there has been immense impact of man on his environment. Environmental pollution is a serious problem of the environment in which human activities have played a prominent role. Various metals and metallic compounds released from anthropogenic activities add up to their natural background levels in water. Some of the trace metals play essential roles in biological processes, but at higher concentrations, they may be toxic to biota [1]. The wastewaters commonly include Cd, Pb, Cu, Ni, Mn and Co etc as pollutants. The industrial effluent containing heavy metals are not biodegradable and their presence in streams and lakes leads to bioaccumulation in living organisms, causing health problems in animals, plants and human beings. Cobalt is irritating to the eyes and mucus membrane, causing severe discomfort in the nose, often leading to formation of the nasal spectrum. The dust causes irritation of the lung, pneumoconiosis and fibrosis [2]. Adsorption has been recognized as an effective method by many researchers for the removal of heavy metal from water [3-7]. The study of adsorption isotherms in water treatment is significant as it provides valuable insights into the application of design. An isotherm describes the relationship between the quantity adsorbed and that remaining in the solution at a fixed temperature at equilibrium [8-9]. In present work, Cobalt was scavenged using F-100 and F-820 in combination with organic ligand. In present investigation 2-hydroxy-5-methoxy benzoic acid has been chosen as a organic ligand for modification of surface of porous carbons. The varying porosity and surface area of GAC reflects on the uptake of ligand and thereby the adsorption of the adsorbate.

MATERIALS AND METHODS

The bituminous coal based granular activated carbon F-100 and F-820 gifted by M/s Calgon Carbon Corporation Ltd Pittusberg, USA was used as adsorbents. These GACs were first subjected to size fractionation. Both carbons were sieved using a sieve shaker wherein the size corresponding to mesh size 16 x 25 (M/s Jayant Test Sieves, Mumbai) were collected for use. The sieved GAC was first stirred in boiling distilled water carefully without leading to any attrition several times until a clear leachate was obtained and then dried in an oven at a temperature of

110^{O}C for 15 hours and later cooled in a desiccators containing anhydrous $CaCl_2$ to ensure complete removal of moisture from the carbon. A stock solution of Cobalt ions was obtained by using a solution of Cobalt sulphate (E. Merck). Beer's law calibration curve was established for Co^{2+} using Nitroso-R-Salt method, spectrophotometrically to calculate concentration of experimental solutions [10].

Analytical grade reagents were used in all experimental work. A sample of 2-hydroxy-5-methoxy benzoic acid (Sigma-Aldrich) was purified and recrystallized by standard method. The experimental melting point of 2-hydroxy-5-methoxy benzoic acid (140.5 ^{o}C) was checked from the literature value (141^{o}C) [11]. The sample was also characterized through determination of molecular weight by the technique of pH titration against standard alkali. To evaluate the adsorption equilibrium data experiments were carried out in batch system. For determining the adsorption isotherm of Cobalt ion on different grades of carbon containing adsorbed ligand such as 2-hydroxy-5-methoxy benzoic acid, it was first essential to fix the amount of 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 five hours using Teflon bladed stirrer at about 500 rpm. The solution was then drained off and the carbon particles were washed thoroughly with distilled water. This loaded carbon was then transferred to same shaking bottle and then 200 ml of Cobalt solution at a pH = 5 were added to it. The contents were stirred for 5 hours at a constant temperature of 25 ± 1^{0}C. The initial and final concentrations of the Cobalt ion in mg/L was then determined spectrophotometrically (Chemito spectrascan UV 2700 Double beam UV Visible spectrophotometer). The experiments were repeated to ensure reproducible results. The concentrations of Co^{2+} ion were calculated using following equation obtained from Beer's Law plot.

$$C = \frac{A + 0.0162}{0.4567} \tag{1}$$

Where,
A = Absorbance
C = Concentration of Cobalt ion.

RESULTS AND DISCUSSION

The adsorption studies were conducted at fixed amount of GAC by varying initial concentration of Cobalt ions. The equilibrium data obtained were analyzed in the light of Langmuir and Freundlich isotherms. The adsorption isotherm describes the relationship between the liquid phase concentration and surface concentration of adsorbate at equilibrium, the amount of Cobalt on the ligand loaded GAC was determined using the equation

$$q_e = (C_o - Ce) \times \frac{V}{W} \tag{2}$$

Where,
q_e = Concentration of Cobalt ion on the ligand loaded GAC in mg/millimoles of ligand,
C_o = Initial concentration of Cobalt ion in solution in mg/L,
C_e = Final concentration of Cobalt ion in solution in mg/L,
V = Volume of solution in liters,
W= Millimoles of the ligand actually present on GAC (0.5 g).

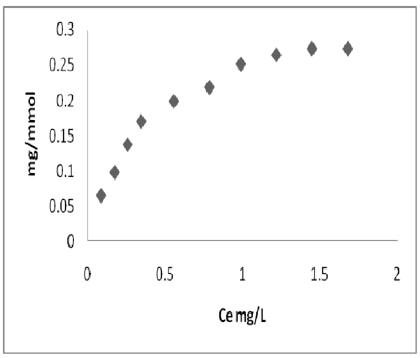

Fig.1. Adsorption isotherm
System: F-100-2-hydroxy-5-methoxy benzoic acid-Co^{2+}

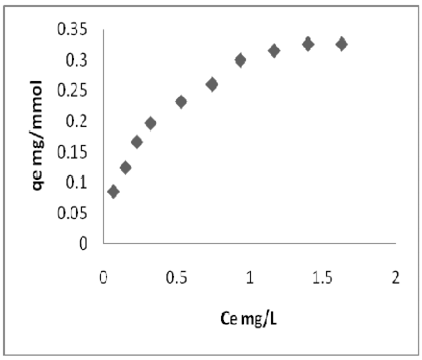

Fig.2.Adsorption isotherm
System: F-820-2-hydroxy-5-methoxy benzoic acid-Co^{2+}

The adsorption isotherms of ligand loaded F-100 and F-820 GAC obtained by plotting q_e versus C_e and shown in Fig.1 and Fig. 2. Using values of q_e versus C_e, the Langmuir equation could be expressed as

$$q_e = Q^0 b \times \frac{C_e}{(1 + bC_e)} \tag{3}$$

Where,
Q^o = amount adsorbed per unit weight of the adsorbent forming a complex monolayer on the adsorbent surface.
b = Langmuir constant.

Rearranging equation (3)

$$\frac{1}{q_e} = \frac{1}{Q^0 b} \times \frac{1}{C_e} + \frac{1}{Q^0} \tag{4}$$

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

$$q_e = k.C_e^{1/n} \tag{5}$$

Where, k and 1/n are constants determine experimentally. Using equation (5)

$$\log q_e = \log k + \frac{1}{n} \log C_e \tag{6}$$

A plot of log q_e versus log C_e fairly showing validity of Freundlich equation over a range of concentrations.

Fig.3 to 6 illustrates the plot of Langmuir and Freundlich isotherms for F-100 and F-820. The plots of $1/q_e$ versus $1/C_e$ 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 were determined.

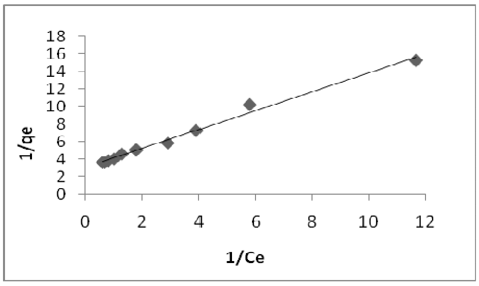

Fig.3 .Langmuir adsorption isotherm
System: F-100 -2-hydroxy-5-methoxy benzoic acid-Co^{2+}

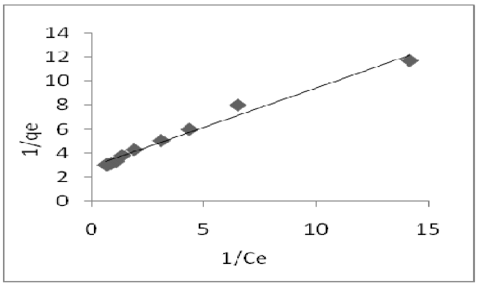

Fig. 4 .Langmuir adsorption isotherm
System: F-820-2-hydroxy-5-methoxy benzoic acid-Co^{2+}

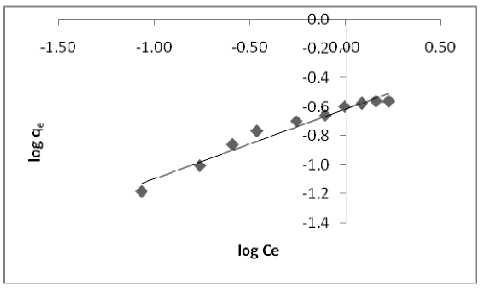

Fig.5. Freundlich adsorption isotherm
System: F-100-2-hydroxy-5-methoxy benzoic acid-Co^{2+}

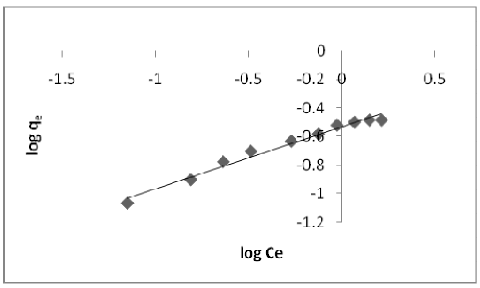

Fig .6. Freundlich adsorption isotherm
System: F-820-2-hydroxy-5-methoxy benzoic acid-Co^{2+}.

The q_e values were used for determination of surface area of the adsorbent. For this purpose a plot of $1/q_e$ versus $1/C_e$ helped in determination of $1/Q^o$ and hence Q^o. The surface area of the carbon through such Cobalt adsorption can then be represented as

$$S' = Na.Q^o.A \tag{7}$$

Where,
S = Surface area of adsorbent, cm^2/g,
Na = Avogadro number and
A = Cross-sectional area of the adsorbent molecule, cm^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 over the entire surface of the adsorbent. Determination of value of S' needed 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.

$$A = 4 \times 0.866 \left[\frac{M}{4\sqrt{2}.Na.d} \right]^{2/3} \tag{8}$$

Where,
M = Atomic weight of the Cobalt
Na = The Avogadro number
d = The density of the Cobalt, [12]

The values of S obtained from $q_{e\ max}$ are found to be fairly comparable with S' (obtained from Q^o) which are reported in Table 1

Table 1 Values of Q^O, A, S and S' for a system GAC-2-hydroxy-5-methoxy benzoic acid –Co^{2+}

Sr. No.	System	Q^0	A (cm^2)	S (cm^2/gm)	*S'* *(cm^2/gm)*	$q_{e\ max}$ (mg/m.mol.)
1	F- 100-2-hydroxy-5-methoxy benzoic acid-Co^{2+}	0.3298	5.4225 x 10^{-16}	0.6068 x 10^3	*0.7311 x10^3*	0.2737
2	F- 820-2-hydroxy-5-methoxy benzoic acid-Co^{2+}	0.3459	5.4225 x 10^{-16}	0.7233 x 10^3	*0.7668 x10^3*	0.3263

CONCLUSION

In this study, results showed that the adsorption of Cobalt ion performed by GAC was very encouraging. From the adsorption isotherm, it is observed 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 Cobalt ion on the surface of adsorbent. The experimental data seen to be of the favorable type and were then subjected for adherence to both Langmuir and Freundlich adsorption isotherm. All adsorption isotherms of the Cobalt ion on different grades of carbons in combination with 2-hydroxy-5-methoxy benzoic acid clearly shows that F-820 adsorbs Cobalt ion to a greater extent as compared to F-100. This may relate to adsorbent characteristics in terms of porosity surface area and functional group that interact with Co^{2+} ions.

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