



EFFECT OF SURFACE MODIFICATION OF GRANULATED CARBON ON REMOVAL OF METAL CONTENT.

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Abstract: In present work the ability of Granular activated carbon in combination with 2-chloro benzoic acid to adsorb Cobalt ions from aqueous solutions has been investigated through batch experiment. The adsorption isotherm of cobalt on Granular Activated Carbon at temperature $25 \pm 1^{\circ}\text{C}$ has been determined and the experimental adsorption data showed good correlation with Langmuir and Freundlich isotherm model. The GAC -300 exhibited a high potential for the removal of Co^{2+} ions as compared to GAC -200 from aqueous solution.

Key words: Adsorption, Cobalt, Granular activated carbon-200,300, 2-chloro benzoic acid.

1. Introduction

Heavy metals and dyes are found in the wastewater streams of industrial processes, including textiles, paper, paint manufacture, leather tanning, battery manufacture, dyeing, and others; their removal has attracted much practical and academic interest owing to increased concern with their environmental impact. Heavy metals cause great harm to the crop growth, yield and quality. So the removal of heavy metals, such as mercury, lead, zinc, copper, cadmium, and arsenic, from natural waters or soils has attracted considerable attention [1]. Cobalt is one of several commonly occurring toxic metals. It is an animal carcinogen producing cancer at various sites. Skin contact with soil or water that contains cobalt may also enhance exposure. When we breathe in too high concentrations of cobalt through air we experience lung effects, such as asthma and pneumonia [2]. Granular Activated Carbon is widely accepted for the removal and recovery of toxic metals because of its low cost and high affinity towards the scavenging of metal ions [3]. The technique of complex formation between the metal ions and ligand was used in this work to enhance the adsorption of Co (II) metal ion on the surface of Granular Activated Carbon. It is now well considered that addition of ligand functioning as a complexing agent could improve the metal recovery from solution by Granular Activated Carbon. Treatable amount of cobalt wastes are growing need in the industrial sector to try and find ways to recover this precious solutions using granular activated carbon [4-5]. In this work, cobalt was scavenged using GAC-200D and GAC-300 D containing adsorbed ligands. For this purpose 2-chloro benzoic acid has been chosen as a organic ligand to modify the surface of GAC.



2. Experimental

Both the Granular Activated Carbons i.e. GAC-200D and GAC-300D gifted by Calgon Corporation Ltd Pittsburg, USA, were first subjected to size fractionation by sieving them using a sieve shaker (M/s Jayant Test Sieves, Mumbai) to obtain particles of mesh size 16 x 25. 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 CaCl₂ desiccator until use. 0.01M stock solution of cobalt ions was prepared by using cobalt sulphate (Loba make). A series of solutions of known concentration of cobalt ions were prepared. Spectrophotometrically, Beer's law calibration curve was established for Co²⁺ [6].

Analytical grade reagents were used in all cases. A sample of 2-chloro benzoic acid (E.Merck) was recrystallized by standard method. The experimental melting point of 2-chloro benzoic acid (140°C) was checked from the literature value (140.3°C) [7]. The sample was also characterized through determination of molecular weight by the technique of pH titration against standard alkali. For determining the adsorption isotherm of cobalt ion on different grades of carbon containing adsorbed ligand such as 2-chloro benzoic acid, it was first essential to fix the amount of ligand on the 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 six hours on a mechanical shaker (Eltek Motor, Type M 56.Elektrocrats India, PVT 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 liter round bottle flask and then 200 ml of cobalt solution at a pH 5 was added to it. The contents were stirred for 6 hours at 25 ± 1 °C. The initial and final concentrations of the cobalt ion in mg/L was then determined spectrophotometrically (Systronics). The concentrations of Co²⁺ ion were calculated using the equation obtained from calibration curve.

The experiments were repeated to ensure reproducible results.

3. Results and Discussion

Equilibrium adsorption isotherms for q_e versus C_e were plotted for different grades of granular activated carbon and are shown in Figs. 1 and 2.

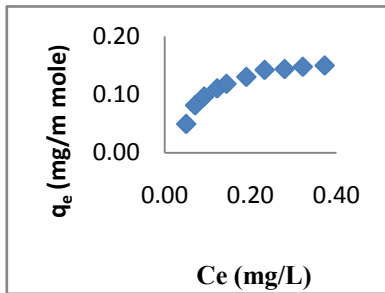


Fig.1. Adsorption isotherm
System: GAC-200 D- 2-chloro benzoic
acid -Co²⁺

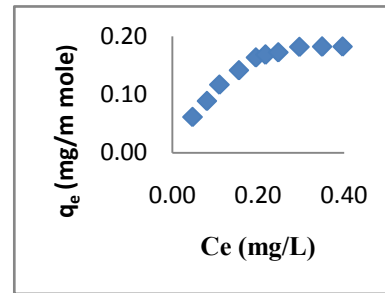


Fig.2. Adsorption isotherm
System: GAC-300 D- 2-chloro benzoic
acid -Co²⁺

The amount of cobalt on the ligand loaded GAC was determined using the equation

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

(i)

Where,

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

C_o = Initial concentration 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 result in Table-1 that cobalt adsorption follows the trend GAC-300D > GAC-200D.

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

$$q_e = Q^0 b \times \frac{C_e}{(1 + bC_e)} \quad \dots (ii)$$

The linearised form of Langmuir isotherm is

$$\frac{1}{q_e} = \frac{1}{Q^0 b} \times \frac{1}{C_e} + \frac{1}{Q^0} \quad \dots (iii)$$

Where Q^0 and b are Langmuir constants. Freundlich equation is on the other hand represented by

$$q_e = \alpha C_e^{1/n}$$

..... (iv)

The above equation may be linearised as

$$\log q_e = \log k + \frac{1}{n} \log C_e \quad \text{..... (v)}$$

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

Figs.3 to 6 illustrates the plot of Langmuir and Freundlich isotherms for GAC-200 D and GAC-300 D. The plots of $1/q_e$ vs $1/C_e$ 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. 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 , $1/n$, Q° and b respectively. The corresponding Freundlich and Langmuir constants obtained are listed in Table-1. The values of k and Q° for GAC-300 D Activated Carbon- 2-chloro benzoic acid - Co^{2+} system were greater than those for GAC-200 D Activated Carbon- 2-chloro benzoic acid - Co^{2+} system, indicating the superiority of the former for this sorption process.

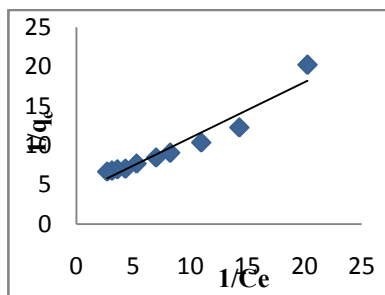


Fig.3. Langmuir adsorption isotherm
System: GAC-200 D- 2-chloro benzoic
acid - Co^{2+}

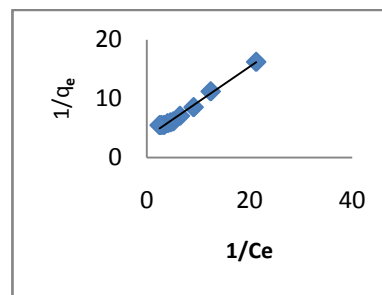


Fig.4. Langmuir adsorption isotherm
System: GAC-300 D- 2-chloro benzoic
acid - Co^{2+}

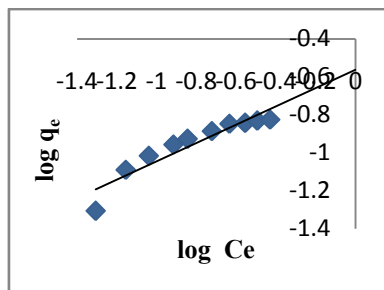


Fig.5. Freundlich adsorption isotherm
System: GAC-200 D- 2-chloro benzoic
acid - Co^{2+}

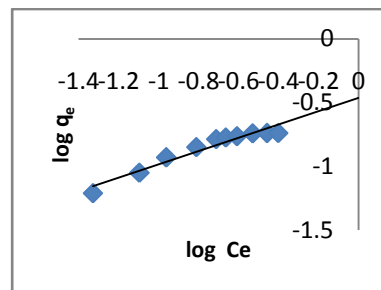


Fig.6. Freundlich adsorption isotherm
System: GAC-300 D- 2-chloro benzoic
acid - Co^{2+}

Table 1: Isotherm Constants

S.No.	System	Langmuir Q^o	Constants b	Freundlich k	Constants $1/n$	q_{max} (mg/m.mol)
1	GAC-200 D - 2-chloro benzoic acid - Co^{2+}	0.2543	5.5694	0.2742	0.4820	0.1497
2	GAC-300 D - 2-chloro benzoic acid - Co^{2+}	0.2899	5.7966	0.3443	0.5210	0.1824

Plot of $\log q_e$ versus $\log C_e$ was fairly linear showing validity of Freundlich equation also over a range of concentrations employed for the ligands as shown in Table-2. All experimental solutions were analyzed using the equation found by regression analysis of absorbance concentration data. In present work order of adsorption followed the trend,

GAC-300 D > GAC - 200 D.

Table 2: Regression Analysis Data

S.No.	Adsorption System	Type of Isotherm	Equation	Reg Coeff
1	GAC-200 D 2-chloro benzoic acid - Co^{2+}	Langmuir adsorption isotherm	$y = 0.706x + 3.932$	0.931
2	GAC-300 D- 2-chloro benzoic acid - Co^{2+}	Langmuir adsorption isotherm	$y = 0.595x + 3.449$	0.991
3	GAC-200 D - 2-chloro benzoic acid - Co^{2+}	Freundlich adsorption isotherm	$y = 0.482x - 0.562$	0.901
4	GAC-300 D- 2-chloro benzoic acid - Co^{2+}	Freundlich adsorption isotherm	$y = 0.521x - 0.463$	0.933

4. Conclusions

On the basis of this study it is concluded that granular activated carbon loaded with 2-chloro benzoic acid has good potential as a cheap



and effective scavenger for cobalt present in aqueous solutions and can be effectively used for environmental protection purposes. The adsorption isotherms of the cobalt on different grades of carbon loaded with 2-chloro benzoic acid clearly shows that GAC-300 D adsorbs cobalt to a greater extent as compared to GAC-200 D. Adsorption was found to be in good agreement with Langmuir isotherm which indicates mono layer adsorption.

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