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ADSORPTION STUDIES OF COBALT IONS ON SURFACE MODIFIED GRANULAR ACTIVATED CARBON

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ABSTRACT

In this study, removal of cobalt ions from aqueous solution by adsorption was investigated. For this purpose the surface modification of granular activated carbon was achieved by using 2-Hydroxy-5-methoxy benzoic acid and 3-Nitro aniline at constant temperature 25 ± 1°C . The adsorption isotherms of cobalt on Granular Activated Carbon (GAC) have been determined and the data were fitted better to the Langmuir and Freundlich isotherm model indicating favorable and monolayer adsorption. The results indicated that GAC in combination with organic ligand 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, 3-Nitro aniline, Filtrasorb 816 (F-816)

INTRODUCTION

Water is vital to the existence of all living organisms, but this valued resource has been highly contaminated due to growing population and rapid industrialization. The presence of toxic heavy metals in wastewaters from industrial effluents, water supplies and mine waters and their removal has received much attention in recent years. Health effects associated with exposures to lead, arsenic, cadmium, mercury and cobalt are well documented by federal and international health and environmental agencies. It is beyond the scope of this report to provide a comprehensive review of the scientific literature on adverse health effects associated with exposures to these chemicals.

The industrial effluent containing heavy metal such as Cd, Pb, Cu, Ni, Mn and Co etc is usually associated with toxicity. They cannot be degraded or destroyed. To a low extent they enter our bodies via food drinking water and air. However at higher concentrations they can lead to poisoning. 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.[1]

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Adsorption using granular activated carbon is technique popular in potable water treatment. Granular activated carbon is effective in removing taste and odour causing compounds and many metals. It is highly porous material provides high surface area for contaminant adsorption. The equivalent surface area of 1 pound of activated carbon ranges from 60 to 150 acres. Adsorption has been recognized as an effective method by many researchers for removal of heavy metal from water.[2-8]

In this connection, work was initiated in laboratory to scavenge cobalt metal using coal based porous granular activated carbon whose adsorption capacity was enhanced by loading organic ligand. An isotherm describes the relationship between the quantity adsorbed and that remaining in the solution at a fixed temperature at equilibrium.

AIMS AND OBJECTIVES

In present work, cobalt was scavenged using F-816 carbon in combination with organic ligands such as 2-hydroxy-5-methoxy benzoic acid and 3-nitro aniline.

MATERIAL AND METHODS

The adsorbent selected in present study was filtrasorb 816 (F-816). It was gifted by M/s

Calgon Carbon Corporation Ltd Pittusberg, USA in adequate amount. This GAC was first subjected to size fractionation 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 collected in glass beaker and stirred in hot 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°C for 15 hours and later cooled in a desiccators containing anhydrous $CaCl_2$ to ensure complete removal of moisture from the carbon. A synthetic cobalt ions solution was obtained by adding 2.811 gm cobalt sulphate (E. Merck). Beer's law calibration curve was established for Co^{2+} using nitroso-r-salt method, spectrophoto metrically to calculate concentration of experimental solutions.[9]

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 °C) was compared with the literature value (141°C).[10] A sample of 3-nitro aniline (Loba Chemie) was purified and recrystallized by standard method. The experimental melting point of 3-Nitro aniline (113.5°C) was compared with the literature value (114°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 mode. For determining the adsorption isotherm of cobaltion on carbon containing adsorbed ligand such as 2-Hydroxy-5-methoxy benzoic acid and 3-Nitro aniline, 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°C. The initial and final concentrations of the cobalt ion in mg/L was then determined spectrophotometrically. Chemito-spectroscan UV 2700 double beams UV Visible spectrophotometer was used for absorbance measurement in present work. The experiments were repeated to ensure reproducible results. The concentrations of Co^{2+} ion were calculated using mathematical equation obtained from Beer's Law plot.

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

$$q_e = (C_o - C_e)\frac{V}{W} \quad (1)$$

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).

The adsorption isotherms of ligand loaded F-816 GAC obtained by plotting qe versus Ce and shown in **Fig. 1.**

Using values of qe versus Ce, the Langmuir equation could be expressed as

$$q_e = Q^o \times b \left[\frac{C_e}{(1+bC_e)}\right] \quad (2)$$

Where,

Q^o = amount adsorbed per unit weight of the adsorbent forming a complex monolayer on the adsorbent surface.

b = Langmuir constant.

Rearranging equation (2)

$$\frac{1}{q_e} = \frac{1}{Q^o b} \times \frac{1}{C_e} + \frac{1}{Q^o} \quad (3)$$

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

$$q_{e=}\mathrm{k.\,C_e^{1/n}} \quad (4)$$

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

$$\log q_e = \log K + \frac{1}{n}\log C_e \quad (5)$$

A plot of log qe versus log Ce fairly showing validity of Freundlich equation over a range of concentrations.

Fig. 2 and **Fig. 3** illustrate the plot of Langmuir and Freundlich isotherms for F-816 loaded separately with 2-Hydroxy-5-methoxy benzoic acid and 3-Nitroaniline.

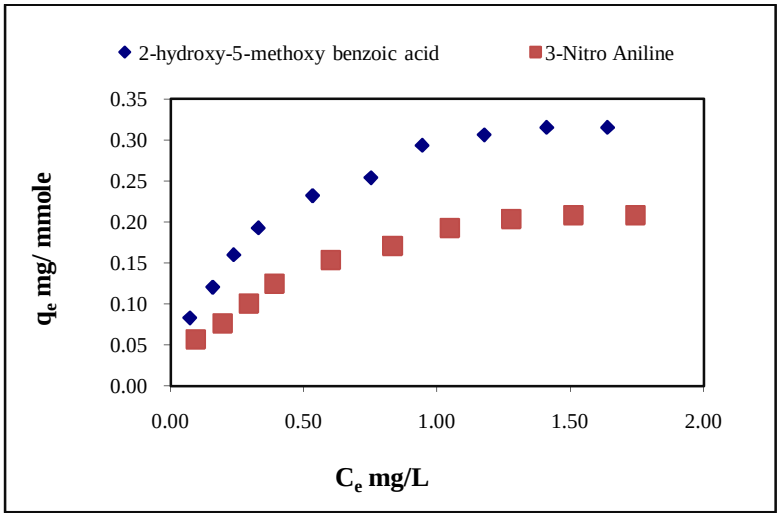

Fig. 1 : Adsorption isotherm system : F-816_Co^{2+} at 298 K

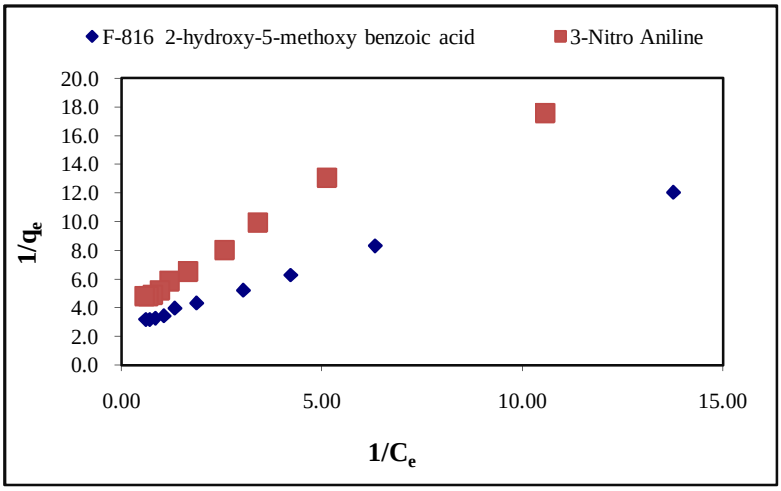

Fig. 2 : Langmuir adsorption isotherm system : F-816_Co^{2+} at 298K

The plots of 1/qe versus 1/Ce 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. The qe values were used for determination of surface area of the adsorbent. For this purpose a plot of 1/qe versus 1/Ce helped in determination of $1/Q^o$ and hence Q^o.

The surface area of the carbon through suchcobalt adsorption can then be represented as

$$S' = Na.Q^0.A \quad (6)$$

Where,

S = Surface area of adsorbent, cm^2/g,

Na = Avogadro number and

A = Cross-sectional area of the adsorbent molecule, cm^2.

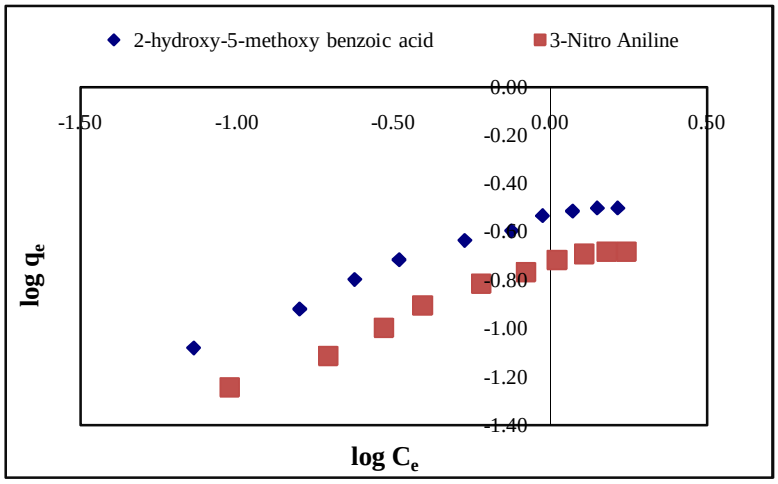

Fig. 3 : Freudlich adsorption isotherm system : F-816_Co^{2+} at 298 K

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. The data are reported in **Table 1**.

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.

$$A = 4 \times 0.866 \left[\frac{M}{4.\sqrt{2}.Na.d}\right]^{2/3} \quad (7)$$

Where,

M = Atomic weight of the cobalt

Na = The Avogadro number

d = The density of the cobalt.[12]

The values of S obtained from qe 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-816-Co^{2+}

S/N	System	Q^o	A(cm^2)	S(cm^2/g)	S'(cm^2/g)	q^e max (mg/m.mol.)
1	F-816-2-hydroxy-5-methoxy benzoic acid-Co^{2+}	0.3396	5.4225×10^{-16}	0.6990×10^3	0.7528×10^3	0.3153
2	F-816-3-Nitro Aniline -Co^{2+}	0.2301	5.4225×10^{-16}	0.4611×10^3	0.5101×10^3	0.208

The values of Q^o needed for calculation of surface area S and S' were calculated from Langmuir equation which are reported in **Table 2**. The validity of both the model also supported from the values of regression coefficient (R^2).[13-16]

Table 2 : Equations and regression analysis data

System	Langmuir equation	Regression coefficient	Freundlich equation	Regression coefficient
F-816-2-hydroxy -5-methoxy benzoic acid-Co^{2+}	y=0.697X+2.945	R^2=0.978	Y=0.437X-0.545	R^2=0.975
F-816-3-Nitro-aniline-Co^{2+}	Y=1.352X+4.345	R^2=0.963	Y=0.472X-0.746	R^2=0.978

CONCLUSION

In this study, results showed that the removal of cobalt ion performed by GAC was very promising. The experimental data correlated reasonably well by Langmuir and Freundlich adsorption isotherms and isotherm parameters were calculated. All adsorption isotherms of the cobalt ion on carbon in combination with 2-Hydroxy-5-methoxy benzoic acid and 3-Nitroaniline clearly shows that GAC F-816 in combination with 2-Hydroxy-5-methoxy benzoic acid adsorbs cobalt ion to a greater extent as compared to 3-nitroaniline. This may related to chelation of cobalt through co-ordining centres of former ligand (2-hydroxy-5-methoxy benzoic acid) loaded on GAC.

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The removal of cobalt ions from aqueous solution using adsorbent like Granular Activated Carbon (GAC) was studied in present study. Batch studies were..Â Batch studies were conducted to obtain adsorption isotherms of Co2+ ions onto Filtrasorb 300 (F-300) loaded by acid at constant temperature 25 Â± 0.5ÂºC and pH 5. GAC surface was modified by using acids such as anthranilic acid, 4-aminobenzoic acid and 2,6- dihydroxybenzoic acid in adsorption study. The adsorption data were analyzed using Langmuir, Freundlich and Temkin isotherms. Adsorption, Cobalt, Granular Activated Carbon (GAC), Filtrasorb 100 (F-100), Filtrasorb 816 (F-. 816), 1,2 Dihydroxybenzene. I. Introduction.Â The adsorption isotherm of Cobalt ion on selected grades of carbon modified with as 1,2 Dihydroxybenzene were carried out . For this 0.5 g of the GAC and 200 ml of the ligand solution of a specified concentration was taken in reagent bottle of 300 ml capacity and it was then shaken for about five hours using Teflon bladed stirrer at about 500 rpm.Â 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 Sâ€™ needed the determination of A the surface area occupied by a single. Keywords: activated carbon; bacteria; adsorption. 1 INTRODUCTION. Granular activated carbon (GAC) Â®lters are used as a Â®nal polishing step in drinking water treatment to remove compounds that are not usually present in the water at high concentrations (algae toxins, pesticides, taste, odours and industrial micropollutants). In addition, this treatment is recognized as an effective process for removing naturally occurring organic material formed by the breakdown of animal and vegetable matter in the environment.Â The surface areas of the activated carbon samples were determined by applying the BET equation to the corresponding adsorption isotherms of N2 at 77 K (SN2). Pore size distributions were obtained from mercury porosimetry experiments.