Adsorption Studies of Cobalt Using Activated Carbon In Presence of 2-Hydroxy-5-Methoxybenzoic Acid

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Abstract:

In present investigation adsorption experiment was conducted for the removal of cobalt ions from aqueous phase using granular activated carbon in presence of 2-Hydroxy-5-methoxybenzoic acid . The adsorption isotherm of cobalt on granular activated carbon was carried out at temperature 25 ± 1°C which maintain constant through the experiment. The experimental adsorption data showed good correlation with Langmuir and Freundlich isotherm model.

Keywords: Adsorption, Cobalt, Granular Activated Carbon (GAC), Filtrasorb 200 (F 200), Filtrasorb 400 (F 400), 2-Hydroxy-5-methoxybenzoic acid.

Introduction

Heavy metal water pollution has become a growing ecological crisis and hence matter of great concern for researcher and scientist. Heavy metal pollution occurs in many industrial wastewaters. Electroplating , battry manufacturing processes, production of paints , metallurgical have greatly enhanced the concentration of heavy metals in industrial wastewater. Heavy metals are not biodegradable, causing health problems in animals , plants and human beings[1]. Hence removal of toxic heavy metal ions such as Cd, Pb, Cu Ni, Mn and Co from sewage and industrial waste water is very important. Cobalt is beneficial for humance because it is part of vitamin B_{12} which is essential for human health. Cobalt is used to treat anemia. However too high concentration of cobalt may damaged human health causing asthma, pneumonia, vomiting, nausea, vision problem, heart problem, thyroid damage etc[2]. The removal of heavy metals from contaminated water bodies has been attempted by several scientist employing a wide variety of techniques including chemical precipitation, ion-exchange, electro- flotation, coagulation, solvent extraction, membrane filtration, reverse osmosis etc. All these methods are generally expensive. For this reason there is need for developing economic and eco-freindly methods for waste minimization and fine tuning of wastewater. Hence it is necessary to develop easily available, inexpensive and equally effective alternatives for wastewater treatment. The adsorption has been shown to be economically feasible and inexpensive alternative for removing metals from waste water[3-12].

MATERIALS AND METHODS :

IR

The surface morphology of Granular Activated Carbon was studied by Fourier Transform Infrared Spectroscopy (FT-IR) (Perkin Elmer-Spectrum One, VNIT, Nagpur.). FTIR spectra of F 200 and F 400 are given in Fig. No.1 and 2. FT-IR study showed the presence of carbonyl, hydroxyl functional groups on the surface of GAC.
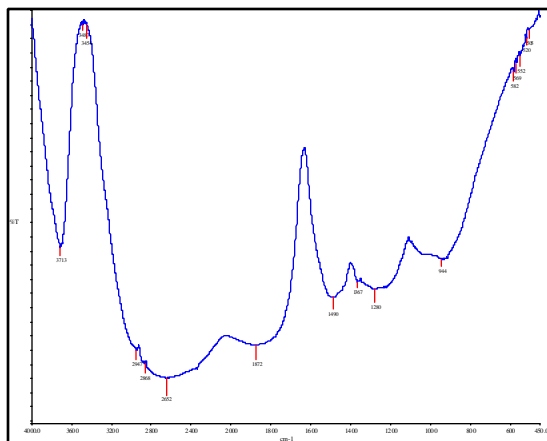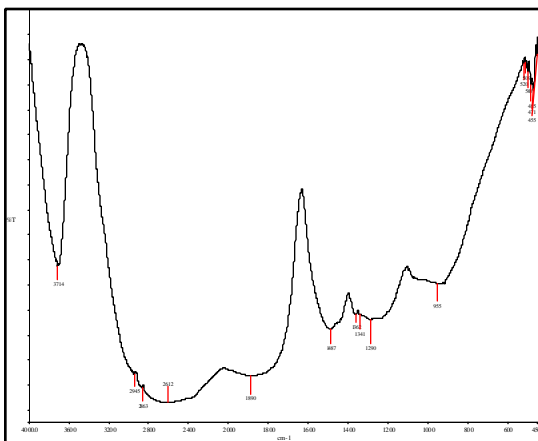

Figure 1 : FT-IR Of F 200 Granular Activated Carbon

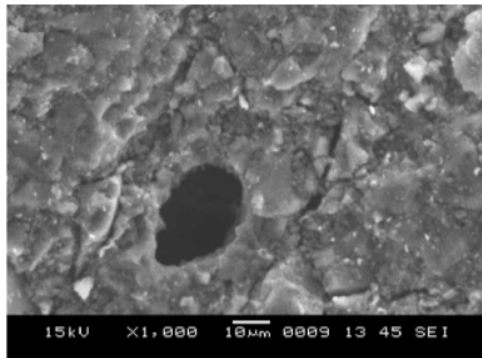Figure 2 : FT-IR Of F 400 Granular Activated Carbon

SEM

Figure 3 : Scanning Electron Micrograph Of F 200 Granular Activated Carbon

Figure 4 : Scanning Electron Micrograph Of F 400 Granular Activated Carbon

The surface morphology of activated carbon was visualized via scanning electron microscopy (SEM) (SEM-JEOL 6380A, VNIT, Nagpur.) and are given in Fig. No. 3 and 4 . The SEM images show that the GAC has a coarse surface with almost non compact structure with large cavities, cracks and pores which makes possible the adsorption of cobalt ions on different parts of the adsorbent. The SEM images show the presence of tiny cavities on granular activated carbon.

Low cost adsorbents such as filtrasorb 200 (F-200) and filtrasorb 400 (F-400) carbons gifted by M/s Calgon carbon Corporation Ltd Pittusberg, USA was selected for present study. These Desired size of carbon particles were obtained by using a sieve shaker wherein the size corresponding to mesh size 16 x 25 (M/s Jayant Test Sieves, Mumbai).All particles were collected in petridish for use. The sieved GAC particles were thoroughly washed with hot distilled water until clear liquid was obtained. It was then dried in an vacuum oven at a temperature of $110^{O}C$ for 15 hours and placed cooled in a desiccators containing anhydrous $CaCl_2$ to ensure complete removal of moisture from the carbon. A stock solution of Cobalt ions was prepared by dissolving requisite $CoSO_4$ (E. Merck) in distilled water. Ten solutions of known concentration of cobalt ions were prepared. Absorbance of all ten solutions were determined using Chemito spectrascan UV 2700 Double beam UV Visible spectrophotometer to construct Beer's law curve. Using mathematical equation the residual concentration of Co^{2+} was established [13].

All reagents used in the adsorption work were of analytical grade. A sample of 2-Hydroxy-5-methoxybenzoic acid (Sigma-Aldrich Chemie, USA) was purified and recrystallized prior to use by standard method. The purity of sample was checked by compairing the melting point of 2-Hydr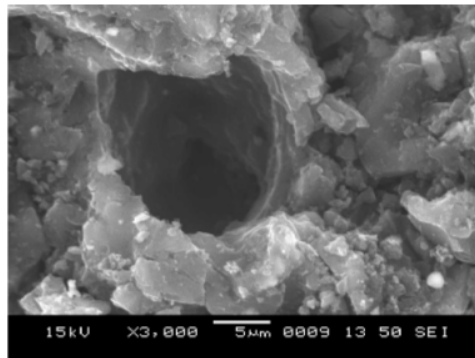oxy-5-methoxybenzoic acid with literature value. The sample was also characterized through determination of molecular weight by the technique of pH titration against standard NaOH. For carrying out adsorption isotherm, 200 ml of 0.001 M solution of 2-Hydroxy-5-methoxybenzoic acid, agitated with 0.5 g of GAC in reagent bottle of 300 ml capacity. Same solution was then shaken for about five hours using Teflon bladed stirrer at about 500 rpm. The solution was then decanted and the carbon particles were washed thoroughly with distilled water. This loaded carbon was then transferred to same reagent bottle and then 200 ml of Cobalt solution at a pH = 5 were added to it. The contents were agitated for 5 hours in a thermostat at a constant temperature of $25 \pm 1^{0}C$. The initial and final concentrations of the Cobalt ion in mg/L was then analysed by measuring absorbance spectrophotometrically. The experiments were repeated twicely to ensure reproducible results.

RESULTS AND DISCUSSION

The experimental data of adsorption of Co^{2+} on GAC 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 estimated using the equation

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

$$\ldots.. (1)$$

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,

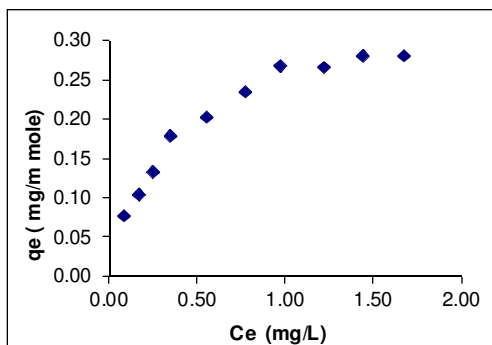W= Millimoles of the ligand actually present on GAC (0.5 g).

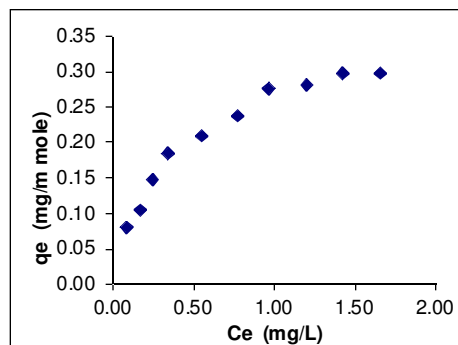**Figure 5**. Adsorption isotherm
2-Hydroxy-5-methoxybenzoic acid -Co^{2+}

Figure 6.Adsorption isothermSystem: F-200-
System: F-400-2-Hydroxy-5-methoxybenzoic
acid -Co^{2+}

The adsorption isotherms of ligand loaded F-100 and F-816 GAC obtained by plotting q_e versus C_e and shown in Fig.5 and Fig. 6. Using values of q_e versus C_e, the Langmuir equation could be expressed as

$$q_e = Q^0 b \times \frac{C_e}{(1 + bC_e)} \quad \text{..... (2)}$$

Where,
Q^o = amount adsorbed per unit weight of the adsorbent forming a complex monolayer on the adsorbent surface.
b = Langmuir constant.
Rearranging equation (3)

$$\frac{1}{q_e} = \frac{1}{Q^0 b} \times \frac{1}{C_e} + \frac{1}{Q^0} \quad \text{..... (3)}$$

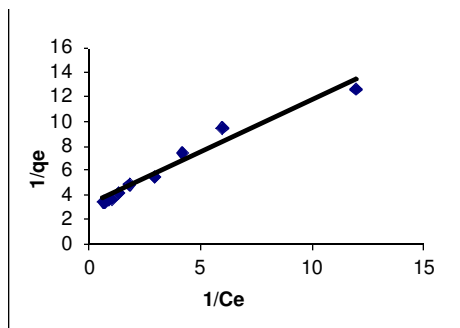A plot of $1/q_e$ versus $1/Ce$ was found to be fairly linear.

Similarly, the Freundlich equation used was

$$q_e = k.C_e^{1/n} \quad \text{..... (4)}$$

Where, k and 1/n are constants determine experimentally. Using equation (4)
$$\log q_e = \log k + \frac{1}{n}\log C_e \quad \text{..... (5)}$$

A plot of log q_e versus log C_e fairly showing validity of Freundlich equation over a range of concentrations.
Fig.7 to 10 illustrates the plot of Langmuir and Freundlich isotherms for F-200 and F-400. 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.

Figure 7 . Langmuir adsorption isotherm
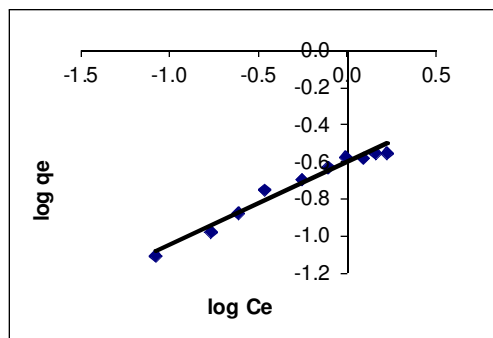System: F-200 -2-Hydroxy-5-methoxybenzoic acid -Co^{2+}
methoxybenzoic acid -Co^{2+}
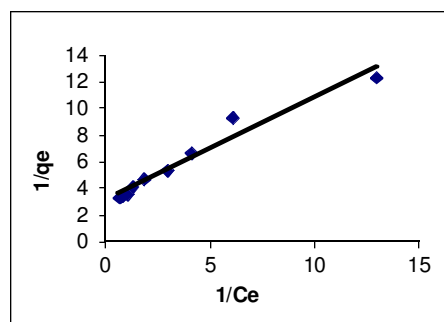
Figure 8 . Langmuir adsorption isotherm
System: F-400-2-Hydroxy-5-

Fig. 9. Freundlich adsorption isotherm
System: F-200-2-Hydroxy-5-methoxybenzoic acid - Co^{2+} methoxybenzoic acid -Co^{2+}

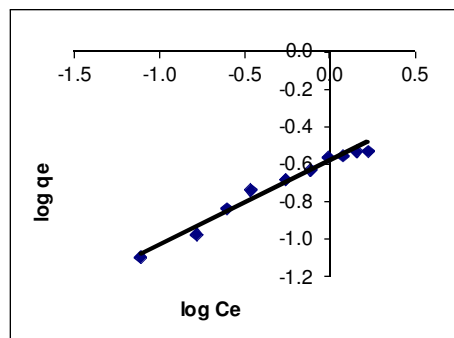**Fig. 10**. Freundlich adsorption isotherm
System: F-400-2-Hydroxy-5-

The plot of $1/q_e$ versus $1/C_e$ helped in determination of Q^o from which the surface area occupied by cobalt ion on GAC can be determined. The surface area of the carbon through such Cobalt adsorption can then be represented as

$S' = Na. Q^o. A$ ... (6)

Where,

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

Na = Avogadro number and

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

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.

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

Where,

M   =   Atomic weight of the Cobalt

Na   =   The Avogadro number

d   =   The density of the Cobalt, [14]

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-methoxybenzoic acid –Co^{2+}

Sr. No.	System	Q^0	A (cm²)	S (cm²/gm)	S' (cm²/gm)	q_e max (mg/m.mol.)
1	F- 200-2-Hydroxy-5-methoxybenzoic acid - Co^{2+}	0.3099	5.4225 x 10⁻¹⁶	0.6263 x 10³	0.6870 x10³	0.2825
2	F- 400-2-Hydroxy-5-methoxybenzoic acid - Co^{2+}	0.3152	5.4225 x 10⁻¹⁶	0.6602 x 10³	0.6987 x10³	0.2978

CONCLUSION

Adsorption by granular activated carbon is inexpensive and effective technique for removal of heavy water from wastewater. 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 presence of 2-Hydroxy-5-methoxybenzoic acid clearly shows that F-400 adsorbs Cobalt ion to a greater proportion as compared to F-200. This is probably due to availability of large active sites on the surface of GAC.

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