PEvaluation of treatment strategies for removal of cobalt from aqueous solution

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ABSTRACT

Application of ligand modified Granular Activated Carbon for adsorption of Cobalt ion from aqueous solution at constant temperature 25 ± 1° C and pH 5 was investigated. In present study Filtrasorb 400 (F-400) Granular Activated Carbon was modified by 2,5-Dihydroxybenzoic acid. Batch experiments were carried out to find the effect of co-metal Zinc on adsorption of Cobalt. The practical performance of GAC as potential adsorbent for Cobalt ion removal from aqueous solution has been proved. The Langmuir isotherm provided a better fit to the experimental data than the other adsorption isotherm models.

Key words: Adsorption, cobalt, Granular Activated Carbon F-400, 2,6-Dihydroxybenzoic acid.
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INTRODUCTION

Heavy metals have been found in harmful concentration level in numerous drinking water systems due to natural or industrial pollution sources. The heavy metals such as Lead (Pb), Cadmium (Cd), Chromium (Cr), Vanadium (V), Bismuth (Bi), Manganese (Mn) and Cobalt (Co) are significantly toxic to human being and ecological environment. The presence of toxic heavy metals in waste waters from industrial effluents, water supplies and mine waters and their removal has been received much attention in recent years. The metal ions do not undergo biodegradation and many of them are soluble in aqueous solution, therefore become more available for living systems and accumulate in the environment [1].

According to the World Health Organization (W.H.O.) about three to four million people die each year in poor countries due to diseases linked to bad water quality. As cobalt is widely dispersed in the environment, human being may be exposed to it by breathing air, drinking water and eating food that contains cobalt. Cobalt 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. It is also irritating to the eyes and mucous membrane, causing severe discomfort in the nose, often leading to perforation of the nasal septum. High concentrations of cobalt may damage human health. Too high concentrations of cobalt in air affect the lung when we breathe and cause asthma and pneumonia. The threshold limit value for cobalt fume and dust exposures is 0.1 mg/m^3 in the U.S [2-3].

There are several methods used for treatment of metal contaminated wastewater such as chemical precipitation [4-5], coagulation, flocculation [6-9], reverse osmosis [10], ultrafiltration [11], electro-dialysis [12], flotation [13], ion exchange [14], membrane processes [15] and adsorption. Adsorption has evolved as one of the most effective physical processes for purification of wastewaters since it can produce high-quality water and also be a process that is economically feasible. The most commonly used adsorbent for metal ions removal is activated carbon. The

adsorption process is most preferred method because of its high efficiency, flexibility in design and cost effectiveness [16]. Activated carbon is effective adsorbent in removing taste and odor causing compounds and many metals [17]. It is highly porous material, hence provide high surface area for metal ion adsorption. The equivalent surface area of 1 pound of activated carbon ranges from 60 to 150 acres [18].

Hence it is essential to remove cobalt from industrial wastewaters using activated carbon before transport and cycling into the natural environment [19-30]. The objective of this study was to explore the potential use of coal based granular activated carbon to remove cobalt from an aqueous solution in batch. To modify the surface of GAC 2,6-Dihydroxybenzoic acid has been chosen as an organic ligand. The effect of co-metal such as Zinc in adsorption of cobalt has also been studied at same temperature.

MATERIALS AND METHODS

A Granular Activated Carbon namely filtrasorb 400 (F- 400) gifted by Calgon Carbon Corporation, Pittsburgh, USA was used as adsorbents. The selected grade of carbon was first subjected to the size fractionation and only the particles of size ranging between 1400 micron to 1600 micron were collected. These GAC particles were then washed with hot distilled water and then dried in an oven at a temperature of 100-110°C for one hour and stored in CaCl$_2$ desiccator until use. All chemical used were of AR grade. 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+}spectophotometrically[31]. A sample of 2,6-Dihydroxybenzoic acid was recrystallised by the routine method. The experimental melting point of 2,6-Dihydroxybenzoicacid (164.5°C)was compared with the literature value (165°C)[32]. All experiments were carried out in batches of five units at a time. For determining the adsorption isotherm of cobalt ion on the carbon containing adsorbed ligand such as 2,6-Dihydroxybenzoicacid, 0.5 gm of the GAC were taken in clean shaking bottles and 200 ml of 0.001M. 2,6-Dihydroxybenzoicacid solution was shaken for about five hours using Remi Stirrers (Type L-157 M/s Remi Udyog, Mumbai, India) in constant temperature bath at around 500rpm. The solution was then filtered off and the carbon was washed thoroughly with distilled water. These carbon particle were then collected in a clean shaking bottle and then 200 ml of cobalt solution at a pH = 5 was added carefully. The system was then stirred for five hours completely with same speed at temperature 25 ± 0.5 °C. The initial and final concentration of the cobalt ion was then determined spectrophotometrically (Type 166 Systronics India Ltd.). To study the effect of co-metal such as Zinc, a solution of Zinc ion was prepared by adding appropriate quantity of Zinc sulphate in Cobalt sulphate solution and 200 ml solution was shaken with carbon previously loaded with same ligand as per procedure outline earlier

RESULTS AND DISCUSSION

Adsorption Isotherm:
Adsorption Isotherm such as Freundlich, Langmuir and Temkin effectively describe the mechanism of adsorption process and the interactions between adsorbent and adsorbate. The experimental data were analyzed using these popular models, to study the best fit in adsorption study. The amount of cobalt on the ligand loaded GAC was estimated using the equation

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

where, q_e = Amount 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 the Cobalt ion in solution in mg/L.
V = Volume of solution in litres
W = Millimoles of the ligand actually present on GAC.

The Langmuir isotherm model is applicable to monolayer adsorption whose adsorbent surface consists of equal number of identical sites. The mathematical expression for the Langmuir model in terms of Cobalt ion concentration in solution Ce (mg/L) in equilibrium with that on ligand loaded GAC q_e (mg/millimoles) is given by

$$q_e = \frac{Q^0 bCe}{1 + bC_e}$$

The linearised form of Langmuir isotherm is given as

$$\frac{1}{q_e} = \frac{1}{Q^0 \ b} \times \frac{1}{Ce} + \frac{1}{Q^0}$$

Where $Q°$ and b are Langmuir constants. The higher values of b and Q^o indicate maximum interaction and greater affinity of cobalt ion with GAC.

The Freundlich adsorption isotherm is based on the assumption that the sites on the surface of adsorbent have different binding energies. This model is applicable for adsorption on heterogeneous surface.

An empirical equation of Freundlich isotherm is given by

$$q_e = K_f C_e^{1/n}.$$

The above equation may be linearised as

$$\log q_e = \log K_f + \frac{1}{n}\log C_e$$

Where,

k_f and n are Freundlich constants relating to adsorption capacity and adsorption favorability.

Fig.2 to 4 illustrate the plot of Langmuir, Freundlich isotherms for GAC F-400. The plots of $1/q_e$ versus $1/C_e$ were found to be linear indicating the applicability of Langmuir model.

Temkin isotherm model considers the effect of indirect adsobent – adsorbate interactions on adsorption and suggests that the heat of adsorption of the entire layer would decrease linearly with coverage due to these interactions. Temkin isotherm assumes that the fall in the heat of adsorption is linear rather than logarithmic as stated in Freundlich expression. The heat of sorption of all the molecules in the layer would decrease linearly with coverage due to sorbate/sorbent interactions. The linear form of Temkin equation is

$$q_e = Bln\, K_T + Bln\, C_e$$

Where,
K_T- equilibrium binding constant (Lmg-1),
B-Temkin constant related to the heat of adsorption

$$B = \frac{RT}{b_T}$$

Temkin constants K_T and B_1 are calculated from the slopes and intercepts of q_e versus $\ln C_e$ are given in Table 3.
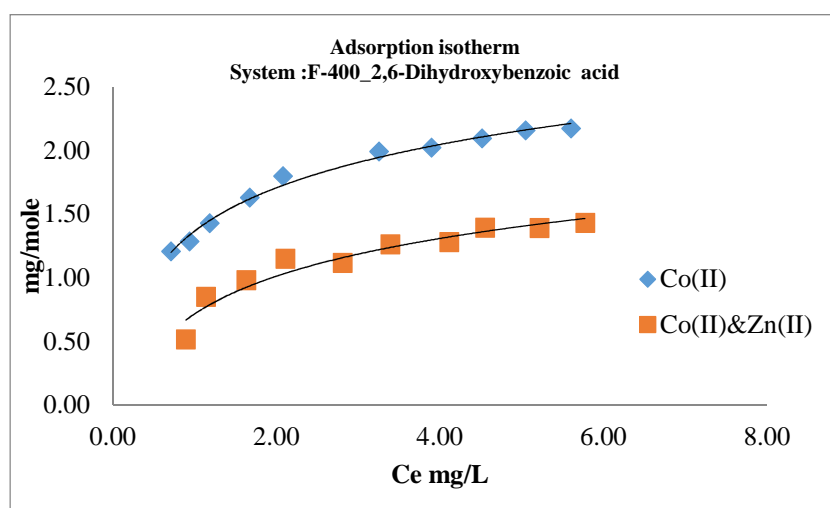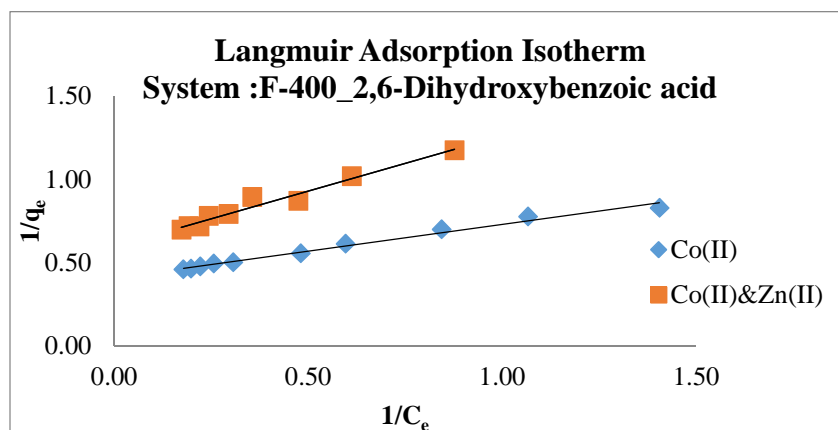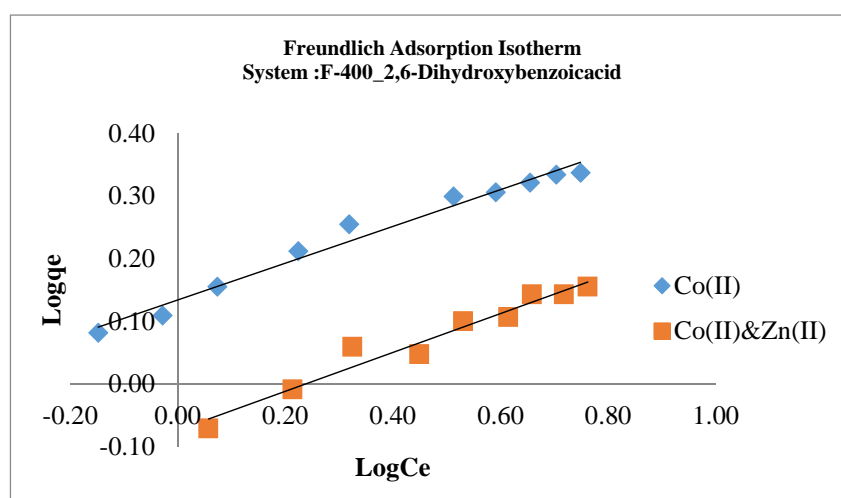

Fig. 1

Langmuir Adsorption Isotherm
System :F-400_2,6-Dihydroxybenzoic acid

Fig. 2

Freundlich Adsorption Isotherm
System :F-400_2,6-Dihydroxybenzoicacid

Fig. 3

Temkin Adsorption Isotherm
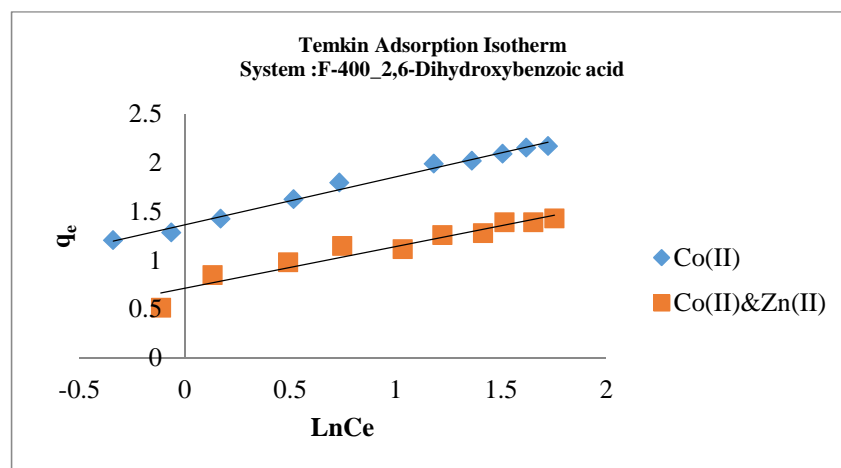**System :F-400_2,6-Dihydroxybenzoic acid**

Fig. 4

Table 1: Values of q_e max (mg/m.mole) ,Langmuir equation and R^2 for adsorption of Cobalt ion from solution by GAC containing adsorbed ligand (2,6-Dihydroxybenzoicacid)

Sr. No.	Adsorption System	F-400_2,6-Dihydroxybenzoicacid_Co^{2+}	F-400_2,6-Dihydroxybenzoicacid_Co^{2+}_Zn^{2+}
1	q_e max	2.1737	1.4313
2	Stat.Parameters R^2	0.9850	0.9650

The comparative adsorption capacities (saturation values of q_e) of Cobalt ion on different grades of GAC used in the present work can be assessed from Fig. 1.

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Table 2 : Equilibrium Isotherm Parameters For Langmuir and Freundlich model

Sr. No.	Adsorption System	Langmuir Constant		Freundlich Constant	
		Q^o	b	K	1/n
1	F-400_2,6-Dihydroxybenzoic acid_Co^{2+}	2.4449	1.2741	1.3583	3.4129
2	F-400_2,6-Dihydroxybenzoic acid_Co^{2+}_Zn^{2+}	1.6750	0.8950	0.8452	3.2258

Table 2 : Equilibrium Isotherm Parameters For Temkin model

Sr. No.	Adsorption System	K_T	b_T	R^2
1	F-400_2,6-Dihydroxybenzoic acid_Co^{2+}	16.1512 L/mg	5.0459 KJ/mole	0.9900
2	F-400_2,6-Dihydroxybenzoic acid_Co^{2+}_Zn^{2+}	10.1563L/mg	7.0985 KJ/mole	0.9610

The presence of co-metal Zn affects the cobalt ion adsorption due to its hindrance, while diffusing cobalt into the pores.

CONCLUSION

The modified GAC employed as adsorbent showed higher removal efficiency as compared to raw carbon. The removal of Cobalt ions from aqueous solution using F-400 was found to be simple and economical process. In present study F-400 modified with 2,6-Dihydroxybenzoic acid as a potential and active adsorbent for removal of cobalt ions from aqueous solution. The adsorption data fitted into Langmuir , Freundlich and Temkin isotherms out of which Langmuir adsorption model was found to have the highest regression value and hence the best fit. The presence of Zn^{2+} suppressed the sorption of Cobalt on GAC. This is probably due to hindrance of co-metal produced while diffusing the cobalt into the pores of adsorbent.

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