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ASSESSMENT OF ADSORPTION PARAMETERS IN THE REMOVAL OF COBALT ION BY ACID LOADED GRANULATED CARBON

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ABSTRACT

The removal of cobalt ions from aqueous solution using adsorbent like Granular Activated Carbon (GAC) was studied in present study. Batch studies were conducted to obtain adsorption isotherms of Co^{2+} ions onto Filtrasorb 300 (F-300) loaded by acid at constant temperature 25 ± 0.5ºC 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.

Key words: Adsorption, Cobalt, Granular activated carbon, Anthranilic acid, 4-Aminobenzoic acid, 2,6-Dihydroxybenzoic acid.

INTRODUCTION

The presence of heavy metals in the aquatic environment has been a big deal to scientists and engineers due to their increased discharge, toxic nature and other adverse effects on receiving waters[1,2]. The rapid pace of industrialization has led to severe problem of water pollution. These metals may include copper, iron, zinc, cadmium, lead, cobalt etc. which cause a number of health problems, diseases and disorders to living being[3]. Cobalt is one of the several commonly occurring toxic metals. Cobalt (II) compounds are essential in many industries. Their applications in nuclear power plants, metallurgy, mining, pigments, paints and electronic are only few examples where the presence of cobalt in waste waters represents a major environmental problem[4,5]. The threshold limit value for cobalt fume and dust exposures is 0.1 mg/m^3 in the US[6].

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Several methods are used for treatment of metal contaminated wastewater such as chemical precipitation[7-9], coagulation, flocculation[10-12], reverse osmosis[13], ultrafiltration[14], electro-dialysis[15], flotation[16], ion exchange[17], membrane processes[18], adsorption etc. They have their innate advantages and limitations in application. Among them, adsorption process is preferred because of its high efficiency, flexibility in design and its cost effectiveness[19].

Activated carbon materials are very popular as adsorptive media in wastewater treatments for removal of many types of heavy metals[20,21]. These materials are black and solid carbonaceous substances, and have porosity, internal surface area of more than 400 m^2/g and relatively high mechanical strength[22]. Activated carbon is effective in removing taste and odor causing compounds and many metals[23-29].

In the present study, the surface of granular activated carbon was modified using organic acids such as anthranilic acid, 4-aminobenzoic acid and 2,6-dihydroxybenzoic acid, which provide negative charge to the surface.

Anthranilic acid is an aromatic acid $C_6H_4OH.NH_2$ consisting of substituted benzene ring, with two adjacent, or ortho- functional groups, a carboxylic acid and an amine. 4-Aminobenzoic acid is an organic compound with the formula $H_2NC_6H_4CO_2H$. It is a white-grey crystalline substance and is only slightly soluble in water. It consists of a benzene ring substituted with an amino group and a carboxyl group. 2,6-Dihydroxybenzoic acid is a dihydroxybenzoic acid with formula $C_7H_6O_4$.

EXPERIMENTAL

Materials and method

In the present investigation, granular activated carbon namely filtrasorb 300 (F-300) (supplied by Calgon Corporation, Pittsburgh, USA) was used. The GAC was sieved to desired particle size 1400-1600 μ. It was washed thoroughly with distilled water to remove the surface adhered particles and water soluble impurities. It was then collected in glass petridish and oven dried at 100-110°C till it reaches to constant weight. The dried particles of GAC were then stored in $CaCl_2$ desiccator for further use. All chemical used were of AR grade. The cobalt sample was prepared by dissolving calculated amount of cobalt sulphate (E-Merck). The solution was used as a stock solution. Beer's law calibration curve was established for Co^{2+} spectophotometrically[30]. Samples of anthanilic acid, 4-aminobenzoic acid and 2,6-dihydroxybenzoic acid were recrystallised by the routine method. The experimental melting point of anthranilic acid (144°C), 4-aminobenzoic acid (189°C) and 2,6-dihydroxybenzoic acid (164.5°C) were compared with the literature value[31-33]. All experiments were carried out in batches of five units at a time. Batch adsorption experiments were performed by contacting 0.5 g of GAC with 200 mL of 0.001 M 2,6-dihydroxybenzoic acid solution. The experiments were performed in clean shaking bottle for 5 hrs at 500 rpm using Remi stirrer at constant temperature 25 ± 0.5^{o}C. The solution was then filtered off and the carbon was washed thoroughly with distilled water. This carbon was transferred to a clean shaking bottle and then 200 mL of cobalt solution at a pH = 5 was added carefully. The system was again stirred for five hours completely with same speed maintaining the temperature at 25 ± 0.5°C. The initial and final concentrations of the cobalt ion were then determined using spectrophotometer (166 Systronics) by measuring absorbances at 425 nm. Same procedure was repeated for the other acids.

The amount of cobalt retained on the acid loaded GAC was determined using the equation:

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

where, q_e = Concentration of cobalt ion on the acid loaded GAC (mg/millimoles)

C_o = Initial concentration of cobalt ion in solution (mg/L).

C_e = Final concentration of the cobalt ion in solution (mg/L).

V = Volume of solution (liters).

W = Millimoles of the acid actually present on GAC.

RESULTS AND DISCUSSION

Langmuir model

The mathematical expression for the Langmuir model in terms of cobalt ion concentration in solution C_e (mg/L) in equilibrium with that od acid loaded GAC q_e (mg/millimoles) is given by –

$$qe = \frac{Q^o b C_e}{1 + bC_e} \quad \ldots(2)$$

The linearised form of Langmuir isotherm is –

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

Where Q° and b are Langmuir constants.

Freundlich model

Freundlich equation is represented by –

$$Q_e = K_f . C_e^{1/n} \qquad \ldots(4)$$

The equation may be linearised as –

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \qquad \ldots(5)$$

Where k_f and 1/n are Freundlich constants.

Figs. 2 and 3 illustrate the plot of Langmuir and Frendlich isotherms for GAC F-300. The plots of $1/q_e$ versus $1/C_e$ 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 equilibrium data were analyzed using the linearized equation (5) using the same set of experimental data by plotting log q_e versus log C_e should be linear bring about the validity of Freundlich equation over a range of concentrations. The Freundlich exponent, *n*, should have values lying in the range of 1 to 0 indicating the favorable adsorption[34]. The Freundlich model was chosen to estimate the adsorption intensity of the sorbate on the sorbent surface.

Temkin model

This model based on assumption that the heat of adsorption of all the molecules in layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the bonding energies, up to some maximum binding energy[35]. The Temkin isotherm is represented as –

$$q_e = \frac{RT}{b} \times \ln (K_T C_e) \qquad \ldots(6)$$

Equation (6) can be literalized as:

$$q_e = B_T \ln K_T + B_T \ln C_e \quad \ldots(7)$$

Where, $B_T = \dfrac{RT}{b}$

T = Absolute temperature (K),

R = Universal gas constant (8.314J/mol.K),

K_T = The equilibrium binding constant (L/mg),

b = Variation of adsorption energy (kJ/mol).

B_T = Temkin constant related to the heat of adsorption (kJ/mol).

The Temkin adsorption isotherm model was chosen to evaluate the adsorption potentials of the adsorbent for adsorbates. The Temkin isotherm plot for the cobalt ion are presented in Fig. 4. The Temkin constant, b related to heat of sorption for Co^{2+} ions was calculated and reported in Table 2. The low values of Temkin constant indicate a weak interaction between sorbate and sorbent, supporting the adsorption mechanism for the present study[36].

The values for the Temkin constants, binding energies (b) and regression coefficients are given Table 2.

Table 1: Values of Langmuir and Freundlich constants q_e max (mg/m.mole) and R^2 for adsorption of cobalt ion containing adsorbed acids

S. No.	Adsorption system	q_e max	Langmuir constant			Freundlich constant		
			Q^o	b	R^2	K_f	1/n	R^2
1	F-300-4-Aminobenzoic acid-Co^{2+}	1.1832	1.8521	0.3042	0.9867	0.3827	0.6850	0.9113
2	F-300-Anthranilic acid-Co^{2+}	1.3836	2.0408	0.5016	0.9514	0.7006	0.4773	0.9532
3	F-300-2,6-Dihydroxybenzoic acid-Co^{2+}	1.7767	2.3446	0.5150	0.9886	0.7698	0.4743	0.9404

Table 2: Equilibrium isotherm parameters for Temkin model

S. No.	Adsorption system	K_T	B_T	b	R^2
1	F-300-4-Aminobenzoic acid-Co^{2+}	5.8386	0.6175	4.0122	0.9673
2	F-300-Anthranilic acid-Co^{2+}	11.9879	0.5203	4.7618	0.9659
3	F-300-2,6-Dihydroxybenzoic acid-Co^{2+}	15.7951	0.4894	5.0624	0.9790

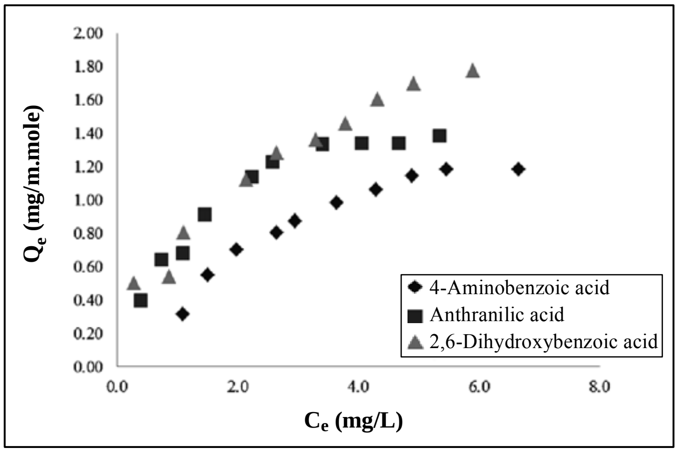

Fig. 1: Adsorption isotherm

System: GAC F-300-Acid-Co^{2+}

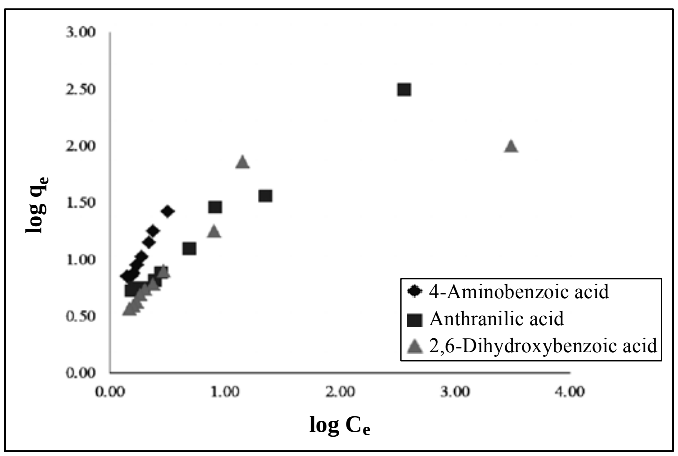

Fig. 2: Langmuir adsorption isotherm

System: GAC F-300-Acid-Co^{2+}

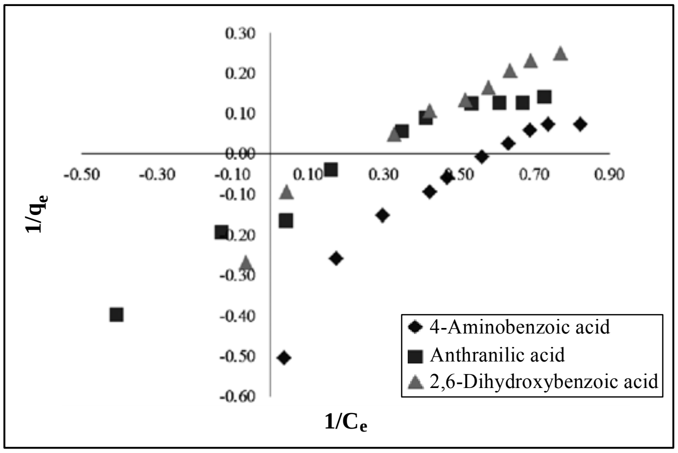

Fig. 3: Frendlich adsorption isotherm

System: GAC F-300-Acid-Co^{2+}

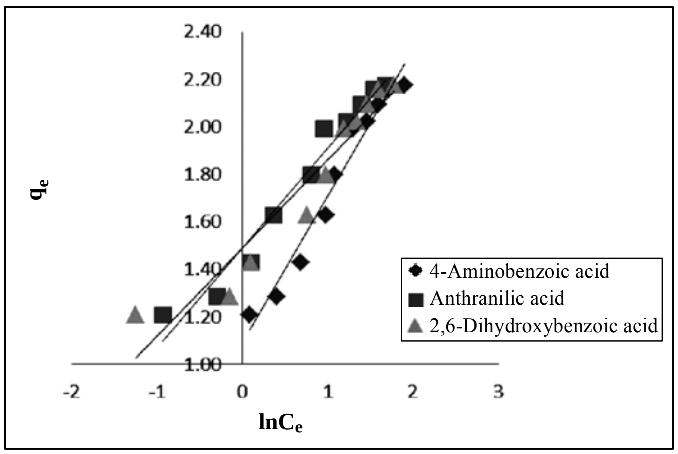

Fig. 4: Temkin adsorption isotherm

System: GAC F-300-Acid-Co^{2+}

The comparative adsorption capacities q_e max of cobalt ion on different grades of GAC used in the present work can be assessed from Fig. 1.

CONCLUSION

The GAC was found to be one of the most promising adsorbent for the removal of cobalt ions from aqueous solution due to its low cost, easy availability and high metal uptake capacity. This study has shown that granular activated carbon is good material for efficient and fast sorption of cobalt. In present study, F-300 modified with 2,6-dihydroxybenzoic acid showed more adsorptive capacity for the removal of cobalt ions from aqueous solution as compared to 4-aminobenzoic acid and anthranilic acid. The adsorption data fitted into Langmuir and Freundlich isotherms and Langmuir adsorption model was found to have the highest regression value and hence, the best fit.

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