A simulation study of the removal efficiency of modified granular activated carbon on Cobalt

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Abstract

The work was carried out to examine the potential and effectiveness of granular activated carbon (GAC) in combination with 3-Nitroaniline to remove heavy metal particularly cobalt through adsorption from the aqueous media. The adsorption isotherm of cobalt on granular activated carbon at constant temperature 25 ± 1^{0}C has been determined by batch technique and the data fitted reasonably well to the Langmuir and Freundlich isotherm. The GAC F-300 exhibited a high potential for the removal of Co^{2+} ions from aqueous solution.

Key words: Adsorption, Cobalt, Granular Activated Carbon (GAC), Filtrasorb 100 (F-100), Filtrasorb 300 (F-300), 3-Nitroaniline.

Introduction

Heavy metal contamination exists in effluents of many industries such as textile, paper, paint, leather tanning, battery manufacturing, dyeing and others. 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, cobalt and arsenic from natural waters or soils has attracted considerable attention [1]. These metals are toxic in both their chemically combined forms as well as in the elemental form. Cobalt is one of several commonly occurring toxic metal. It is an animal carcinogen producing cancer at various sites. When we breathe in too high concentrations of cobalt through air we experience lung effects, such as asthma and pneumonia [2-3]. Studies on the treatment of effluent bearing heavy metals have revealed adsorption to be a highly effective technique for the removal of heavy metals from waste streams and therefore, activated carbon has been widely used as an adsorbent. It is found to be superior to other techniques for water re-use in terms of the initial cost, high affinity towards metal, simplicity of design, ease of operation and insensibility to toxic substances [4]. The process of complexation 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 metal using granular activated carbon [4-6]. The objectives of this study were to determine the effectiveness of GAC to remove heavy metals from aqueous solution. In this work, cobalt was scavenged using F-100 and F-300 containing adsorbed ligand. For the modification of GAC surface, 3-Nitroaniline has been selected as a ligand.

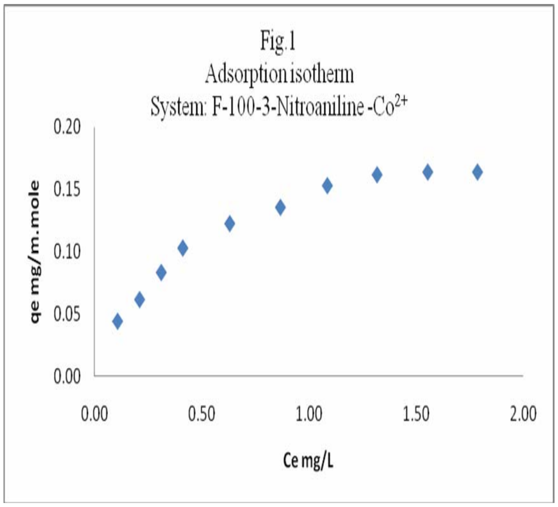
Experimental

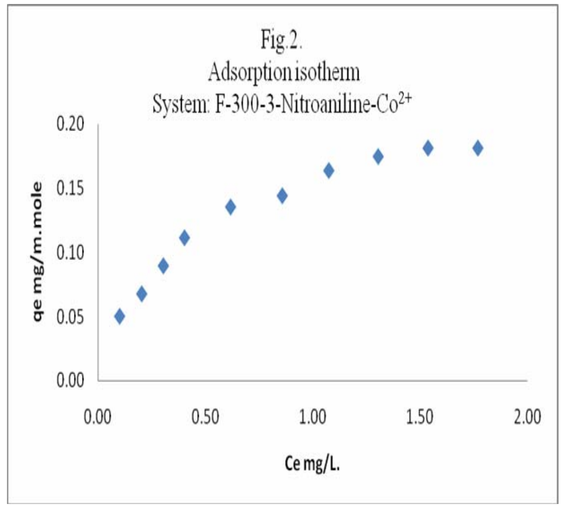
Two granular activated carbons namely F-100 and F-300 gifted by M/s Calgon Carbon Carporation Ltd Pittusberg, USA were used in this study. To get the carbon particles of the desired size range, the selected grades of carbon were first subjected to size fractionation by sieving them through 16 x 25 mesh (M/s Jayant Test Sieves, Mumbai). In order to remove any leachable matter, GAC was washed with boiled distilled water. The GACs were considered to be fit for use when the distilled water obtained after washing was visibly clear. After washing, these were dried in an oven at a temperature of 110 ^{O}C and stored in a $CaCl_2$ desiccator until use. A stock solution of cobalt ions was obtained by using a solution of cobalt sulphate (E.Merck). Spectophotometrically, Beer's law calibration curve was established for Co^{2+} ion using Nitroso-R-Salt method[7].

All the chemicals used were of AR grade. A sample of 3-Nitroaniline (Loba Chemie) was recrystallized by standard method. The experimental melting point of 3-Nitroaniline (113.5^{o}C) was checked from the literature value (114^{o}C)[8]. 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 3-Nitroaniline, 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 five hours on a mechanical shaker (Eltek Motor, Type M 56.Elektrocrats India, PVT LTD Mumbai.) at around 500 rpm. The solution was then filtered off and the carbon was washed thoroughly with distilled water. This carbon was then transferred to a same shaking bottle and then 200 ml of cobalt solution at a pH 5 was added to it. The contents were stirred for 5 hours at a temperature 25 ± 1 ^{0}C. The initial and final concentrations of the cobalt ion in mg/L was then determined spectrophotometrically (Chemito spectrascan UV 2700 Double beam UV Visible spectrophotometer). The concentrations of Co^{2+} ion were calculated using the equation obtained from Beer's law plot. The experiments were repeated to ensure reproducible results.

Results and Discussion

Adsorption isotherm describes the relationship between the liquid phase concentration and surface concentration of adsorbate at equilibrium. The Langmuir and Freundlich isotherms are the most common models used to describe such a relation. Equilibrium adsorption isotherms for q_e versus C_e were plotted for these grades of GACs and are shown in Fig.1 and 2.





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

$$q_e = (C_o - Ce) \times \frac{V}{W} \qquad \text{..... (1)}$$

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).

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

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

The linearised form of Langmuir isotherm is

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

where , Q^0 is the Langmuir constant related to the adsorption capacity and b is the other Langmuir parameter related the energy of adsorption . Freundlich equation is on the other hand represented by

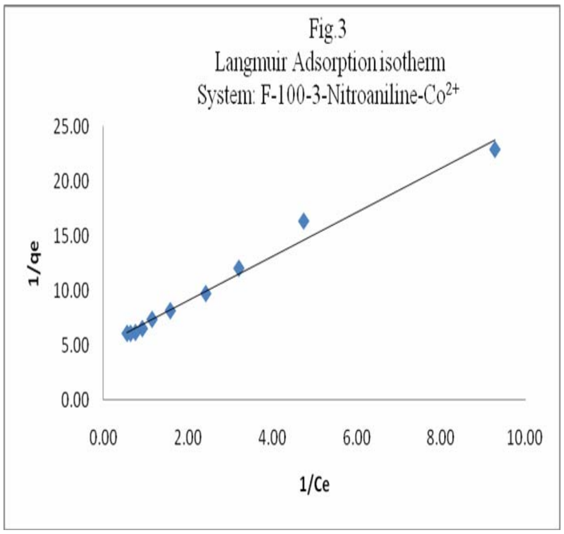
$$q_e = k.C_e^{1/n} \qquad \text{..... (4)}$$

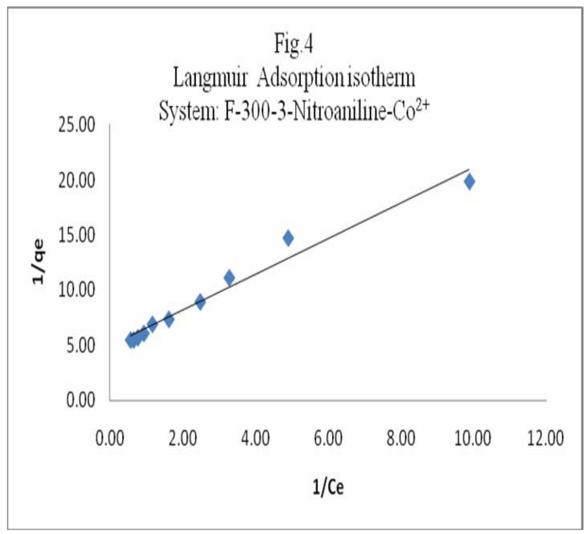
The above equation may be linearised as

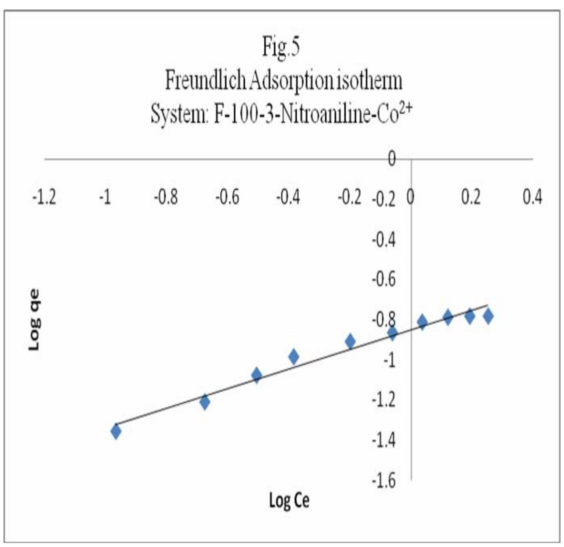
$$\log q_e = \log k + \frac{1}{n} \log C_e \qquad \text{..... (5)}$$

Where, k and 1/n are Freundlich constants.

Figs.3 to 6 illustrate the plot of Langmuir and Freundlich isotherms for F-100 and 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^o 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 versus log C_e and of $1/q_e$ versus $1/C_e$ under given set of experimental conditions provide values of k, 1/n, Q^o and b respectively.The values of k and Q^o for F-300 - 3 –Nitroaniline-Co^{2+} system were greater than those for F-200 - 3 –Nitroaniline-Co^{2+}system, indicating the superiority of the former for this sorption process. The corresponding Freundlich and Langmuir constants obtained are listed in Table-1







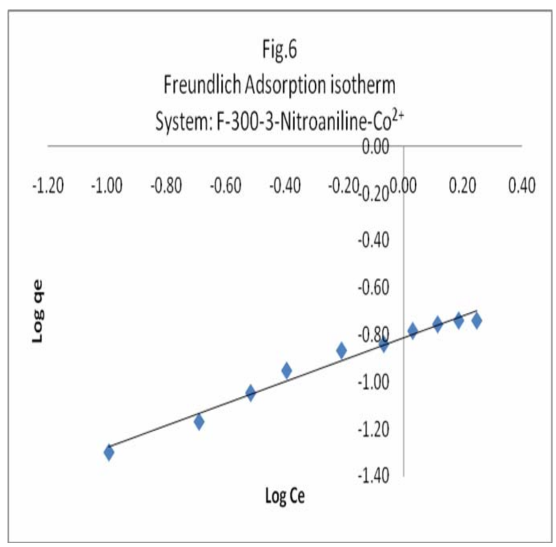


Table1: Adsorption Isotherm Constants

S.No.	System	Langmuir Q^o	Constants B	Freundlich K	Constants 1/n	q_{emax} (mg/m.mol)
1	F-100 -3-Nitroaniline -Co^{2+}	0.1987	2.4988	0.1406	0.4860	0.1642
2	F-300 - 3-Nitroaniline -Co2+	0.2031	3.0395	0.1542	0.4670	0.1817

Plot of log q_e versus log C_e was fairly linear showing validity of Freundlich equation over a range of concentrations employed for the ligand which was supported from the values of R^2. The linear equations and regression coefficient(R^2) are shown in Table-2. In present work order of adsorption followed the trend, GAC-F-300-3-Nitroaniline > GAC - F-100 -3-Nitroaniline.

Table 2: Adsorption Equation and Regression Coefficient

S.No.	Adsorption System	Type of Isotherm	Equation	Reg Coeff
1	F-100- 3-Nitroaniline -Co^{2+}	Lanngmuir adsorption isotherm	y = 2.014x + 5.032	0.984
2	F-300- 3-Nitroaniline -Co^{2+}	Lanngmuir adsorption isotherm	y = 1.620x + 4.923	0.969
3	F-100- 3-Nitroaniline -Co^{2+}	Freundlich adsorption isotherm	y = 0.486x - 0.852	0.969
4	F-300- 3-Nitroaniline -Co^{2+}	Freundlich adsorption isotherm	y = 0.467x - 0.812	0.977

Conclusion

The experimental data correlated reasonably well by the Langmuir and Freundlich adsorption isotherms and the isotherm constants were calculated. The present study brings out clearly the fact that granular activated carbon could function very effectively in scavenging metal ions from aqueous solution. The adsorption isotherms of the cobalt on different grades of carbon loaded with 3-nitroaniline clearly shows that F-300 adsorbs cobalt to a greater extent as compared to F-100 .

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