



STUDIES ON REMOVAL OF METAL CONTENT USING COAL BASED ADSORBENT THROUGH WASTEWATER.

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Abstract:

This paper presents the observations of the study on cobalt removal from a waste water by adsorption onto granular activated carbon. Similar study has also been done in presence of other metal namely zinc for comparison. The removal of cobalt ions by adsorption using granular activated carbon (GAC) in combination with Anthranilic acid was studied at constant temperature 25 ± 0.5 °C and pH 5. The equilibrium sorption isotherms are analyzed by the Freundlich and the Langmuir isotherms .

Keywords:

Adsorption, Cobalt, GAC F-200 , GAC F-400, Anthranilic acid, Zinc

Introduction:

Metal ion contamination of drinking water and wastewater especially with heavy metal ions such as cobalt, is a serious and ongoing problem. As a result of this pollution water bodies become a major environmental problem of the modern world. According to WHO[1] organization, about 80% of all diseases in human beings are caused by water. Cobalt is beneficial for humans because it is a part of vitamin B12, which is essential for human health. However, too high concentrations of cobalt may damage human health. When plants grow on contaminated water they will accumulate very small particles of cobalt, especially in the parts of the plant we eat, such as fruits and seeds. Water effluent of ceramic industry contains very high amounts of cobalt may cause serious health effects on human being [2]. The threshold limit value for cobalt fume and dust exposure is 0.1 mg/m³ in the U.S [3]. Even though heavy metal ions can be removed by physicochemical methods such as chemical precipitation, membrane separation [4-5] and ion exchange but adsorption has been shown to be economical alternative for removing metals from water [6-8].





Adsorption is an important technique in separation and purification processes which is useful in water and waste water industry to removal of color, odor and organic pollutant [9-10]. Among many types of adsorbent materials, activated carbons which can be produced from almost any carbonaceous materials are the most widely used, because of their large adsorptive capacity and low cost [11]. Adsorption is not always a single process. Often a combination of interaction is responsible for the association between a particular chemical (sorbate) and solid (sorbent)[12-19] . In the present work cobalt was removed using granular activated carbon Filtrasorb-400 (F-400) and Filtrasorb-200 (F-200) containing adsorbed organic ligand such as Anthranilic acid and the effect of Zn^{2+} (co-metal) on adsorption was also studied.

Material and Method:

Granular Activated Carbon namely F-200 and F-400 gifted by Calgon Corporation, Pittsburgh, USA were used as adsorbents. These carbons showed very good resistance to abrasion and stability in form when they were used for long periods of time in contact with aqueous solutions. The selected grades of carbons were first subjected to the size fractionation and only the particles of size ranging between 1400 micron to 1600 micron were recovered. The GAC was then washed several times with warmed distilled water carefully without leading to any attrition and water then decanted with care. After decanting much of water, the entire lot of the carbon sample was then transferred to a glass petridish. The carbon sample was dried in an oven at a temperature of 100-110°C for twelve hours and stored in $CaCl_2$ desiccator until use. All chemicals used were of AR grade. A stock solution of cobalt ions was prepared by dissolving required quantity of cobalt sulphate (E. Merck) in distilled water with a drop of sulphuric acid to prevent hydrolysis. The standardized cobalt solution was utilized for establishing a Beer's law plot of absorbance versus concentration of solutions. For this purpose 10 ml of the standard solution was diluted to one liter and various compositions with distilled water of total





volume 20 ml were made. To these solutions 1 ml of 1% sodium acetate trihydrate and 2 ml 0.2 % Nitroso-R-salt was added. The liquid was boiled for one minute and 2 ml 1:1 nitric acid was added to stabilize the red orange complex [20]. The solution was cooled ,diluted to 50 ml and absorbance measured at 425 nm against a blank using Digital Systronic Spectrometer Model 166. A sample of Anthranilic acid was recrystallised by the routine method. The experimental melting point of 145 °C was compared with the literature value 144.5 °C[21]. All experiments were carried out in batches of five units at a time. For determining the adsorption isotherms of cobalt ion on the different grades of carbon containing adsorbed ligand such as Anthranilic acid ,0.5 gm of the GACs were taken in clean shaking bottles and 200 ml of 0.001M Anthranilic acid 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 500 rpm. The solution was then filtered off and the carbon was washed thoroughly with distilled water. The carbon particles were then transferred to a clean shaking bottle and then 200 ml of cobalt solution at a pH = 5 was added carefully. The pH of the adsorptive solutions was adjusted using nitric acid, sodium hydroxide and buffer solutions when required. The systems were then stirred for five hours completely with same speed maintaining the temperature at 25 ± 0.5 °C. The initial and final concentration of the cobalt ion was then determined spectrophotometrically.

Result and Discussion:

The correlation of experimental adsorption data with the adsorption models was undertaken to gain an understanding of adsorption behavior and the heterogeneity of the adsorbent surface. The mathematical interpretation of the adsorption isotherms is studied using the two common models, namely Freundlich and Langmuir. The adsorption isotherms for different grades of granular activated carbon are shown in Fig.1 and 2. The amount of cobalt on the GAC chemically modified by ligand Anthranilic acid was determined using





the equation $q_e = (C_o - C_e) \times V/W$ 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 the cobalt ion in solution in mg/L. V = Volume of solution in liters W = Millimoles of the ligand actually present on 0.5 gm of GAC. It is observed from the result in Table-1 that cobalt adsorption follows the trend $F-400 > F-200$. The mathematical expression for the Langmuir model in terms of cobalt ion concentration in solution C_e (mg/L) in equilibrium with that on ligand loaded GAC q_e (mg/millimoles) is given by $q_e = (Q^o b C_e) / (1 + b C_e)$ It can be written in its linearized form as follows $1/q_e = 1/(Q^o b) \times 1/C_e + 1/Q_0$ Where, Q^o is the Langmuir constant related to the adsorption capacity b is the other Langmuir parameter related to the energy of adsorption. The Freundlich model can take the following form. $q_e = K_f (C_e)^{1/n}$ The equation may be linearised as

Langmuir $\log(q_e) - \log(K_f) = 1/n \log(C_e)$ Where, k_f and $1/n$ are

Freundlich constants. Fig.3 to 6 illustrate 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. The intercept and slope of the linear plots of $1/q_e$ vs. $1/C_e$ and of $\log q_e$ vs $\log C_e$ under given set of experimental conditions provide values of Q_0 , b , k_f , and $1/n$ respectively. The corresponding Freundlich and Langmuir constants obtained are listed in Table-2. The values of k_f and Q_0 for F-400-Anthranilic acid - Co^{2+} system were greater than those for F-200-Anthranilic acid- Co^{2+} system, indicating the superiority of the former for this sorption process. The presence of co-metal (Zn) results in the lowering of the cobalt ion adsorption due to hindrance caused by the co-metal ions while cobalt diffuses into the pores. The values of q_e in presence of Zn^{2+} follows the trend $F-400-Co^{2+} > F-400 (Co^{2+}-Zn^{2+})$ and $F-200-Co^{2+} > F-200-(Co^{2+}-Zn^{2+})$





Conclusion:

From the adsorption isotherms it is seen that as C_e increases q_e increases but at high concentration q_e tends to be constant which indicates the formation of a monolayer of cobalt ions on the surface of GAC. The ligand adsorbed granular activated carbon showed high adsorption capacity in the removal of cobalt ion from aqueous solution. In present work the GAC F-400 adsorbs cobalt to a greater extent as compared to F-200. In the presence of zinc the amount of cobalt adsorbed on GAC decreases Adsorption was found to be in good agreements with Langmuir isotherm which indicates monolayer adsorption. Application of the Freundlich and Langmuir isotherm models gave good representations of the experimental data for cobalt sorption by GAC .

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Table-1 VALUES OF $q_e \text{ max}$ (mg/mmol) FOR ADSORPTION OF COBALT ION FROM SOLUTION BY GAC CONTAINING ADSORBED LIGAND (ANTHRANILIC ACID)

Sr. No.	System	$q_e \text{ max}$ (mg/mmol)
1	GAC F-200-Anthranilic Acid- Co^{2+}	0.9313
2	GAC F-400-Anthranilic Acid- Co^{2+}	1.5160
3	GAC F-200-Anthranilic Acid- Co^{2+} - Zn^{2+}	0.8852
4	GAC F-400-Anthranilic Acid- Co^{2+} - Zn^{2+}	0.8244

Table-2 ISOTHERM CONSTANTS

Sr. No.	System	Langmuir Constant		Freundlich Constant	
		Q°	b	Kf	1/n
1	GAC F-200-Anthranilic Acid- Co^{2+}	1.7667	0.2254	0.3572	0.5990
2	GAC F-400-Anthranilic Acid- Co^{2+}	1.8867	0.6567	0.7870	0.3480
3	GAC F-200-Anthranilic Acid- Co^{2+} - Zn^{2+}	1.7452	0.2208	0.3459	0.6060
4	GAC F-400-Anthranilic Acid- Co^{2+} - Zn^{2+}	1.1454	0.4298	0.3926	0.4330





