



Research Article

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Kinetic models for the adsorption of cobalt from aqueous phase using granular activated carbon

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ABSTRACT

This study investigated the removal of Cobalt ions from aqueous solution using Granular Activated Carbon (GAC) such as Filtrasorb-400 (F-400) in presence of different organic complexing agent, Batch mode experiments were carried out to obtain adsorption kinetics of Co^{2+} ions onto granular activated carbon F-400 loaded with Salicylic acid, 3,5-Dinitrosalicylic acid and 5-Sulphosalicylic acid one by one at constant temperature 25 ± 0.5 °C and pH 5. Three different kinetic models namely pseudo first order, pseudo second order and Weber-Morris intra particle diffusion models were applied to experimental results. The experimental study revealed that 300 min of contact time was enough to achieve equilibrium for the adsorption of cobalt. The experimental results indicated a significant potential of the GAC as an adsorbent for cobalt ions removal.

Keywords: Adsorption, cobalt, Granular Activated Carbon, 3,5-Dinitrosalicylic acid, 5-Sulphosalicylic acid, Salicylic acid.

INTRODUCTION

It is well known that some metals can have toxic or harmful effects on many forms of life. Metals, which are significantly toxic to human beings and ecological environments, include chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), manganese (Mn), cadmium (Cd), nickel (Ni), zinc (Zn), cobalt (Co) and iron (Fe), etc. Cobalt is one of the naturally occurring element that has properties similar to those of iron and nickel. Small amounts of cobalt are naturally found in most rocks, soil, water, plants, and animals, typically in small amounts. Cobalt has both beneficial and harmful effects on human health. Cobalt is beneficial for humans because it is part of vitamin B₁₂, which is essential to maintain human health. At very high exposure levels cobalt increases red blood cell production in healthy people. It is also essential for the health of various animals, such as cattle and sheep.

Acute exposure to high levels of cobalt by inhalation in humans and animals results in respiratory effects, such as a significant decrease in ventilatory function, congestion and hemorrhage of the lung. Chronic exposure to cobalt by inhalation in humans results in effects on the respiratory system, such as respiratory irritation, wheezing, asthma, decreased lung function, pneumonia, and fibrosis[1-2]. The threshold limit value for cobalt fume and dust exposures is 0.1 mg/m³ in the US [3]. Unlike organic pollutants the majority of which are susceptible to biological degradation, heavy metal ions will not degrade into harmless end-product[4].

There are several methods employed for treatment of metal contaminated wastewater such as chemical precipitation [5-7], coagulation, flocculation [8-10], reverse osmosis [11], ultrafiltration [12], electro-dialysis [13], flotation [14], ion exchange [15], membrane processes [16] and adsorption are employed for the treatment of toxic metals. These methods have their inherent advantages and limited applications. Among them adsorption process is preferred

because of its high efficiency, flexibility in design and its cost effectiveness [17]. Activated carbon is effective in removing taste and odor causing compounds and many toxic metals [18-24].

In terms of kinetics numerous models have been investigated among which three models such as pseudo first order, pseudo second order and Weber-Morris intra particle diffusion models have been investigated. The study of adsorption dynamics describes the solute uptake rate which in turn governs the residence time of adsorbate uptake at the solid solution interface [25]. The adsorption rate constant can be used to compare the performance of activated carbons. The various kinetic models have been adopted to describe the behavior of sorption process under different experimental conditions [26].

Activated carbons are characterized by their strong adsorption capacity, which can be diameter as high as 10 \AA° - 1000 \AA° which occurs mostly in cavities of molecular dimensions called micro-pores [27]. In present study diffusion mechanism and kinetics of adsorption of cobalt by modified GAC study how various derivatives of Salicylic acid effect on adsorption of cobalt metal on GAC F-400. For this work we have selected Salicylic acid, 3,5-Dinitrosalicylic acid and 5-Sulphosalicylic acid as complexing agents to improve the adsorption capacity of granular activated carbon.

EXPERIMENTAL SECTION

In the present work commercially available Granular Activated Carbon namely filtrisorb 400 (F-400) supplied by Calgon Corporation, Pittsburgh, USA was used as a adsorbent. It was first subjected to the size fractionation and only the particles of size ranging between 1400 micron to 1600 micron were recovered by siever (M/s Jayant Test Sieves, Mumbai). The GAC was then washed with boiled distilled water and then dried in an oven at a temperature of $100\text{-}110^{\circ}\text{C}$ 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 prepared using cobalt sulphate (E. Merck) in distilled water. The experimental solutions were prepared by diluting the stock solution with distilled water when necessary. Beer's law calibration curve was established for Co^{2+} spectrophotometrically [28]. A sample of Salicylic acid, 3,5-Dinitrosalicylic acid and 5-Sulphosalicylic acid were purified by the routine method. The experimental melting point of Salicylic acid (157.5°C), 3,5-Dinitrosalicylic acid (169°C) and 5-Sulphosalicylic acid (121°C) were compared with the literature value [29-31]. All experiments were carried out in one unit at a time. For determining the adsorption kinetics of cobalt ion on the carbon containing adsorbed complexing agent such as Salicylic acid, 3,5-Dinitrosalicylic acid and 5-Sulphosalicylic acid, 1gm of the GAC were taken in clean shaking bottles and 400 ml of 0.001M. organic ligand solution was shaken for about five hours using Remi Stirrers (Type L-157 M/s RemiUdyog, 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. This carbon was then transferred to a clean shaking bottle and then 400 ml of cobalt ion solution at a pH 5 was added carefully. The system was then stirred with same speed maintaining the temperature at $25 \pm 0.5^{\circ}\text{C}$. After 15 minutes interval 5 ml of an aliquot of cobalt ion solution was withdrawn and then analyzed using UV-Visible spectrophotometer (Type 166 Systronics India Ltd.). Same procedure was repeated after 30min, 45 min, 60min, 90 min, 120min, 180 min and 240 min for determination of adsorption of cobalt ion.

RESULTS AND DISCUSSION

The mathematical interpretation of the adsorption kinetics was studied using the three popular models, namely pseudo first order, pseudo second order and Weber-Morris intra particle diffusion model. The adsorption kinetics for different derivatives of salicylic acid on granular activated carbon (F-400) is shown in Fig.1. The amount of cobalt adsorbed was calculated using the following relation

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

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 the cobalt ion in solution in mg/L.

V = Volume of solution in liters

W = Millimoles of the ligand actually present on GAC.

All the experiments were performed in duplicate and the average value have been used in calculations. The correlation of the experimental adsorption data with pseudo first order, pseudo second order and Weber-Morris intra particle diffusion model was undertaken to gain an understanding adsorption behavior and the heterogeneity of the adsorbent surface.

i) Pseudo First Order Kinetic Model.

The pseudo first order rate expression of Lagergren is widely used kinetics model for adsorption of solute from a liquid solution. This kinetic model is used for reversible reaction with an equilibrium being established between liquid and solid phase [32-33]. It is represented by

$$\frac{d\bar{q}}{dt} = K_1(\bar{q}_e - \bar{q}_t) \quad \text{--(2)}$$

Integrating equation for the boundary $t=0$ to $t=t$ and $q=0$ to $q=q$ result for the following equation.

$$\ln \frac{(\bar{q}_e - \bar{q}_t)}{\bar{q}_e} = k_1 t \quad \text{--(3)}$$

Above equation may be rearranged to form

$$\bar{q}_t = \bar{q}_e(1 - e^{-K_1 t}) \quad \text{--(4)}$$

Equation may be rearranged to obtained linear form

$$\log(\bar{q}_e - \bar{q}_t) = \log \bar{q}_e - \frac{K_1}{2.303} t \quad \text{--(5)}$$

K_1 and \bar{q}_e values obtained by plotting $\log(\bar{q}_e - \bar{q}_t)$ versus t . The metal uptake capacities of GAC at equilibrium and rate constant for pseudo first order model calculated from graph are reported in Table 1.

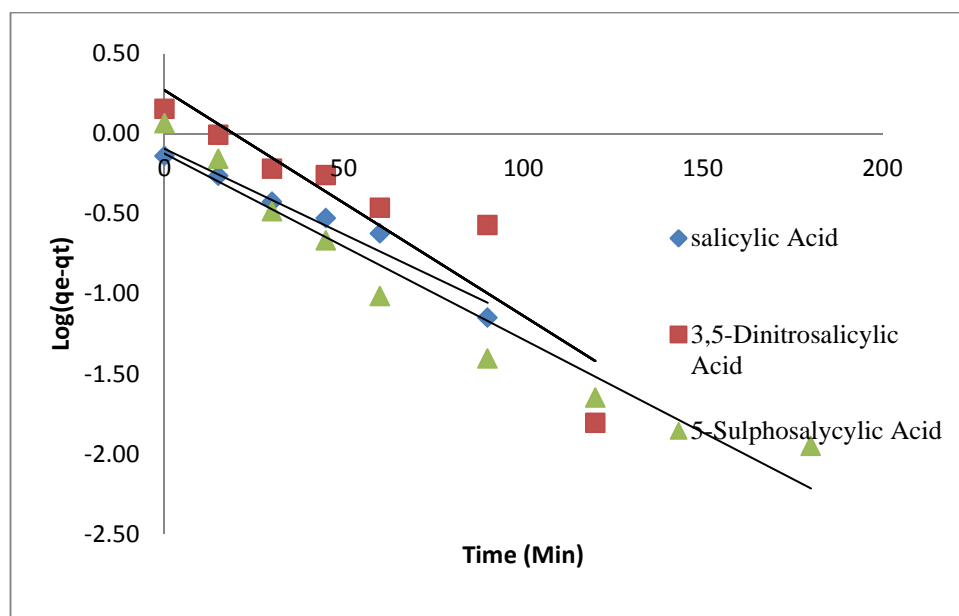


Fig 1.: Lagergren Pseudo First Order Rate Equation Model

ii) Pseudo Second Order Kinetic Model:

Ho and McKay presented the pseudo second order kinetic model which is based on the assumption that rate limiting factor may be chemical adsorptions. Chemical adsorptions, the metal ion stick to the adsorbent surface through chemical bond and tend to find sites that maximize their coordination number with surface. A kinetic model is only concerned with the effect of observable parameters on the overall rate. Pseudo-second order model is derived on the basis of the sorption capacity of the solid phase, expressed as

$$\frac{d\bar{q}}{dt} = k_2(\bar{q}_e - \bar{q}_t)^2 \quad \text{--(6)}$$

Integrating this for the boundary conditions $t=0$ to $t=t$ and $q=0$ to $q=q_t$, gives,

$$\frac{1}{(\bar{q}_e - \bar{q}_t)} = \frac{1}{\bar{q}_e} + k_2 t \quad \text{--(7)}$$

Equation may be rearranged as

$$\bar{q}_t = \frac{k_2 \bar{q}_e^2}{1 + k_2 \bar{q}_t} t \quad \text{--(8)}$$

Equation may be rearranged to obtained linear form

$$\frac{t}{q_t} = \frac{1}{k_2 \bar{q}_e^2} + \frac{1}{\bar{q}_e} t \quad \text{--(9)}$$

The plot of $\frac{t}{q_t}$ as a function of t yield a straight line from which k_2 and \bar{q}_e are calculated. The metal uptake capacities of GAC at equilibrium and rate constant for pseudo second order model calculated from graph are reported in Table 1. The R^2 values for pseudo first order are less than that of pseudo second order, which indicates that the data obtained from the study at different time interval fits the pseudo second order model better than pseudo first order. This gives an idea that the adsorption process followed the pseudo second order kinetics.

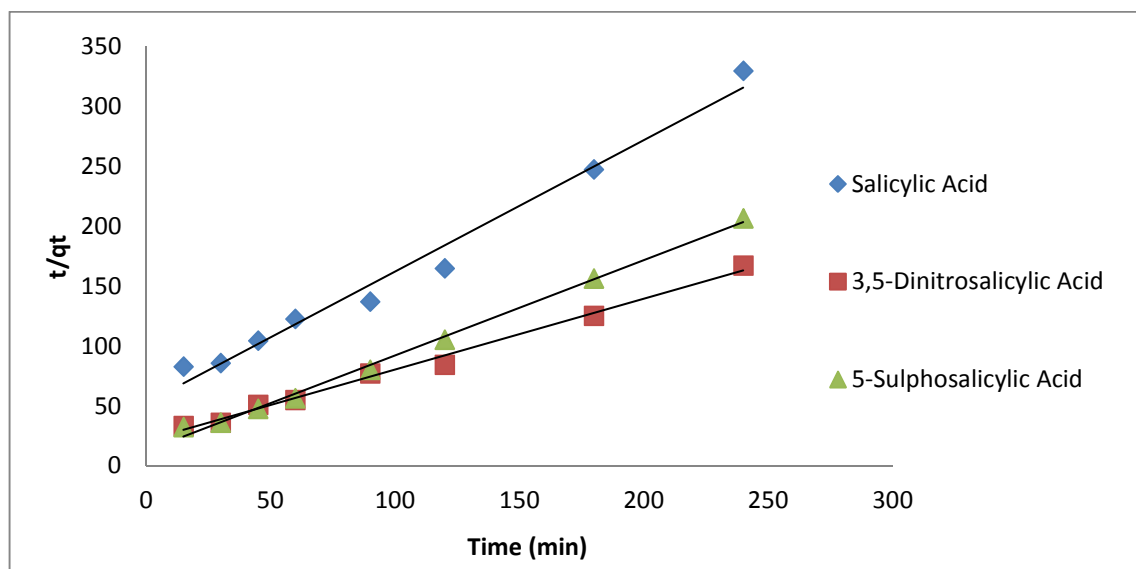


Fig 2.: Lagergren Pseudo Second Order Rate Equation Model

iii) Weber-Morris Intraparticle diffusion model

The Weber and Morris model or intraparticle diffusion model is of major interest because the internal diffusion determines the adsorption rate in most of the liquid systems. The most widely applied intraparticle diffusion equation is given by Weber-Morris.

$$q = k_{in} t^{0.5} \quad \text{--(10)}$$

The external mass transfer from the solution to the liquid-solid interface and the diffusion of the adsorbed species inside the porous particle both these processes are observed for adsorption kinetics on activated carbons. This model describes the time evolution of the concentration in adsorbed state, where the rate constant (k_{in}) is obtained from the plot of q versus $t^{0.5}$ and is related to the respective intraparticle diffusion coefficient (D) according to equation

$$k_{in} = 6 \frac{q_0}{R} \sqrt{\frac{D}{\pi}} \quad \text{--(11)}$$

The different mechanisms of mass transfer are manifested as different slopes in the linear plot of q versus $t^{0.5}$, obtained by piecewise linear regression. They correspond to different consecutive stages of mass transport with decreasing rate: external mass transfer and intraparticle diffusion in the macro-, meso- and microporous structure of the adsorbent [34].

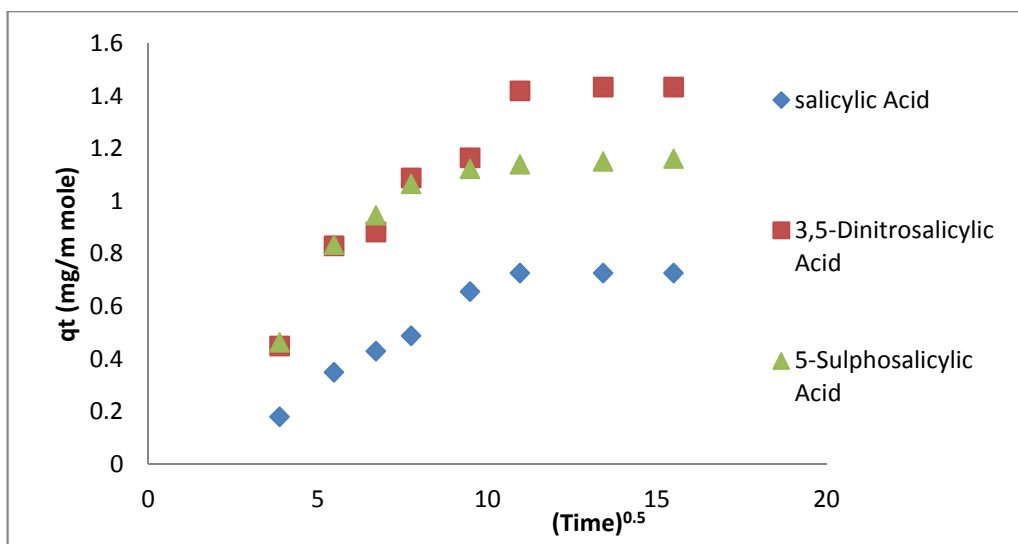


Fig. 3 : Weber-Morris Intraparticle diffusion model

Table-1 Values of rate constant; metal uptake capacity of GAC at equilibrium and regression correlation coefficient (R^2) for Pseudo First and Second Order Kinetic Model

Sr. No	System	q_{exp}	Pseudo First Order Kinetic Model			Pseudo Second Order Kinetic Model		
			q_{cal}	K_1	R^2	q_{cal}	K_2	R^2
1	F-400_Salicylic acid_Co ²⁺	0.7274	0.8087	24.6421×10^{-3}	0.9589	0.9113	22.9635×10^{-3}	0.9813
2	F-400_3,5,Dinitrosalicylic acid_Co ²⁺	1.4348	1.2612	41.9146×10^{-3}	0.9505	1.6889	16.6730×10^{-3}	0.9922
3	F-400_5-Sulphosalicylic acid_Co ²⁺	1.1621	1.0064	34.0844×10^{-3}	0.9801	1.2559	50.9401×10^{-3}	0.9959

Table-2 Weber-Morris Intra-particle Model Constants

Sr.No.	System	K_{id}	D	R^2
		(mg/m. mole min ^{1/2})	(cm ² min ⁻¹)	
1	F-400_Salicylic acid_Co ²⁺	0.0652	3.7685×10^{-4}	0.9648
2	F-400_3,5,Dinitrosalicylic acid_Co ²⁺	0.1232	7.1203×10^{-4}	0.9126
3	F-400_5-Sulphosalicylic acid_Co ²⁺	0.1103	6.3752×10^{-4}	0.7227

CONCLUSION

The present work showed that GAC surface was effective in the removal of cobalt from the aqueous solution. The adsorption kinetics of Co²⁺ with granular activated carbon was successfully described by the pseudo second order model. Kinetics data were best fitted by the pseudo second order model and the result indicated that GAC is excellent in the removal of cobalt from aqueous solution at different concentrations.

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