



Surface Modified Granular Activated Charcoal With Anionic Surfactant For Scavenging of Co(II) Metal Ions From Aqueous Solution : Thermodynamics and Kinetics

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Abstract:

Paper describe the adsorption of Co(II) metal ion from aqueous solutions by Sodium Dodecyl Sulfate an anionic surfactant species on granular activated charcoal. The contact time and pH were determined and adsorption isotherms were obtained for Co(II) metal ion. Capacity of the activated charcoal to adsorb Co(II) metal ion increased in proportion to the quantity of surfactant with which they were impregnated. The adsorption process follows pseudo second order reaction kinetics as well as validated to Freundlich, Langmuir adsorption isotherms. The paper discusses the thermodynamic and kinetic parameters. Results demonstrate that maximum removal efficiency was found to be 95% for Co(II) at pH 4.

Keywords: Granular Activated Carbon, Sodium dodecyl sulphate, Surface modification, Adsorption kinetics, Cobalt(II) Metal Ion.

Introduction:

The presence of aqueous metal ions in effluent from various related industries has been proven hazardous and poses a threat to the environment. The aqueous metal ions are known toxic in nature, non-biodegradable and more likely to accrue in human body, thus causing a number of health problems, diseases and disorders. Among the toxic and hazardous metal ions are copper, cobalt, lead, mercury, cadmium and chromium^[1]. Several efforts to convert carbonaceous materials into activated carbon particularly for heavy metals remediation have been reported in literature^[2]. And to name but just a few, coconut shell^[3], sawdust^[4], corncob^[5], apricot stone^[6] and pecan shell^[7]. In most cases, one-step chemical activation is a method of choice by researchers in this area to activate the carbonaceous materials. Activating agents such as H₃PO₄, H₂SO₄, ZnCl₂, KOH and NaOH are known to produce a larger surface area and high yield^[8-9].

In the recent years, it has been increasingly used for the prevention of environmental pollution and antipollution laws have increased the sales of AC for control of air and water pollution^[10-11]. AC is a broad-spectrum agent that effectively removes toxic and bio-refractive substances such as insecticides, herbicides, chlorinated hydrocarbons, heavy metal ions, and phenols, typically present in many water supplies^[12-14]. AC in fact is a microcrystalline, non-graphitic form of carbon with porous structure that has been processed to develop its internal porosity. AC has a high degree of porosity, an extensive surface area, and a high degree of surface reactivity. The most important physical property of AC which allows the physical adsorption of gases or vapours and dissolved or dispersed substances from liquids^[15]. It has large number of very fine pores (microspores)





gives the AC a large inner surface, which is the basis of its remarkable adsorption properties. Consequently, they are effective adsorbents for many pollutant compounds (organic, inorganic, microbial and biological) of concern in water and wastewater treatment^[16-17].

EXPERIMENTAL

Surface Modification Of GAC and Batch Experiment for Co(II) Metal Ion:

The activated carbon was washed several times with deionised water, and then dried for several days in an oven at 60 °C. The capacities of virgin GAC and SDS-GAC to adsorb Co(II) metal ion were examined by measuring the initial and final concentrations of Co(II) metal ion in a batch system. To evaluate the adsorption equilibrium data experiments were carried out in batch mode. For determining the adsorption isotherm of cobalt ion on carbon containing adsorbed anionic surfactant Sodium Dodecyl Sulfate, it was first essential to fix the amount of anionic surfactant on the GAC. This process of fixing of anionic surfactant on GAC was denoted as loading of GAC. The resulting GAC were designated as SDS-GAC. For this purpose 0.5 g of the GAC was taken in clean shaking bottles and 200 ml of the anionic surfactant solution of a specified concentration was shaken at 100rpm at 20±1°C for 48 h. Then adjusting the pH to 2, 3, 4, 5 or 6 by adding 1N NaOH or H₂SO₄ as required.

Effect Of pH On Co(II) Adsorption

As initial pH increases, the extent of removal Co(II) metal ion increases reaches a maximum value. The removal efficiency was 95% for Co(II) metal ion because of the interactions between adsorbent and adsorbate. The optimum pH for removal of Co(II) metal ion is fixed as 4 pH shown in fig-I. Batch adsorption experiments with virgin GAC and SDS-GAC were conducted at various pH from 2 to 6. The virgin GAC removed Co(II) metal ion poorly at all pHs. Thus, the low capacity of virgin GAC to adsorb Co(II) metal ion is a result of its low acidity. Impregnating activated carbon with SDS anionic surfactant increased the number of active sites capable of binding the Co(II) metal ion

Effect Of Contact Time

The percentage removal increases with increase in contact time due to more amounts of Co(II) metal ion removed due to effective contact and due to the availability of active sites. The effect of contact time is shown in Fig-II. The result indicates the equilibrium was attained in about 360 min. The extent of removal of Co(II) metal ion by SDS-GAC and GAC was found to increase, reach a maximum value with increase in contact time.

Effect Of Ligand Loading

To understand the effect of Sodium Dodecyl Sulfate as a ligand on Co(II) metal ion removal, virgin GAC was impregnated with eight different amounts of SDS. As the amount of SDS on the surface of activated carbon increased, its specific surface area decreased. The amount of anionic surfactant dose varies from 200mg/200ml to 1000mg/200ml in SDS-GAC system. The retrieval efficiency is





maximum at anionic surfactant dose of 1000 mg/200ml which is up to 95% shown in Fig.-III

ADSORPTION ISOTHERMS

Freundlich Isotherm

In 1906, Freundlich studied the sorption of a material onto animal charcoal. He found that if the concentration of solute in the solution at equilibrium, C_e , was raised to the power $1/n$, the amount of solute sorbed being q_e , then $C_e^{1/n} / q_e$ was a constant at a given temperature. This fairly satisfactory empirical isotherm can be used for non ideal sorption and is expressed by the following equation: $q_e = K_f C_e^{1/n}$

The equation is conveniently used in the linear form by taking the logarithm of both sides as:

$$\log q_e = \log K_f + 1/n \log C_e$$

The parameters are represented in Table-1. Results show that the adsorption of Co(II) metal ion are best explained by Freundlich and Langmuir model as the value of correlations factor r^2 for Cobalt metal are 0.985 and 0.979. The results are shown in Fig- IV and V.

Langmuir Isotherm

The Langmuir adsorption isotherm plot for $1/q_e$ versus $1/C_e$ is shown in Fig. IV. The essential characteristics of Langmuir isotherm can be described by a separation factor or equilibrium constant R_L , which is defined as,

$$R_L = \frac{1}{(1 + bC_i)}$$

Where C_i is the initial concentration of heavy metal ions (mg/l) and b , Q_0 is Langmuir constant which indicates the nature of adsorption. The separation factor R_L indicates the isotherm shape and whether the adsorption is favourable or not, as per the criteria given below.

R_L Values	Adsorption
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

First order kinetics: -

The pseudo first-order equation (Lagergren, 1898) is generally expressed as follows:

where:
$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

q_e and q_t are the adsorption capacity at equilibrium and at time t , respectively (mg.g⁻¹),

k_1 is the rate constant of pseudo first-order adsorption (l.min⁻¹).





It is found that as initial Co(II) metal ion concentration increases, Lagergren rate constant decrease. This indicates that, adsorption does not follow the 1st order kinetics.

Pseudo Second order Model:

The pseudo second-order adsorption kinetic rate equation is expressed as :

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$$

Where,

k_2 is the rate constant of pseudo second-order adsorption ($g \cdot mg^{-1} \cdot min^{-1}$).

Results indicates that adsorption of Co(II) metal ion on SDS-GAC System obey the 2nd order kinetics. Also the concentration of Co(II) metal ion increasing from 15mg/L to 45 mg/L, equilibrium sorption capacity q_e increase.

Elovich Model: - The Elovich model equation is generally expressed as

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \text{ ----- (Eq-1)}$$

Where,

α is the initial adsorption rate ($mg \cdot g^{-1} \cdot min^{-1}$)

β is the desorption constant ($g \cdot mg^{-1}$) during any one experiment

To simplify the Elovich equation, Chien and Clayton (1980) assumed $\alpha\beta t \gg 1$ and by applying the boundary conditions $q_t=0$

at $t=0$ and $q_t=q_e$ at $t=t$ (Eq-1) becomes:

$$q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln(t)$$

As the concentration of Co(II) metal ion increases from 15mg/L to 45mg/L. value of α increase and β decreases. This favoured the adsorption phenomenon.

Thermodynamics Parameters

The negative value of free energy change ΔG indicates feasibility and spontaneous nature of adsorption of Co(II) metal ion. ΔH value suggested endothermic nature of Co(II) metal ion on SDS-GAC. Positive value of ΔS is due to increase randomness during adsorption of Co(II) metal ion

Table.1

Metal Ions	Langmuir Constants				Freundlich Constants		
	$Q_0 mg/g$	$b L/mg$	R_L	r^2	k_f	B	r^2
Cobalt (II)	6.862	0.071	0.45	0.979	0.681	8.951	0.985

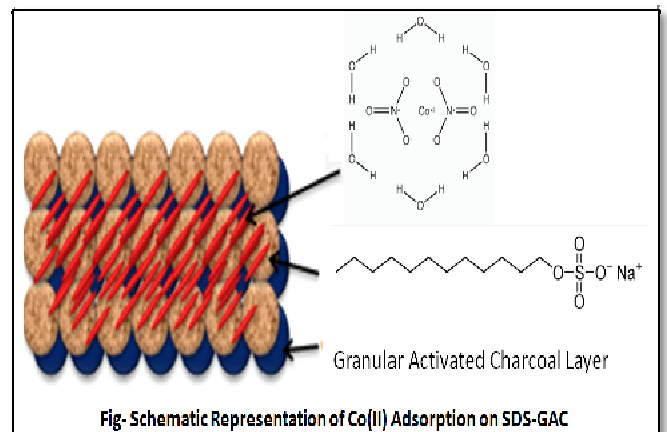
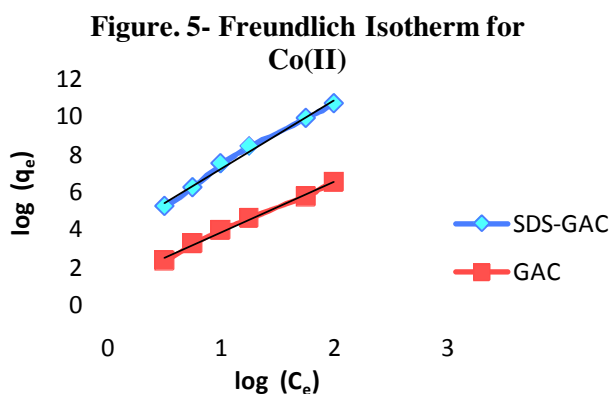
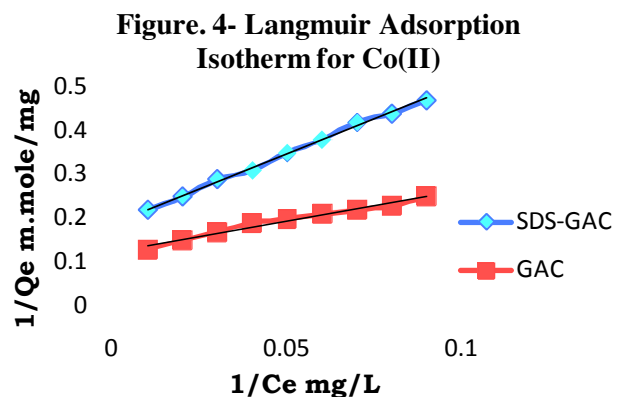
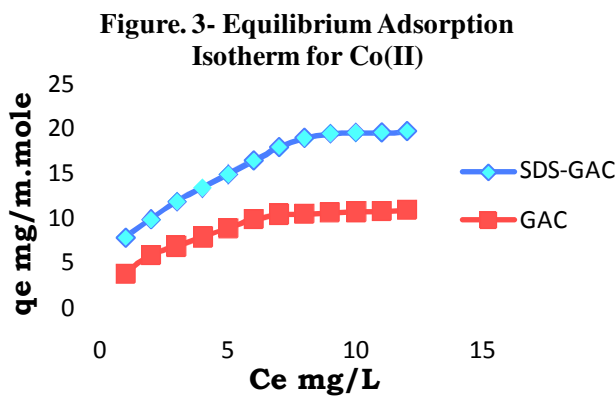
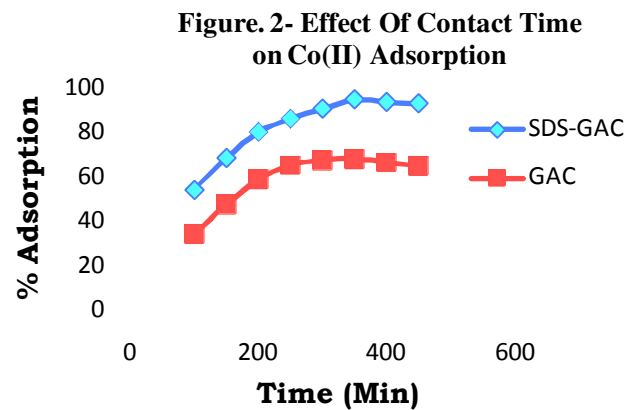
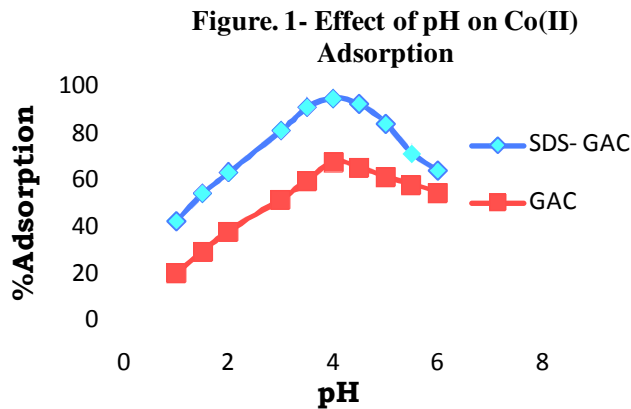


Table. 2-Kinetic Model Value for Adsorption of Co(II) metal ion on SDS-GAC System

Concentration	1 st Order			Pseudo Order			Elovich		
	K_L	q_e	r^2	q_e	k_2	r^2	α	β	r^2
15mg/L	0.1281	7.89	0.971	8.576	0.0018	0.990	0.531	0.1376	0.9893
30mg/L	0.0683	12.33	0.992	12.282	0.0015	0.994	1.513	0.0951	0.9867
45mg/L	0.0236	16.71	0.995	17.981	0.0012	0.996	2.641	0.0742	0.9861

Table. 3- Thermodynamics Parameters

Temperature	ΔH	ΔS	ΔG
20°C	23.1241	0.0815	-0.7652
25°C	25.7521	0.3067	-68.295
30°C	31.5201	1.0605	-298.235





Conclusion:

The pH variation studies showed that the adsorption process for Co(II) metal ion on SDS-GAC is highly pH dependent. The optimum pH range for the removal was found to be 4. Increase in adsorbent dosage leads to increase in Co(II) metal ion adsorption due to increased number of adsorption sites. The adsorption process found to follow 2nd-order kinetics and Elovich model. The adsorption isotherm studies showed that both Langmuir and Freundlich adsorption isotherm model fits well with the experimental data. Thermodynamic studies indicated the spontaneous nature of adsorption process and it increases with increase in temperature showing endothermic nature of the adsorption process. The maximum removal efficiency was found to be 95%. Hence it is conclude that surface modification of granulated activated charcoal is the best way to remove Co(II) metal ion from aqueous solution.

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