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COBALT (II) ION REMOVAL BY ADSORPTION ONTO GRAPHENE NANOSHEETS: KINETIC AND THERMODYNAMIC STUDIES

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ABSTRACT

In this work, the graphene nanosheets (Gns) were firstly prepared by modified Hommer's method. Subsequently, Gns properties such as functional groups and homogeneity were identified by FTIR and TEM. Then, a batch adsorption study was used to investigate the kinetics and thermodynamic of adsorption of Co²⁺ ions in the concentration range of 10-60 mg L⁻¹.from aqueous solution by Gns. The effect of different conditions including pH, contact time (t_c), adsorbent dosage (m) and temperature (T) on adsorption of Co²⁺ ions onto Gns were studied. Kinetic analysis shows that absorption of Co²⁺ ions obeys a pseudo first-order kinetic. Absorption mechanism was investigated using a three-step mechanism proposed by weber–morriss in order to find rate-limiting step. Different isothermal absorption models including Langmuir, Freundlich, Temkin, Dubinin-radushkevich (D-R), and Brunauer-Emmett-teller (BET) were applied to describe the absorption behavior of Co²⁺ ions. The results showed that experimental data could be well described by Langmuire equations. From relationship between kinetic model and thermodynamic parameters was used to predict the absorption process. The results showed that the overall adsorption process was endothermic and spontaneous in nature. Moreover, it can be suggested that Co²⁺ ions adsorption may be chemisorptions and physisorption onto Gns.

Keywords: Graphene Nanosheets; Cobalt (II) Ions; Adsorption; Isotherm; Kinetics

INTRODUCTION

Heavy metal contamination exists in the aqueous waste streams of many industries, such as metal plating facilities, mining operations, nuclear power plant and tanneries. Some metals associated with these activities are cadmium, chromium, cobalt, lead and mercury (Netzer *et al.*, 1984). Cobalt, a natural element present in certain ores of the Earth's crust, is essential to life in trace amounts. Pure cobalt is a steely-grey, shiny and brittle metal. Everyone is exposed to low levels of cobalt in air, water and food. An average of 2g L⁻¹ in drinking water has been estimated. Cobalt and its salts are used in nuclear medicine, enamels and semiconductors, grinding wheels, painting on glass and porcelain, in vitamin B12 manufacture, and as a catalyst for organic chemical reactions. The permissible limits of cobalt in the irrigation water and livestock watering are 0.05 and 1.0 mg L⁻¹, respectively. The effects of acute cobalt poisoning in humans are very serious, among them are asthma like allergy, damage to the heart, causing heart failure, damage to the thyroid and liver. Many methods have been developed for heavy metal ions removal from water, such as precipitation, reverse osmosis, Reduction, filtration, membrane processes, ion exchange, coagulation and adsorption on solid sorbent such as activated carbon or coal fly ash (Poon 1986). Similarly, Gns, consisting of two-dimensional (2D) material of carbon atoms packed densely in a hexagonal crystal lattice. In this lattice are carbon atoms with sp²-hybridized single-atom-layer structure. Carbon atoms covalently bonded has been theorized to have a huge specific surface area (Sen *et al.*, 1987). In particular, single grapheme layer has as ultrathin thickness as 0.5-1.5 nm which enables it to be applicable on a stretchable substrate (Singh *et al.*, 2009). Gns is a newly emerging has unique physical, chemical, electrical and mechanical properties. Recently graphene has been used as adsorbent to remove methyl orange, naphtalen, Fluoride ion and Hg²⁺ ion from aqueous solutions (Wang *et al.*, 2003). To our knowledge, no investigation has been carried on using graphene as an adsorbent to remove Co²⁺ from aqueous solutions. The aim of this study is to investigate the adsorption behavior of Co²⁺ ions onto Gns as

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an adsorbent. Many works have reported absorption of heavy metals on carbon-based nanosheets. However, most of them have been done on surface of graphene oxide. Despite there are many reports, lack of a comprehensive study of absorption cobalt ions on surface of graphene exist. The main aim of this paper is providing of universal understanding for absorption cobalt ions aiding relationship between kinetics models and thermodynamic parameters. For this propose, the cobalt ion adsorption on surface of graphene was studied through investigating experimental parameters such as pH, adsorbent dosage, temperature, and contact time. Moreover, adsorption kinetics, isotherm models and thermodynamic parameters have been estimated from experimental results.

MATERIALS AND METHODS

Preparation of Gns

Firstly, graphene oxide (GO) was synthesized from natural graphite powder by a modified Hummers method (Huang *et al.*, 2012). In a typical reaction, 5 g graphite, 5 g NaNO₃, and 230 mL H₂SO₄ (98%) were stirred together in an ice bath. KMnO₄ (15 g) was slowly added while stirring, and the rate of addition was controlled to prevent the mixture temperature from exceeding 20°C. The mixture was then transferred to a 35°C water bath and stirred for about 0.5 h, forming a thick paste. Subsequently, 230 mL de-ionized water was added gradually, causing an increase in temperature to 98°C. After 15 min, the mixture was further treated with 700 mL de-ionized water and 50 mL 30% H₂O₂ solution. The warm solution was then filtered and washed with de-ionized water. To reduce graphene oxide to Gns, 0.1 g GO was dried in a vacuum oven at 80°C for 12 h and then dispersed into 100 mL de-ionized water and reduced with hydrazine (Huang *et al.*, 2012). Upon reduction, the solution changed from brown to black in color. The product Gns was obtained by filtration, then washed with methanol, water and oven-dried for further use. Natural flake graphite used in this study was kindly provided by Asbury Carbons (grade 3240).

Characterization of Gns

The morphology and structure of Gns was characterized by Transmission electron microscopy (TEM) JEOL 2100 model. Fourier transform infrared (FTIR) spectra were recorded by a FTIR spectrophotometer (Bruker Optics) over the wave number range from 4000 to 100 cm⁻¹. Pressed disks were prepared by grinding the powdered grapheme with KBr in an agate mortar. X-ray diffraction (XRD) analyses is powerful tools was used to study the crystal structures of the CuO nanoparticles.

Batch Adsorption Experiments

Adsorption experiments were conducted by batch method in stoppered glass conical flasks. A stock solution of 500 mg L⁻¹ of Co (II) was prepared by dissolving 2.4705 g of Co (NO₃)₂ in 1000 ml of deionized water. The solution was diluted as required to obtain standard solution containing 10-100 mg L⁻¹ of Co (II). 100 ml of Co (II) solution of a desired concentration adjusted to a desired pH of the solution was adjusted by using 0.1 M hydrochloric acid or dilute sodium hydroxide solutions (Ion meter, model-686). The solutions were agitated for a predetermined period at 298±1 K in a shaking incubator (Jeio Tech SI-900R) with speed 220 rpm for 120 min. The suspension was filtered through a 0.2 µm membrane filter. The filtrate was analyzed by an atomic absorption spectrophotometer (AA-220, Shimadzu Co., Ltd) for cobalt content. All the chemicals used were of analytical grade and obtained from Aldrich chemical, USA.

To study the kinetic of Co²⁺ adsorption by Gns, 0.04, 0.06, and 0.07 g Gns was added to each glass vial containing 100 mL of 20, 40, and 60 mg L⁻¹ Co²⁺ solution. Experiments were carried out at temperature 298 K by placing the glass vials on a temperature controlled shaker. Samples were collected at 10 to 120 min added with a step size of 10 min for Co²⁺ analysis. The amount of uptake at time *t*, *q_t* (mg g⁻¹), was calculated by (Benguella *et al.*, 2002):

$$q_t = \frac{(C_o - C_t)V}{m} \quad (1)$$

Where C_o and C_t are Co²⁺ concentration (mg L⁻¹) at time 0 and *t*, respectively, *V* is the volume of the solution (L), and *m* is the mass of Gns (g).

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Isotherms studies were carried out with different initial concentration of Co (II) from 10 to 90 mg L⁻¹ in 100 mL vials with 0.03 to 0.08 g Gns at three temperatures (298, 308, and 318 K). The samples were collected at 120 min for Co⁺² analyses. The uptake of the adsorbate at equilibrium, q_e (mg g⁻¹), was calculated by:

$$q_e = \left(\frac{C_o - C_t}{m} \right) V \quad (2)$$

which C_e is the equilibrium concentration (mg L⁻¹).

RESULTS AND DISCUSSION

Characterizations of Gns

Graphite, graphite oxide (GO), and graphene nanosheets (Gns) were characterized by X-ray diffraction (XRD) as well. Figure 1 shows the XRD spectra of graphite, GO, and Gns. the powder X-ray diffraction patterns of graphite show a very sharp diffraction peak at 26.6° which shift to 13.5° on chemical reforming, indicating the formation of Gns. The FTIR spectra of the GO and Gns (Figure 2) displayed some absorption peaks belonging to various functional groups or different vibration modes. The band at about 3400 cm⁻¹ is indicative of the appearance of the stretching of –OH. The band at about 2900 cm⁻¹ assigned to the aliphatic C-H groups. The band at about 1600 cm⁻¹ can be ascribed to stretching mode of amide type C=O bond introduced by oxidation treatment of graphite by H₂SO₄ and H₂O₂. The bond at about 1100 cm⁻¹ can be ascribed to the appearance of C-N group, which is possibly introduced on the surface of graphene by hydrazine treatment. The surface morphology of Gns was characterized by TEM (Figure 3). TEM image shows that Gns film is transparent, which is usually rippled and entangled due to partial overlapping of Gns sheets.

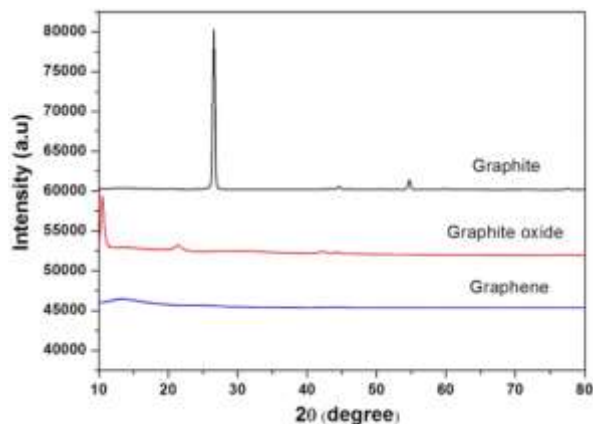


Figure 1: XRD plots for graphite, GO and Gns.

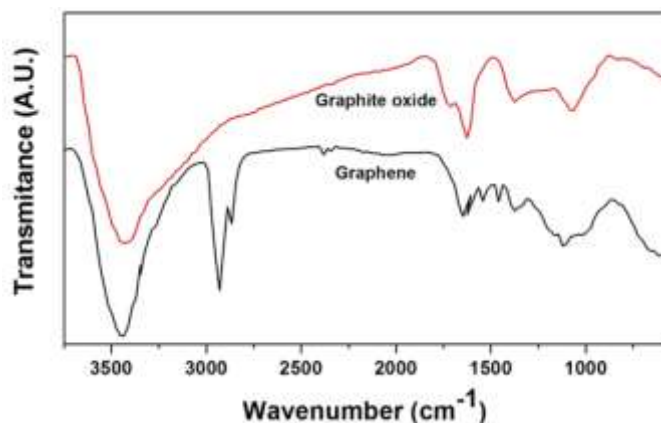


Figure 2: FTIR plots for GO and Gns.

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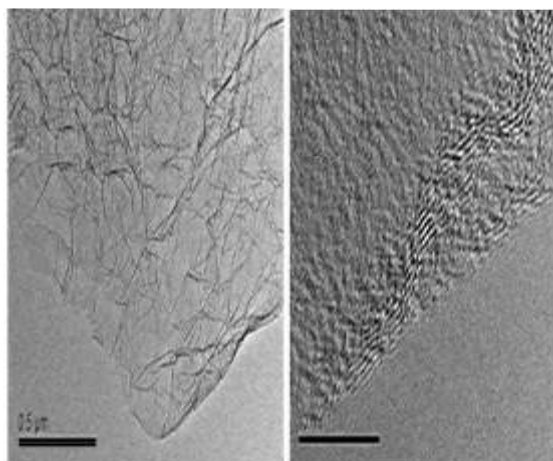


Figure 3: Micrographs of TEM images of prepared Gns.

Effect of Gns Dosage

The effect of Gns dosage on the percentage Co (II) removal at different initial Co (II) ions concentrations shown in figure 4. The experimental results revealed that Co (II) ions percent increases up to the optimum dosage, then percent removal dose not change with Gns dosage. As expected, the equilibrium concentration decreases with increasing adsorbent doses for a given initial Co (II) concentration, because for a fixed initial solute concentration, increasing adsorbent dose provides a greater surface area or more adsorption sites. After optimum dosage, all active sites are entirely exposed and the adsorbent surface is saturated. It is evident that for the noticeable removal of 20, 40, and 60mg L⁻¹ of Co (II) in 100 ml, minimum Gns dosage is 0.04, 0.06, and 0.07 mg.

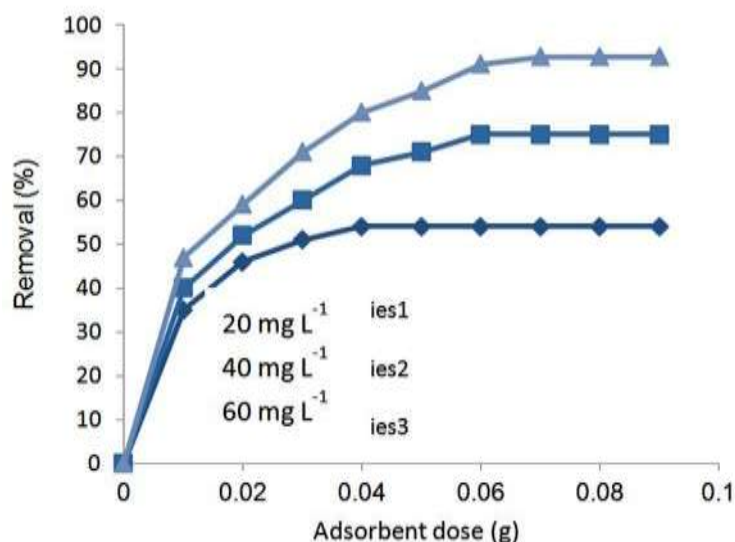


Figure 4: The effect of Gns dosage on Co (II) removal
Condition: pH=7, t_c=2h, T=298 k

Effect of pH

Solution pH is one of the most important parameters to determine the adsorption property of an adsorbent that it controlled the kind and amount surface charge of the adsorbent (Jimenez-Reyes *et al.*, 2010) Also

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amount pH reveals degree of ionization and speciation of adsorbate. Figure 5 illustrate the effect of the pH of the solution on the adsorption percentage of Co (II) ions adsorbed onto Gns. it is evident that increasing solution pH significantly increases the percent removal in the pH range from 2 to 7.0. The percent removal correspondingly increase from 32 and 40 to 51.5 and 71.1, respectively, for initial Co (II) concentration of 20 and 40 mg L⁻¹. At pH=2, the surface charge of Gns is positive because the H⁺ ion concentration in solution is high, competition between H⁺ and Co(II) reduces the adsorbent-adsorbate interaction.

Thus, the decrease of the adsorption percentage in acidic pH can be attributed to the repulsion between positive charges of Gns and Co (II) solution. Increasing solution pH increases the number of hydroxyl groups and negatively charged sites, thus, adsorption increases with the increase of pH solution.

For Gns isoelectric point pH (pH_{IEP}) is 4.7 thus, at pH >4.7, Gns surface is negatively charged and the surface functional groups on Gns are deprotonated, thus, increases adsorption) Li *et al.*, (2001).

The decrease of the adsorption capacity in alkaline pH may be attributed to the precipitation Co (OH)₂ (Hiemstra *et al.*, 2000).

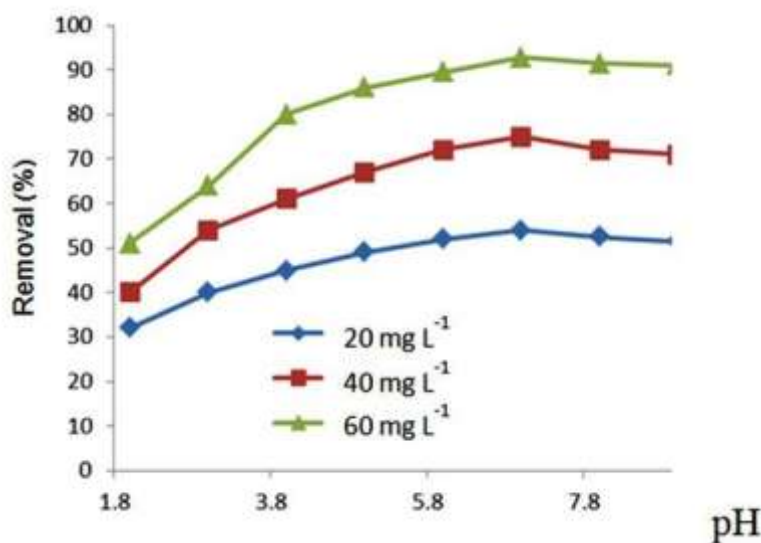


Figure 5: The effect of pH on Co (II) removal by Gns.

Condition: T=298, t_c=2h, Gns dosage=0.05 g.

Effect of Contact Time

The effect of contact time (t_c), on the adsorption percentage of Co (II) ion onto Gns was studied and shown in Figure 6.

A rather fast uptake occurs during the first 20 min of the adsorption process followed by a slower stage as the adsorbed amount of Co (II) reaches its equilibrium value. The figure reveals that increased agitation time increased the uptake of Co(II) and attained equilibrium in 60 min for 10 and 20, 80 min for 30 and 40, and 105 min for 50 and 60 mg L⁻¹ Co(II) solutions.

The removal curves are single, smooth, and continuous, indicating the possibility of the formation of monolayer coverage of Co (II) at the outer surface of Gns. According to the results, the equilibrium time was fixed at 120 min for the rest of the batch experiments to make sure that equilibrium is reached.

The percent removal was found to be 54, 75, and 92.75 at the initial concentrations of 20, 40, and 60 mg L⁻¹ of Co (II) solutions, respectively.

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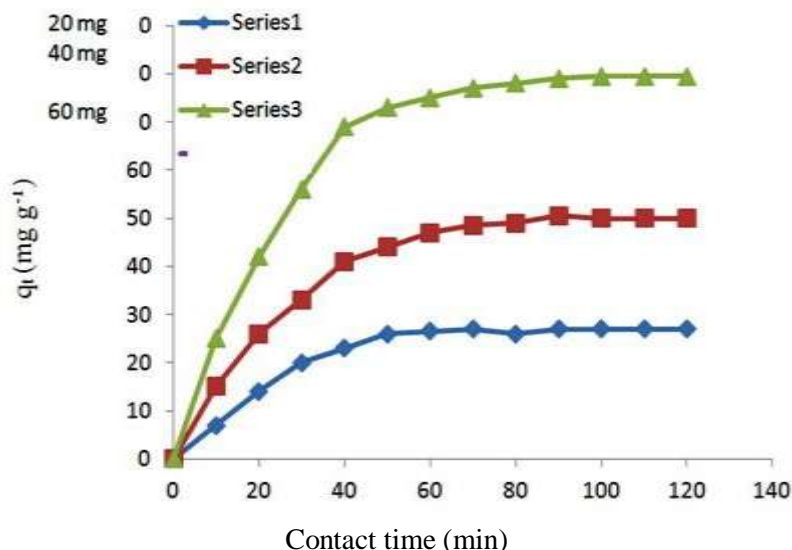


Figure 6: The effect of contact time on Co (II) adsorbed by Gns. Condition: pH=7, Gns dosage=0.05 (g), T=298 K.

Kinetic Studies

To evaluate the potential rate controlling steps such as chemical reaction, diffusion control and mass transport processes, the pseudo first-order, pseudo second-order, Elovich and intra-particle diffusion models were tested at the 298 K to slope and interpret the experimental data.

The linear form of pseudo first-order model is expressed as follows (Ho *et al.*, 2003).

$$\log (q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \tag{3}$$

Where q_e and q_t (mg g^{-1}) are the adsorption capacities at equilibrium and at time t (min) and k_1 (min^{-1}) is the pseudo first-order rate constant respectively. Lagergren's equation (3) describes adsorption in solid-liquid systems based on the sorption capacity of solids (Ho 2004). In the present study a concentration of Co^{2+} over the range 20 to 60 mg g^{-1} was examined and the k_1 and q_e were calculated using the slope and intercept of plots of $\log (q_e - q_t)$ vs. t (Figure 7A, Table 1).

The pseudo second-order model can be represented by the following linear from (Ho, 2005)

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

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

The values k_2 and q_e are determined from the intercept and slope of the plot of t/q_t vs. t (Figure 7B, Table 1). This model assumes that adsorption occurs on localized sites with no interaction between adsorbed material, maximum adsorption represents saturated monolayer adsorption and negligible rate of desorption compared to adsorption rate leading to the chemisorption through sharing or exchange of valence electrons between adsorbate-adsorbent via covalent bond formation (Ho *et al.*, 1999). The Elovich model is presented by the following equation (Li *et al.*, 2005):

$$q_t = \frac{1}{\beta} \ln \alpha \beta + \frac{1}{\beta} \ln t \tag{5}$$

Where α (mg/g min) is the initial adsorption rate and β (g/mg) desorption constant. The values α and β are determined from the intercept and slope of the plot of q_t vs. $\ln t$ (Figure 7C, Table 1). As it can be seen from Table 1, absorption rate increases while de-absorption rate decrease with increase of Co^{+2} concentration.

The validity of each kinetic model was checked by the fitted straight lines and depicted in Figure 7 and Table 1. Furthermore the correlation coefficient (R^2) for the pseudo first-order kinetic model fit is 0.9939, much higher the correlation coefficients derived from pseudo second-order and Elovich model fits. This suggests that Co^{2+} adsorption followed pseudo first-order model.

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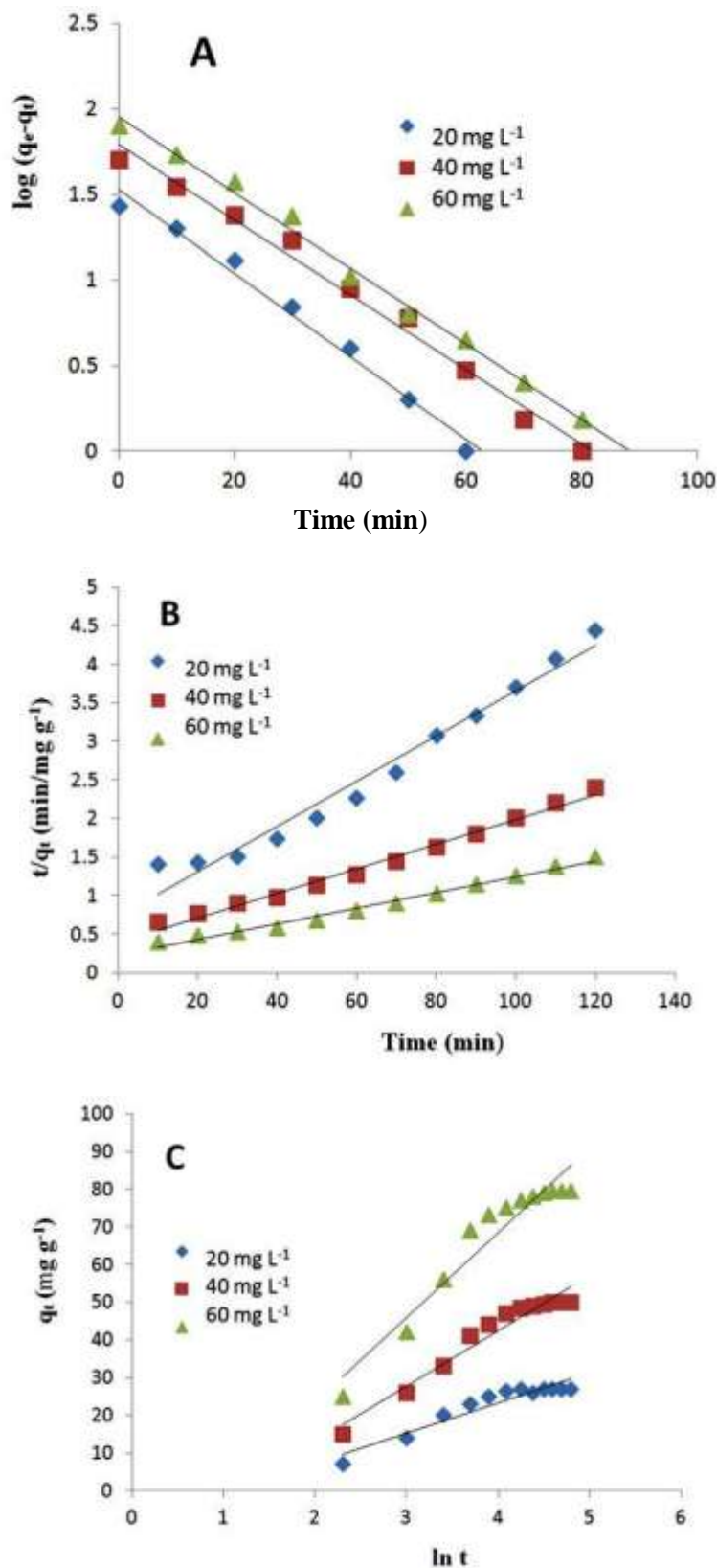


Figure7: Kinetic analysis of cobalt (II) adsorbed by Gns: (A) pseudo first-order model, (B) pseudo second-order model, (C) Elovich model.

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Table 1: Parameters of three kinds of kinetic models

Kinetic model	Parameter	Values		
		20 (mg/L)	40 (mg/L)	60 (mg/L)
Experimental data	$q_{e,exp}$ (mg g ⁻¹)	27.10	50.01	79.80
Pseudo first-order	$q_{e,cal}$ (mg g ⁻¹)	33.550	61.810	89.990
	k_1 (min ⁻¹)	0.0560	0.0504	0.0509
	R^2	0.9862	0.9879	0.9939
Pseudo second-order	$q_{e,cal}$ (mg g ⁻¹)	34.010	62.890	98.030
	k_2 (g/ mg min) × 10 ⁻³	1.20	0.630	0.460
	R^2	0.9710	0.9869	0.9861
Elovich	α (mg/g min)	1.56	4.79	8.70
	β (g/mg)	0.210	0.068	0.044
	R^2	0.9042	0.9504	0.9273

Adsorption Mechanisms

The adsorption mechanism of adsorbate onto adsorbent follows three steps (Chingombe *et al.*, 2006): (1) Surface diffusion where the sorbate is transported from the bulk solution to the external surface of sorbent, (2) Intra-particle diffusion, where sorbet molecules move into the interior of sorbent particles, (3) Adsorption on the interior sits of the sorbent. The slowest of the tree steps controls the overall rate of the process. The weber –morris model is a widely used intra-particle diffusion model to predict the rate controlling step (Taqvi *et al.*, 2007). The rate constant of intra-particle diffusion (k_i) at the stage i was determined using the following equation:

$$q_t = K_i t^{0.5} + C \tag{6}$$

Where C is the intercept at stage i. The value of C is related to the thickness of the boundary layer. The values C and k_i at different initial C_0 (II) concentrations are determined from the intercept and slope of the plot of q_t vs. $t^{1/2}$ (Figure 8, Table 2). Given the multi-linear of this plot for adsorption of Co (II) on Gns particles, this suggests that adsorption occurred in three phases. The first steeper section represents film diffusion, the second subdued portion is the gradual adsorption stage, where intra-particle diffusion is rate-limiting and the third section is final equilibrium stage. The intra-particle diffusion rate constant k_i was calculated from the slope of the second section. The intercept values increased with the increasing C_0 (II) initial concentration (Table 2).

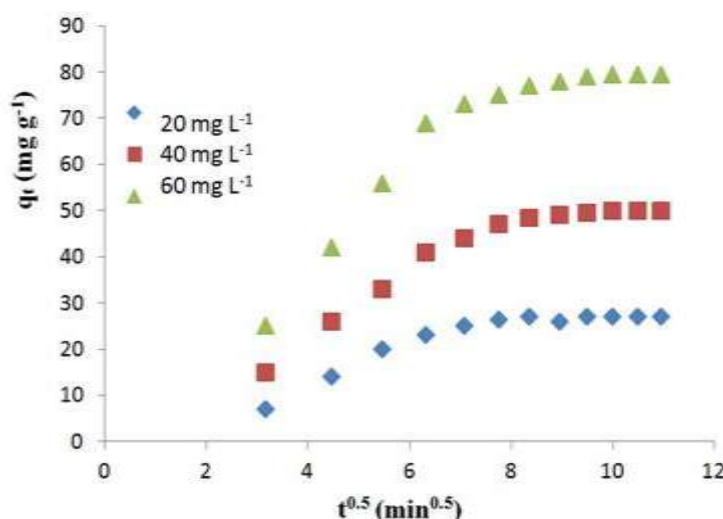


Figure 8: Intra-particle diffusion plots for Co⁺² adsorption on Gns.

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Table 2: Intra-particle diffusion coefficients and intercept values (C) for Co⁺² adsorption on Gns particles at different concentrations of Co (II)

Concentration of Co(II) (mg L ⁻¹)	k _i (mg g ⁻¹ min ^{-0.5})	C
20	1.5489	14.032
40	0.8768	41.162
60	1.7537	62.328

Adsorption Isotherm

An adsorption isotherm is characterized by certain constant values, which express the surface properties of the adsorbent, and could also be used to compare the adsorptive capacities of the adsorbent for different pollutants. Equilibrium data can be analyzed using the Langmuir, Freundlich, Temkin, Dubinin-radushkevich (D-R), and Brunauer- Emmett - teller (BET) isotherm models.

The Langmuire isotherm assumes monolayer on a homogeneous surface without any interaction between adsorbed ions and with uniform binding sites and equivalent sorption energies (Tan *et al.*, 2009). The linear form of Langmuire equation is expressed as (Langmuir, 1916):

$$\frac{1}{q_e} = \frac{1}{K_L C_e q_m} + \frac{1}{q_m} \tag{7}$$

where q_m (mgg⁻¹) is the maximum adsorption capacity corresponding to complete monolayer coverage and K_L (L/mg) is the Langmuire constant related to adsorption capacity and energy of adsorption [18]. The slope and intercept of plot of 1/q_e versus 1/C_e at different temperatures, were used to calculated L and q_m (Figure 10A). Langmuire isotherm parameters fit (Table 3) for Co⁺² adsorption on Gns yielded isotherm that were in good agreement with observed behavior.

The essential characteristic separation constant factor, R_L, for the Langmuire adsorption is defined as follows:

$$R_L = \frac{1}{1+K_L C_o} \tag{8}$$

The value of R_L illustrate the shape of the isotherm to be either unfavorable (R_L>1), linear (R_L=1), favorable (0<R_L<1) or irreversible (R_L=0). The R_L values between 0 and 1 indicate favorable adsorption [20]. In the present study, the calculated values of R_L are observed to be in the range.0.52-0.15 at all studied temperatures (Figure 9), indicating that the adsorption of Co (II) onto Gns is favorable.

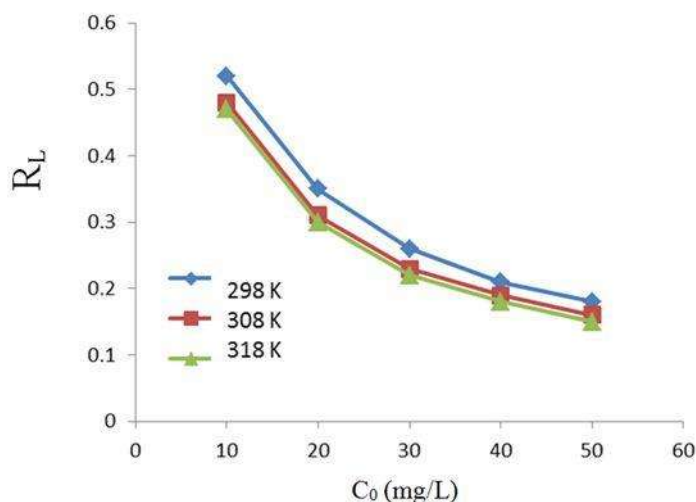


Figure 9: The effect of Co (II) initial concentrations on R_L.

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The Freundlich equation is an empirical equation based on adsorption on a heterogeneous surface. This isotherm is applicable to both monolayer (chemisorption) and multilayer adsorption with interaction between adsorbed molecules. The linear form of the Freundlich isotherm model is described as;

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (9)$$

K_F (L/g) and n are the Freundlich constants related to adsorption capacity and adsorption intensity (Celebi *et al.*, 2007). The values of K_F and n are determined from the intercept and slope of a plot of $\log q_e$ versus $\log C_e$ at different temperatures, were used to calculate the K_F and n (Figure 10B), and are listed in Table 3. The correlation coefficients (0.9480-0.9775) and lower n values of this model show that the Freundlich model has lower efficiency compared to the Langmuir model.

The Temkin isotherm model assumes that the adsorption energy decreases linearly with the surface coverage due to adsorbent-adsorbate interaction (Freundlich 1906) Linear plots for Temkin model, which consider chemisorption of an adsorbate onto the adsorbent (Wang *et al.*, 2005). The linearized form of the Temkin isotherm model is given by the equation:

$$q_e = B_T \ln A_T + B_T \ln C_e \quad (10)$$

$$B_T = \frac{RT}{K_T} \quad (11)$$

A_T (Lmg⁻¹) is Temkin isotherm constant. A_T is related to binding constant and K_T (Jmol⁻¹) is the Temkin constant that is related to the heat of sorption (Akkaya *et al.*, 2010). K_T and A_T are determined from the slope and intercept of a plot of q_e versus $\ln C_e$, at different temperatures (Figure 10C), and are listed in table 3. The heat of Co²⁺ adsorption onto Gns was found to decrease from 18.80-18.07 Jmol⁻¹ with increase in temperature from 298-318 K. The correlation coefficient (R^2) obtained from Temkin model were comparable to that obtained for Langmuir and Freundlich equations, which explain the inapplicability of Temkin model to the adsorption of Co²⁺ onto Gns.

The D-R isotherm model is a semi-empirical equation. It assumes that the adsorption has a multilayer character (Gupta *et al.*, 2010). The linear form of D-R equation is expressed as:

$$\ln q_e = \ln q_d - \beta \varepsilon^2 \quad (12)$$

Where q_d is the D-R constant (mg g⁻¹), ε is Polani potential (J/mol), which is defined as:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (13)$$

β (mol J⁻¹)² is the D-R isotherm constant related to free energy:

$$E = -0.7\beta^{-0.5} \quad (14)$$

It has been reported that the adsorption should be of chemisorption if adsorption energy has value between -8.0 and -16.0 kJ mol⁻¹ or physisorption if the value is below 8.0 kJ mol⁻¹. In the present study, the calculated values of E are observed to be in the range -127.70 to -154.84 J mol⁻¹ (Hutson *et al.*, 1997). In all temperatures, q_d and β are determined from the intercept and slope of a plot of $\ln q_e$ versus ε^2 (Figure 10D) and are listed in Table 3. The magnitude of the correlation coefficients for the D-R isotherm is low when compared to the Langmuir isotherm model (Table 3). This suggests that the Co (II) adsorption onto Gns can be physisorption.

The BET isotherm model is assumed to be multilayer adsorption. The linear form of the BET isotherm is described as (Brunauer *et al.*, 1938):

$$\frac{C_e}{(C_s - C_e)q_e} = \frac{1}{K_B q_m} + \frac{K_B - 1}{K_B q_m} \left(\frac{C_e}{C_s} \right) \quad (15)$$

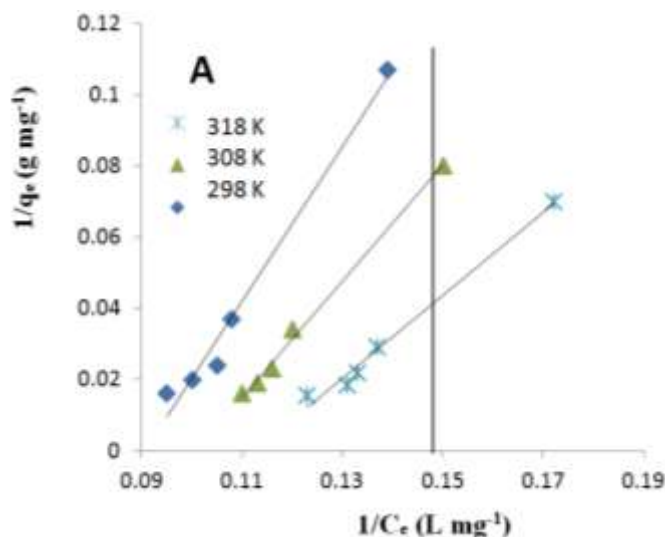
$$C_s = C_0 - C_e \quad (16)$$

C_s is adsorbed concentration (mg L⁻¹) and K_B (g/mg) is BET isotherm constant related with surface interaction energy. K_B and q_m are determined from the intercept and slope of a plot of $\frac{C_e}{(C_s - C_e)q_e}$ versus $\frac{C_e}{C_s}$ (figure 10E) and are listed in Table 3. According to the experimental data, with increase of temperature, Co²⁺ ions adsorb physically onto Gns.

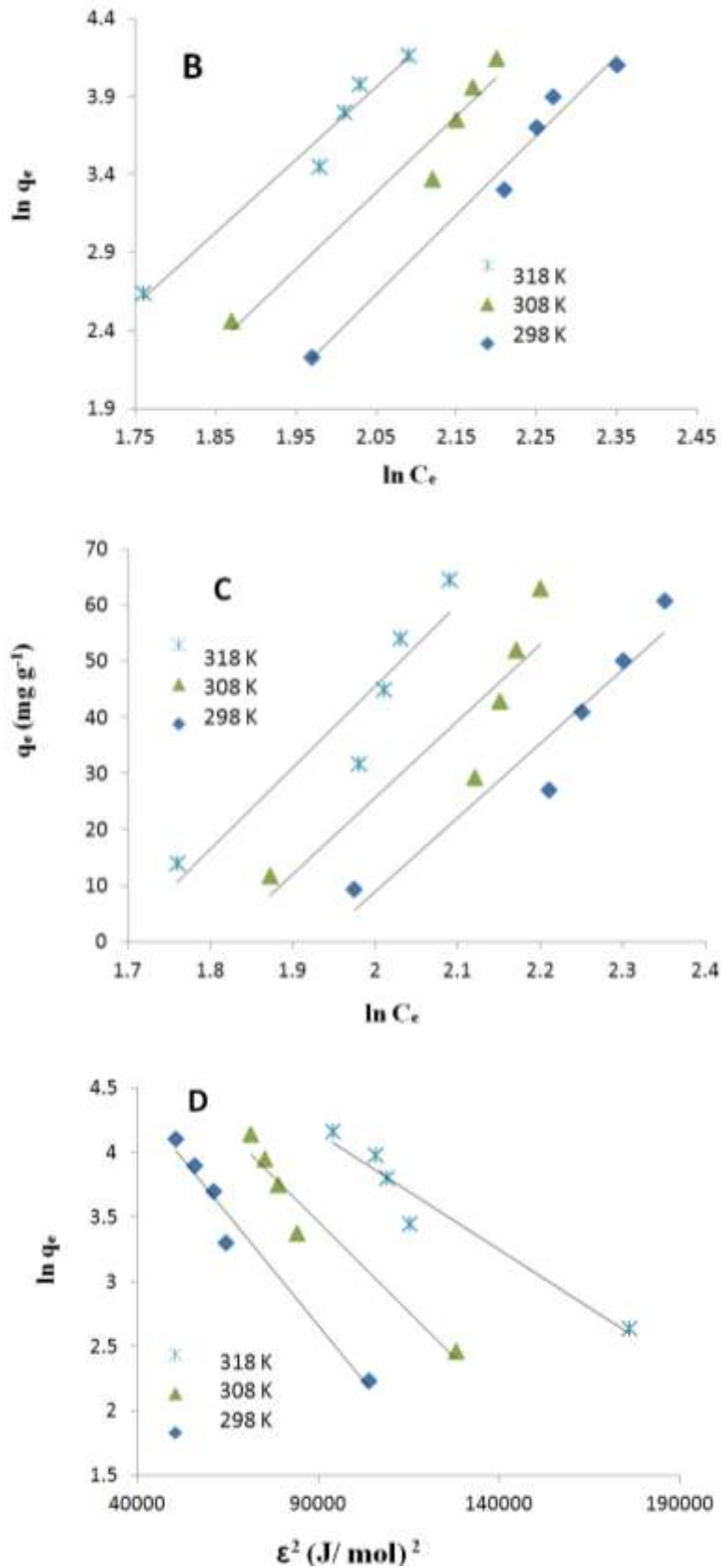
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Table 3: Langmuire, Freundlich, Temkin, D-R, and BET isotherm model parameters and correlation coefficients for adsorption of cobalt (II) ion on Gns particles

Isotherm	Temperature(K)	Parameters		
		q_m (mg/g)	K_L (L/mg)	R^2
Langmuire	298	5.08	0.09	0.9828
	308	6.10	0.10	0.9956
	318	7.60	0.112	0.9879
		Parameters		
		$K_F \times 10^4$ (L/g)	n	R^2
Freundlich	298	3.90	0.196	0.9775
	308	12.00	0.205	0.9480
	318	36.00	0.214	0.9664
		Parameters		
		A_T (L mg ⁻¹)	K_T (J mol ⁻¹)	R^2
Temkin	298	0.145	18.80	0.9122
	308	0.163	18.76	0.8130
	318	0.184	18.07	0.8800
		Parameters		
		q_d (mg g ⁻¹)	$\beta \times 10^{-5}$ (mol J ⁻¹) ²	R^2
D-R	298	315.38	3.0	0.9678
	308	394.61	3.0	0.9441
	318	322.56	2.0	0.9427
		Parameters		
		q_m (mg g ⁻¹)	K_B (g mg ⁻¹)	R^2
BET	298	4.50	-3.51	0.8309
	308	11.00	-4.04	0.9610



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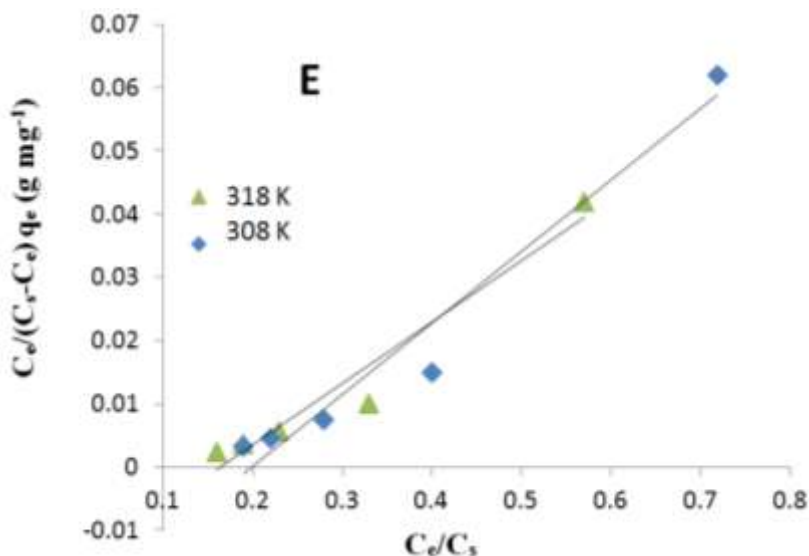


Figure 10: Linearized (A) Langmuir, (B) Freundlich, (C) Temkin, (D) D-R, and (E) BET isotherm for Co²⁺ adsorption on Gns particles at different temperatures.

Thermodynamic Parameters

The thermodynamic parameters of adsorption process can be determined from the variation of thermodynamic equilibrium constant, K_o . Which K_o is defined as follow (Calvet *et al.*, 1989):

$$K_o = \frac{a_s}{a_e} = \frac{v_s C_s}{v_e C_e} \tag{17}$$

Where a_s is the activity of adsorbed Co²⁺ and a_e is the activity of Co²⁺ in solution at equilibrium, C_s is the amount of Co²⁺ adsorbed by per mass of Gns (mg g⁻¹), v_s is the activity coefficient of adsorbed Co²⁺ and v_e is the activity coefficient of Co²⁺ in solution at equilibrium.

The expression of K_o Can be simplified by assuming that the C_s and C_e approaches to zero thus v_s and v_e approaches unit. K_o at different temperatures was determined by plotting $\ln(C_s/C_e)$ versus C_s (Figure 11) and extrapolating C_s to zero.

The calculated values of K_o at temperatures of 298, 308, and 318 K are 1.107, 1.281, and 1.546, respectively. K_o increased with temperature indicating that the adsorption was endothermic.

The adsorption standard free energy change (ΔG^0), average standard enthalpy change (ΔH^0), and average standard entropy change (ΔS^0) were calculated using the equations (18), (19), and (20).

$$\Delta G^0 = -RT \ln K_o \tag{18}$$

$$\ln K_o (T_3) - \ln K_o (T_1) = -\frac{\Delta H^0}{R} (T_3^{-1} - T_1^{-1}) \tag{19}$$

$$\Delta S^0 = -\frac{\Delta G^0 - \Delta H^0}{T} \tag{20}$$

The thermodynamic parameters are listed in Table 4. Negative values of ΔG^0 indicate spontaneous adsorption and the degree of spontaneity of the reaction increases with increasing temperature. The positive standard enthalpy change suggests that the adsorption Co²⁺ by Gns is endothermic, which is supported by the increasing adsorption of Co²⁺ with the increase in temperature.

The positive standard entropy change indicated increased randomness at the adsorbent-solution interface during the adsorption of Co²⁺ onto Gns.

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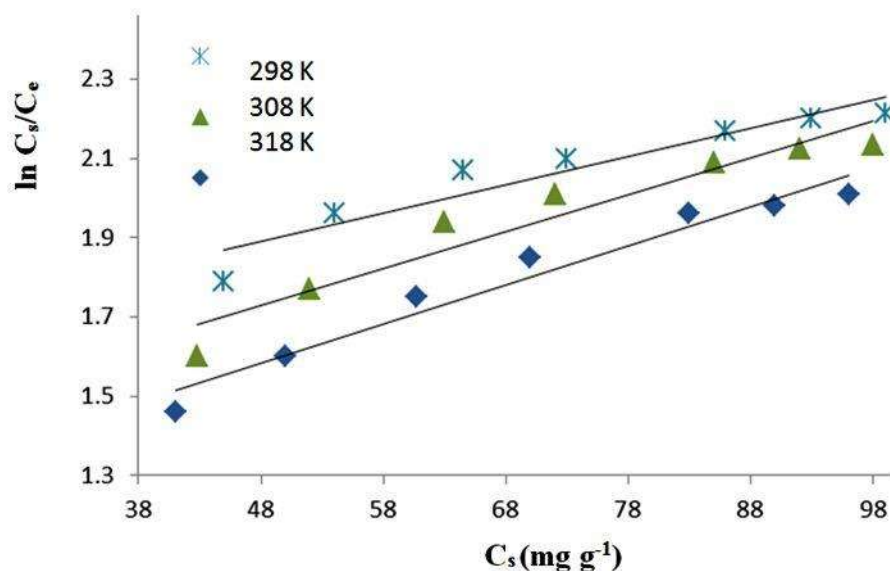


Figure 11: Plots of $\ln(C_s/C_e)$ versus C_s for Co (II) at different temperatures

Table 4: Thermodynamic parameters for adsorption of Co (II) onto nG particles

Temperature (K)	ΔG^0 (kJ mol ⁻¹)	ΔH^0 (kJ mol ⁻¹)	ΔS^0 (J mol ⁻¹ K ⁻¹)
298	-0.253	1.738	6.68
308	-0.635	1.738	7.70
318	-1.153	1.738	9.09

ACKNOWLEDGEMENT

Graphene nanosheets (Gns) can be used as an effective adsorbent for removing Co (II) from aqueous solutions. Increasing the Co (II) initial concentration decrease the cobalt adsorption rate. Co²⁺ removal investigated through adsorption at pH=7 condition at t_c=120 min in equilibrium-batch mode system. Increasing the initial Co²⁺ concentration decreased the Co²⁺ adsorption rate but the adsorption capacity was increased. The pseudo first-order kinetic model accurately described the adsorption kinetics. According to the rate-mechanism the second section contributes to the intra-particle diffusion as rate-limiting step. The Langmuire isotherm gave a better fit than the Freundlich and Temkin isotherm, thus indicating the applicability of monolayer coverage of Co²⁺ion on Gns surface. The experimental data for the D-R and BET model showed that the adsorption of Co²⁺ions onto Gns can be multilayer. Thermodynamic analysis showed that the adsorption process was endothermic and spontaneous in nature.

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