Kinetics and Thermodynamics Studies of Cobalt (II) Adsorption onto Alumina

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Abstract

Adsorption for alumina-cobalt (II) ions solution system was investigated as a function of adsorbent dose, contact time, temperature, pH of solution and initial concentration of adsorbate. The optimum conditions for removal of cobalt (II) ions were found as pH 7.5-8.5, adsorbent dose of solution 20 gl^{-1}, equilibrium time 90 minutes and initial concentration range 5-50 mgl^{-1}. Pseudo-second-order kinetics was observed for adsorption of cobalt while cobalt removal process does not seem to control the intra-particle diffusion. Langmuir, Freundlich and Dubnin-Radushkevich isotherm models were applied to analyze the equilibrium isotherms for adsorption of cobalt (II) ions onto alumina. The experimental results indicated that equilibrium data follows the Langmuir model within used concentration range.

Keywords: Cobalt, Alumina, Adsorption kinetics, Isotherms, Thermodynamics

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Introduction

Exposure to cobalt ions (II) is natural and anthropogenic due to tremendous use in last few decades in many industries such as electroplating, mining, electronics, pigments and paints. As a result, cobalt (II) ions have found its way to water and soil which are used by humans. Cobalt and its salts may be highly soluble to practically insoluble in water [1]. The adsorption of cobalt (II) ions in the soil can occur rapidly within 1 to 2 hrs. Various mineral oxides such as manganese and iron oxides, goethite, alumino-silicates and some organic substances can retain cobalt [2]. Cobalt can move easily from soil to underground water and is stable in water with half-life of more than 200 days [3].

Cobalt has both harmful as well as beneficial effects on human health. Although there is no standard regarding cobalt maximum permissible concentration (mgl^{-1}) in portable water, however, it is always desirable that industrial wastewater must be treated for cobalt (II) ions removal before being discharged into ecosystem. Among the various available methods, the adsorption seems to be the most cost effective, efficient and reliable especially for treating domestic and industrial effluents with low to moderate concentration [4, 5]. Alumina (Al_2O_3) is extensively used as an adsorbent to remove metal ions, dyes and organic solvents from solutions because of its higher porosity, surface area and adsorption capacity [6]. Therefore, alumina was applied as an adsorbent for the removal of cobalt (II) ions from aqueous medium in this study. α-alumina specifically was used for this study. Various studies already have been conducted on the adsorption of heavy metals and other toxic materials from aqueous solutions using alumina [7-10].

The aim of present investigation was to explore the possibility and extent of removing cobalt (II) ions from aqueous medium employing alumina as an adsorbent. For this purpose, the effect of various parameters affecting the adsorption process like adsorbent dose, contact time, temperature, pH of solution and initial concentration of adsorbate was evaluated. The Freundlich, Langmuir and Dubinin-Radushkveich

adsorption isotherms models were applied to define the adsorption equilibrium. The thermodynamics and kinetics of adsorption process were also evaluated with the adsorption equilibrium data.

Materials and Methods
Adsorbent

Calcined alumina dried was of AR grade (BDH Chemicals Ltd. England), having a surface area significantly over 200 m^2/g. Impurities were minimized by washing with hot distilled water. The washed alumina was dried in electric oven maintained at $105^{\circ}C$ and applied as adsorbent without any further chemical treatment.

Adsorbate

AR grade cobalt chloride hexa-hydrate ($CoCl_2.6H_2O$) was dissolved in distilled water to prepare stock solution of cobalt (II) ions (1000 mgl^{-1}). The concentration range of cobalt (II) ions was varied from 5 to 50 mgl^{-1} by diluting the stock solution. The cobalt concentration in the solution was determined by complexometric titrations using standard EDTA solution [22].

Adsorption studies

Adsorption of cobalt (II) ions onto alumina was investigated by batch type tests [23]. Alumina (0.5g) was equilibrated with cobalt solution (25ml) of known concentration in Pyrex beakers for a known period of time in a Gallen Kamp thermostated water bath shaker (Model: BKS No.305-166, UK) at a fixed temperature. After attaining the equilibrium the suspension was put in a test tube fitted with stopper and centrifuged for 5 min at 4500 rpm in Wirowka-Type WE-1 centrifuge. It was filtered using medium fast filter paper # 41. The pH of solution was checked with the help of Hanna digital pH meter (Model: HI8417). All adsorption experiments were done at natural pH except where the pH was varied. To investigate the effect of pH, the pH of suspension was maintained by NH_4OH and HNO_3 in one set of tests. The pH of supernatant solution was measured after equilibration. Initial concentration 'C_i, and equilibrium concentration 'C_e, of cobalt (II) ions in the solution was determined by volumetric method

with standard EDTA (0.05M) solution. The adsorption as percentage extraction of cobalt (II) ions onto alumina and the quantity of cobalt (II) ions adsorbed per unit weight of the alumina, q_e, were determined by following equations.

$$\% \text{ Adsorption} = \frac{(C_i - C_e)}{C_i} \times 100 \qquad (1)$$

$$q_e = \frac{(C_i - C_e)V}{W} \qquad (2)$$

Where 'C_i, is initial concentration (mgl^{-1}) and 'C_e, is equilibrium concentration (mgl^{-1}) of cobalt solution respectively, 'W' is the weight (g) of substrate where as 'V' is the volume (l) of solution. Adsorption capacity of cobalt species has been evaluated from Langmuir, Freundlich, and Dubinin-Raduskevich (D-R) isotherm models at three different temperatures (263K, 289K and 306K). The concentration of cobalt (II) ions was studied in the range of *5 to 50 mgl^{-1}*.

Effect of pH

The influence of pH of solution was investigated within the range from 2.5 to 12.5 keeping all other parameters constant (contact time = 90 min, adsorbent dose = 0.5 g, temperature = 306 K and cobalt concentration = 10 mgl^{-1}). The results (Fig. 1b) showed that the adsorption of cobalt ions on alumina depends upon pH. A much greater adsorptive capacity of cobalt (II) ions was observed at natural pH of the solution i.e. 7.5- 8.5. It is due to the fact that pH of cobalt solution greatly influences the surface charge of adsorbent. Surface charge of particles become positive with reduced pH leading to competition between the cobalt ions and of hydrogen ions for the binding sites of adsorbent. As a result of this competition, metal ions desorbs from the binding sites of adsorbent at lower pH value. Similarly, a decreasing trend in adsorption of cobalt (II) ions was observed at a pH greater than 9. At higher pH, soluble cobalt complexes are formed leading to decreased adsorption.

Effect of initial concentration of adsorbate

The effect of initial concentration of adsorbate onto alumina was investigated by

varying the initial concentration of cobalt (II) in solution from 5 to 50 mgl^{-1}. As is evident from the results (Fig. 1c & 1d) the adsorption capacities 'q_e' (mg/g) of alumina increases with increasing cobalt concentration, whereas the percentage of cobalt (II) ions adsorption showed opposite trend. It is due to the fact that the initial concentration of cobalt (II) ions provides the necessary driving force to overcome the resistance to mass transfer of cobalt (II) ions between solid phase and liquid phase. By increasing the initial concentration of cobalt (II) ions the interaction between cobalt (II) ions and alumina is produced. Similarly, cobalt adsorption increases with rise in initial concentration of cobalt (II) ions. This effect may be attributed to enhancement in driving force of concentration gradient generated by increment in initial concentration of cobalt (II) ions leading to greater adsorption capacity 'q_e' mg/g [11].

Results and Discussion
Effect of contact time

The effect of contact time on the adsorption of cobalt (II) ions onto alumina was studied at 360 K by varying it from 10 to 120 min for different initial concentrations of cobalt (II) ions within the range from 5 to 50 mgl^{-1}. (Fig. 1a) illustrates the variation of adsorption percentage with contact time. The results showed that the rate of cobalt (II) ions adsorption onto alumina is fast at 306 K and equilibrium is reached instantaneously after mixing. No significant change in percentage removal of cobalt ions was observed up to 90 min. Therefore, equilibrium contact time of 90 min was selected for next series of tests.
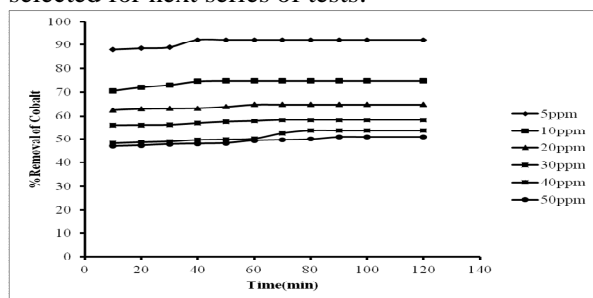

Figure 1a: **Effect of contact time (t) on the adsorption of Co (II) ions**

Experimental conditions:

Initial Conc. (C$_i$)	=	5-50 ppm
Temperature (T)	=	306 K
Adsorbent conc. (m)	=	20 g/l
pH of solution	=	7.5
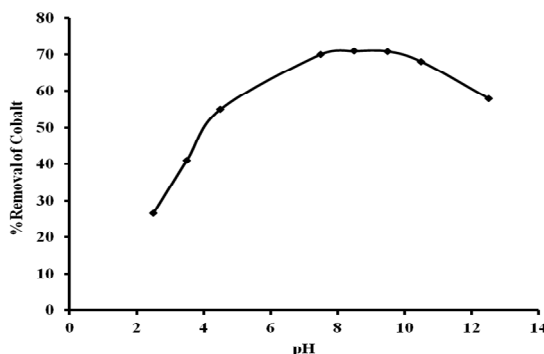
Figure **1b: Effect of pH on the adsorption of Co (II) ions.**
Experimental conditions:

Initial Conc. (C$_i$)	=	10 ppm
Temperature (T)	=	306 K
Adsorbent conc. (m)	=	20 g/l
pH of solution	=	varied

Effect of pH

The influence of pH of solution was investigated within the range from 2.5 to 12.5 keeping all other parameters constant (contact time = 90 min, adsorbent dose = 0.5 g, temperature = 306 K and cobalt concentration = 10 mgl^{-1}). The results (Fig. 1b) showed that the adsorption of cobalt ions on alumina depends upon pH. A much greater adsorptive capacity of cobalt (II) ions was observed at natural pH of the solution i.e. 7.5- 8.5. It is due to the fact that pH of cobalt solution greatly influences the surface charge of adsorbent. Surface charge of particles become positive with reduced pH leading to competition between the cobalt ions and of hydrogen ions for the binding sites of adsorbent. As a result of this competition, metal ions desorbs from the binding sites of adsorbent at lower pH value. Similarly, a decreasing trend in adsorption of cobalt (II) ions was observed at a pH greater than 9. At higher pH, soluble cobalt complexes are formed leading to decreased adsorption.

Effect of initial concentration of adsorbate

The effect of initial concentration of adsorbate onto alumina was investigated by varying the initial concentration of cobalt (II) in solution from 5 to 50 mgl^{-1}. As is evident from the results (Fig. 1c & 1d) the adsorption capacities 'q_e' (mg/g) of alumina increases with increasing cobalt concentration, whereas the percentage of cobalt

(II) ions adsorption showed opposite trend. It is due to the fact that the initial concentration of cobalt (II) ions provides the necessary driving force to overcome the resistance to mass transfer of cobalt (II) ions between solid phase and liquid phase. By increasing the initial concentration of cobalt (II) ions the interaction between cobalt (II) ions and alumina is produced. Similarly, cobalt adsorption increases with rise in initial concentration of cobalt (II) ions. This effect may be attributed to enhancement in driving force of concentration gradient generated by increment in initial concentration of cobalt (II) ions leading to greater adsorption capacity 'q_e' mg/g [11].
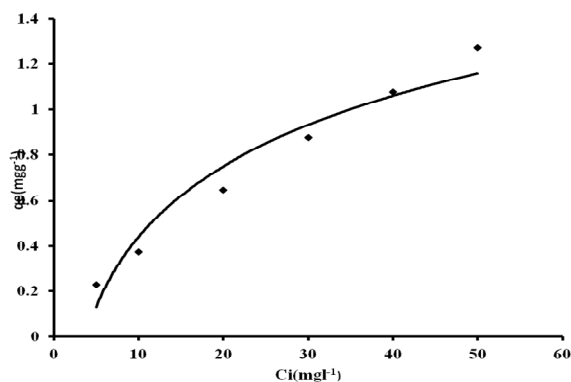

Figure 1e: **Effect of initial concentration (C_i) of Co (II) ions on adsorption capacity**
Experimental conditions:

Initial Conc. (C_i)	=	5-50 ppm
Temperature (T)	=	306 K
Adsorbent conc. (m)	=	20 g/l
pH of solution	=	7.5
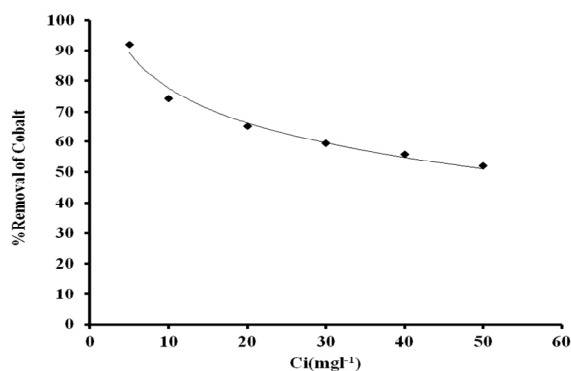
Figure 1d: **Effect of initial concentration (C_i) of Co (II) ions on % removal of Co (II) ions**

Experimental conditions:		
Initial Conc. (C_i)	=	10 ppm
Temperature (T)	=	306 K
Adsorbent conc. (m)	=	20 g/l
pH of solution	=	7.5

Effect of adsorbent amount (m)

Effect of cobalt adsorption onto alumina amount (*m*) was studied at 306 K at the 10 mgl^{-1} and 20 mgl^{-1} initial concentrations of cobalt (II) and varying the adsorbent amount and keeping the volume of the metal solution constant. The result obtained is presented in Fig. 1e. It can be seen that removal of cobalt became almost constant after increasing up to a certain limit. The increase in cobalt adsorption with increasing in amount of alumina (*m*) may be due to enhanced surface area leading to more adsorption sites. At $m < 15$ gl^{-1} (i.e. 0.375g /25 ml for the batch experiment), the surface of adsorbent gets almost saturated with cobalt (II) ions and consequently the residual concentration of cobalt (II) ions in the solution is greater. The cobalt removal increases with an increase in *m*, due to increased contents of adsorbent. At m > 20 gl^{-1} (i.e. 0.5 g/25 ml for the batch experiment) the cobalt removal became low because surface concentration and solution concentration of cobalt (II) ions are equilibrated with each other. It can be seen that at about $m = 20$ gl^{-1}, the removal efficiency remains nearly consistent.
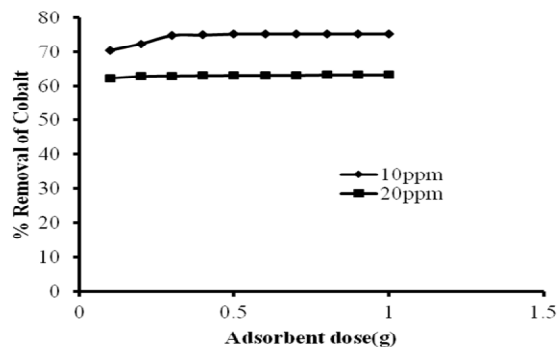

Figure 1e: **Effect of adsorbent dose (m) on % removal of Co (II) ions**
Experimental conditions:

Initial Conc. (C_i)	=	10 and 20 ppm
Temperature (T)	=	306 K
Adsorbent conc. (m)	=	20 g/l
pH of solution	=	7.5

Adsorption kinetic studies

Five kinetic model equations were used for interpretation of the experimental results. These include Lagergren first-order equation and pseudo-second-order equation, Elovich equation,

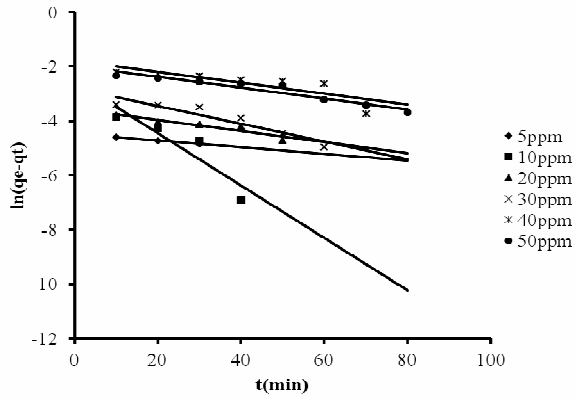Bangham's equation and intra-particle diffusion equation.

Figure 2a: **Pseudo-first-order kinetics plot**
Experimental conditions:
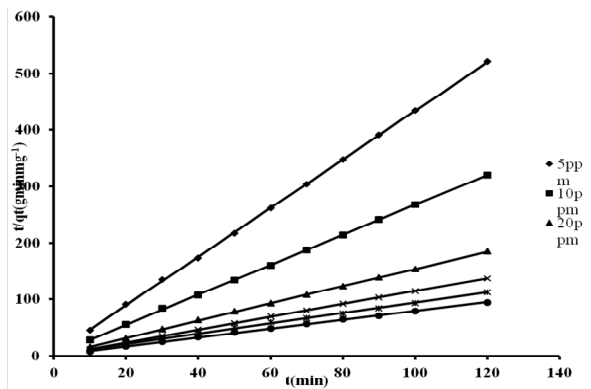Temperature (T) = 306 K
Adsorbent conc. (m) = 20 *g/l*

Figure 2b: **Pseudo-second-order kinetics plot**
Experimental conditions:
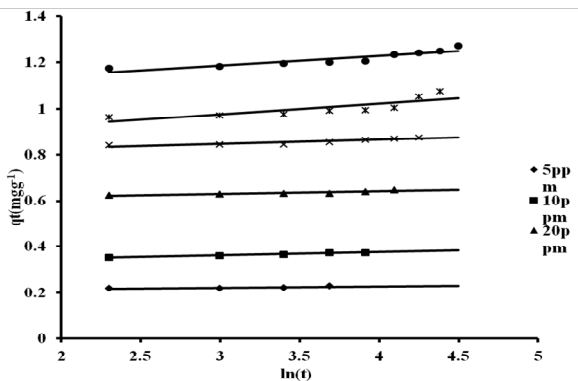Temperature (T) = 306 K
Adsorbent conc. (m) = 20 *g/l*

Figure 2c: **Elovich kinetic model**
Experimental conditions:
Temperature (T) = 306 K
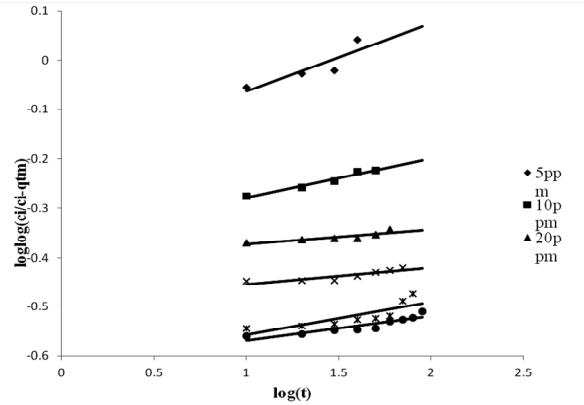Adsorbent conc. (m) = 20 *g/l*

Figure 2d: **Bangham kinetic model**
Experimental conditions:
Temperature (T) = 306 K
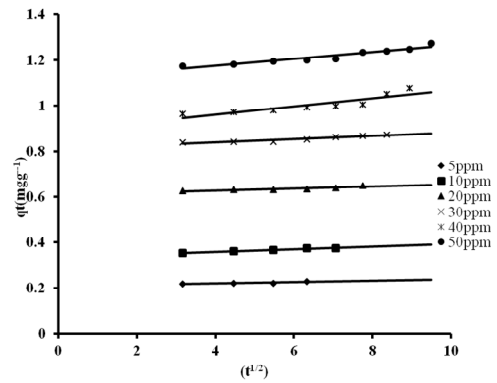Adsorbent conc. (m) = 20 *g/l*

Figure 2e: **Intra-particle diffusion model**
Experimental conditions:
Temperature (T) = 306 K
Adsorbent conc. (m) = 20 *g/l*

The Lagergren first-order rate equation [12] is shown as follows:

$$\ln(q_e - q_t) = \ln q_e - k_f t \qquad (3)$$

The pseudo-second-order equation [13] is given as follows:

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{1}{q_e} t \qquad (4)$$

The simple Elovich equation [14] is written as below:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \qquad (5)$$

The Bangham's equation [15] is explained as follows:

$$\log\log\left(\frac{C_i}{C_i - q_t m}\right) = \log\left(\frac{k_o m}{2.303 V}\right) + \alpha_B \log(t) \quad (6)$$

The intra-particle diffusion equation [16] is described as follows:

$$q_t = k_{id} t^{1/2} + 1 \quad (7)$$

Where 'q_t' refers to the amount of cobalt (II) ions adsorbed by adsorbent at different times 't' (mgg⁻¹) and 'q_e' at equilibrium respectively, k_f and k_s are rate constants for the adsorption process of Lagergren first-order model (min⁻¹) and pseudo-second-order model (gmg⁻¹min⁻¹) respectively, α is the rate of initial adsorption (mgg⁻¹min⁻¹), β is the constant of desorption (gmg⁻¹) for Elovich equation. "V" stands for the volume (ml) of solution, $\alpha_B (< 1)$ and k_0 are Bangham's equation constants. I is the intercept and 'k_{id}, is the rate constant for intra-particle diffusion (mgg⁻¹min⁻¹/²). The straight-lined plots of ln (q_e-q_t) versus t for Lagergren first-order model (Fig. 2a), t/q_t against t for pseudo-second-order model (Fig. 2b), 'q_t' against ln (t) (Fig. 2c) for Elovich model and $\log\log\left(\frac{c_i}{c_i - q_t m}\right)$ versus log(t) for Bangham's model (Fig. 2d) were plotted to get rate parameters for the adsorption of cobalt (II) ions onto alumina. Table-2 shows the kinetic parameters obtained from these plots. The correlation coefficients (R²) for Lagergren first-order kinetic model vary from 0.665 to 0.998, for the pseudo-second-order kinetic model are near to 1, for Elovich kinetic model are between 0.6259 and 0.8187 and for Bangham's equation are between 0.7800 and 0.8182. Therefore, present adsorption system more likely does not follow the kinetic models of Lagergren first-order, Bangham and Elovich. It rather follows pseudo-second-order kinetic model. The calculated 'q_e' values well match with experimental 'q_e' values. The correlation coefficients of plots for pseudo-second-order kinetic model are high. Likewise, according to Bangham's kinetic model the double logarithmic plot Equation (6) did not produce the required linear curves for the removal of cobalt (II) ions by alumina indicating that the diffusion of adsorbate into the pores of adsorbent was not the sole rate-limiting step. The possibility of intra-particle diffusion for rate controlling step was explored further by subjecting the kinetics results to intra-particle diffusion model (Fig. 2e). The deviation of straight lines from origin shows that the diffusion through the pores is not the only rate-determining step as presented by Bangham's equation. The values of intra-particle diffusion constant k_{id} shown in Table-1 were attained from slopes of linear portions of plots. The values of correlation coefficients for the intra-particle diffusion model (R²) were found between 0.7067 and 0.9130.

Table 1: **Kinetic parameters (T=306 K, t = 120 min, C_i = 5-50 mgl⁻¹, solution to adsorbent ratio = 50:1 therefore m = 20 gl⁻¹).**

Pseudo-first-order

C_i (mgl⁻¹)	$q_{e,exp}$ (mgg⁻¹)	$q_{e,calc}$ (mgg⁻¹)	k_f (min⁻¹)	R^2
5	0.2301	0.0114	0.0123	0.9998
10	0.3740	0.0804	0.0964	0.8329
20	0.6480	0.0288	0.0206	0.8872
30	0.8740	0.0614	0.0327	0.8824
40	1.0760	0.1657	0.0199	0.6665
50	1.2725	0.1387	0.0199	0.9206

Pseudo-Second-order

C_i (mgl⁻¹)	$q_{e,calc}$ (mgg⁻¹)	h (mgg⁻¹min⁻¹)	k_s (gmg⁻¹min⁻¹)	R^2
5	0.2320	0.3478	6.4640	0.9999
10	0.3772	0.4856	3.4130	0.9999
20	0.6530	0.8322	1.9500	0.9999
30	0.8830	0.8970	1.1500	0.9999
40	1.1074	0.3062	0.2496	0.9983
50	1.2940	0.5380	0.3210	0.9994

Elovich

C_i (mgl⁻¹)	α(mgg⁻¹min⁻¹)	β(gmg⁻¹)	R^2
5	0.0393	166.66	0.6259
10	-	71.43	0.9682
20	0.0202	93.46	0.7763
30	0.0369	56.18	0.8042
40	-	21.59	0.6741
50	0.0579	24.15	0.8187

Bangham

C_i (mgl⁻¹)	α_B	k_o(g)	R^2
5	0.1370	1.8160	0.7800
10	0.0782	1.2680	0.9647
20	0.0288	1.1400	0.7955
30	0.0326	0.9390	0.8069
40	0.0665	0.6845	0.6798
50	0.0479	0.6974	0.8182

Intra-particle diffusion

C_i (mgl⁻¹)	k_{id} (mgg⁻¹min⁻¹/²)	I(mgg⁻¹)	R^2
5	0.0028	0.2097	0.7067
10	0.0058	3.3341	0.9788
20	0.0044	0.6095	0.8522
30	0.0070	0.8120	0.8989
40	0.0177	0.8904	0.7842
50	0.0148	1.1160	0.9130

Effect of temperature

Temperature greatly affects the adsorption capacity of adsorbents. (Fig. 3a) presents the results of adsorption isotherms, q_e vs C_e for cobalt (II)-alumina system at a set of three different temperature values, i.e. 263, 289, 306 K. It indicates that adsorption of cobalt (II) ions onto alumina increases directly with rise in temperature of solution. This behavior is because of increased surface activities which suggest that adsorption of cobalt (II) ions onto alumina is endothermic process.
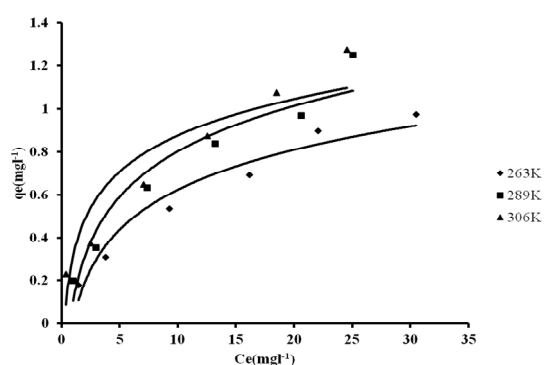

Figure 3a: **Equilibrium adsorption isotherms for cobalt-alumina system**
Experimental conditions:
Time (t)   =   90 min
Adsorbent conc. (m)   =   20*g/l*

Adsorption isotherms

Three most widely used isotherm equations such as Freundlich [17], Langmuir [18] and Dubinin-Radushkevich [19] were applied to explain equilibrium characteristics of the adsorption process [20]. The related parameters of these models are presented in (Table-2). Freundlich adsorption isotherm gives an empirical expression, which was used for the study of cobalt (II) ions adsorption onto alumina in the following linearized form.

$$\log q_e = K_F + \frac{1}{n} \log C_e \qquad (8)$$

Where 'q_e' refers to the amount of adsorbate adsorbed per unit weight of the adsorbent (mgg^{-1}), 'C_e' is the equilibrium concentration. 1/n and k_F are constants indicating the adsorption intensity and adsorption capacity

respectively. The plot of $\log C_e$ against $\log q_e$ results in straight line (Fig. 3b).

The intercepts and slopes of the straight lines (Table-2) give the values of 1/n and k_F. The affinity and heterogeneity of adsorbent sites is directly proportional to 1/n. Values of 1/n < 1 indicate that the adsorption of cobalt ions (II) onto alumina is favourable in nature.
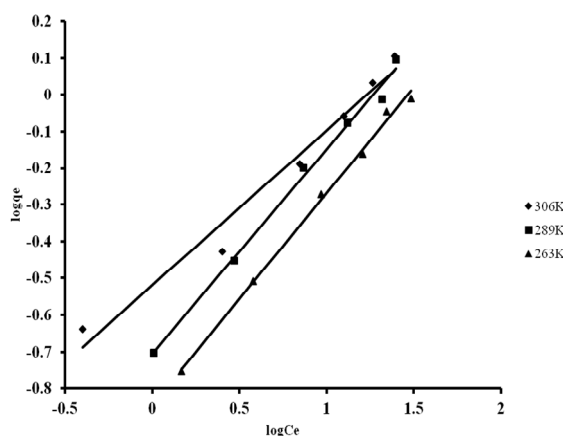

Figure 3b: **Freundlich adsorption isotherms**
Experimental conditions:
Time(t)   =   90 min
Adsorbent conc.(m)   =   20*g/l*

The Langmuir isotherm relates the equilibrium distribution of adsorbate between solid and liquid phases. The Langmuir equation is applied as:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_L \, q_m} \qquad (9)$$

Where 'q_m' stands for maximum adsorption capacity (mgg^{-1}) of the adsorbent with adsorbate while 'K_L' represents the binding constant related to heat of adsorption. Results showed that Langmuir isotherm is followed very well by the adsorption data as the plot of 'C_e/q_e, against 'C_e' (Fig. 3c) yielded straight lines for cobalt (II) ion alumina adsorption system. The values of 'q_m' (mgg^{-1}) were calculated from slopes of linear plots while the values of 'K_L' were estimated from intercept of plots. The data obtained is given in (Table 2).
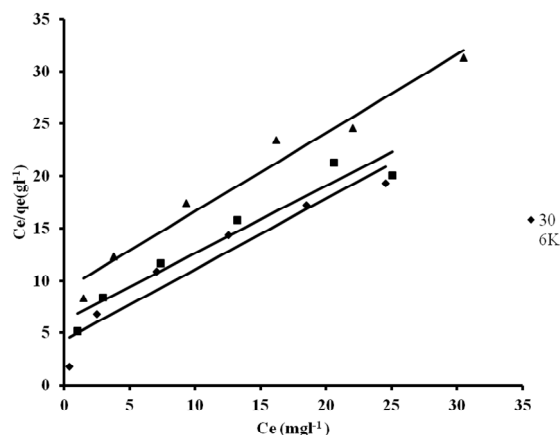
Figure 3c: **Langmuir adsorption isotherms**
Experimental conditions:
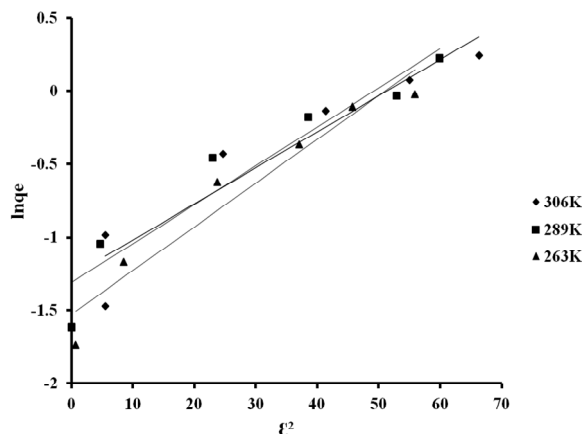Time (t)   =   90 min
Adsorbent conc. (m)   =   20g/l

Figure 3b: **Dubinin-Radushkevich adsorption isotherms**
Experimental conditions:
Time (t)   =   90 min
Adsorbent conc. (m)   =   20g/l

Table 2. **Linear Isotherms and related parameters for the removal of cobalt (II) ions by alumina from the aqueous solution (t = 90 min, Ci = 10-50 mgl^{-}, solution to adsorbent ratio = 50:1 therefore m = 20gl^{-}).**

Isotherm	T (K)	306	289	263
Freundlich	K_F [(mg/g)(mgl^{-1})]$^{-1/n}$	0.3027	0.1976	0.1435
	$\frac{1}{n}$	0.4212	0.555	0.5749
	R^2	0.9735	0.9933	0.9966
Langmuir	K_L (lmg^{-1})	0.1570	0.1048	0.0818
	q_m (mgg^{-1})	1.4779	1.5490	1.3360
	R^2	0.9224	0.9376	0.9682
Dubinin-Radushkevich	q_{D-R} (mgg^{-1})	0.2830	0.2168	0.2698
		0.0246	0.0299	0.0266
	E ($KJmol^{-1}$)	4.504	4.089	4.336
	R^2	0.9007	0.9394	0.9147

Fig. 3d represents the application of Dubinin-Radushkevich isotherm to adsorption results in following equation:

$$\ln q_e = \ln q_{D-R} - \beta\varepsilon^2 \tag{10}$$

Where 'q_{D-R}' shows the maximum adsorption capacity of adsorbent (mgg^{-1}), 'β' is constant with dimension of energy and 'ε' is the Polanyi adsorption potential, which is equal to

$$\varepsilon = RT\ln\left(1 + \frac{1}{C_e}\right) \tag{11}$$

Where 'Ce' is the concentration of adsorbate in solution (mgl^{-1}), T is a temperature (K) and 'R' is a gas constant ($KJmol^{-1}k^{-1}$). The plots of '$\ln q_e$' versus 'ε^2' give the values of 'β' and 'q_{D-R}', which were obtained from intercepts and slopes of concerned plots. Adsorption energy represented by E is determined using following equation [21].

$$E = \frac{1}{\sqrt{-2\beta}} \tag{12}$$

Where 'E' describes the nature and type of adsorption. If the value of 'E' is within the range of 8-16 $KJmol^{-1}$, then the type of adsorption is guessed by ion exchange while if the value of 'E' is less than 8 $KJmol^{-1}$ then the type of adsorption is physical in nature. The value of E found in this study is between 4.089 $KJmol^{-1}$ and 4.504 $KJmol^{-1}$ suggesting physical nature for cobalt (II) ions adsorption on alumina. Further by making comparison in terms of "q_m (mgg^{-1})values" with previous reported data for Co^{2+} adsorption on other adsorbents (Table-3) it is possible to conclude that the alumina removal of cobalt.

Table 3: **Comparison of "q_m (mgg^{-1}) for removal of Co^{2+} by various adsorbents.**

Adsorbent	q_m (mgg-1)	References
Mesoporous Silica	9.73	[24]
Oxalated Treated Activated Carbon	5.33	[25]
Sugarcane bagasse	1.14*	[26]
PET-g-(MAA/AAm)	0.461*	[27]
α-Alumina	1.4**	This study

* : mmol/g, **>90% adsorption with respect to initial concentration.

Estimation of thermodynamic parameters

The changes in free energy (ΔG^O), entropy (ΔS^O) and enthalpy (ΔH^O) during adsorption process were calculated from the equations given below.

$$K_C = C_{Ae} / C_e \qquad (13)$$

$$\Delta G^O = - RT\ln K_C \qquad (14)$$

$$\log K_C = \frac{\Delta S^O}{2.303R} - \frac{\Delta H^O}{2.303RT} \qquad (15)$$

Where 'K_c, is the equilibrium constant, 'C_e, is the equilibrium concentration in solution (mgl^{-1}) and 'C_{Ae}, is equilibrium concentration (mgl^{-1}) of the solid phase. ΔG^O (*$KJmol^{-1}$*), ΔS^O (*$Jmol^{-1}K^{-1}$*) and ΔH^O (*$KJmol^{-1}$*) are respective Gibbs free energy, entropy and enthalpy changes (Table-3), T is a temperature (K) and R is a gas constant ($8.314Jmol^{-}K^{-}$).

Table 3: **Thermodynamic parameters for the adsorption of cobalt (II) ions on to alumina.**

Initial cobalt(II) Conc.	ΔH^O	ΔS^O	ΔG^O		
(mg/l)	(KJ/mol)	(J/mol/K)	(KJ/mol)		
10	10.782	49.95	306 K	289 K	263 K
			- 2.7603	- 2.0930	- 1.0709

The ΔH^o and ΔS^o were found from intercept and slope of the plot of '$\log K_c$, vs 1/T (Fig. 4). The ΔG^o was determined from equation 14. It shows that adsorption of cobalt (II) ions onto alumina increased when the temperature of solution was raised from 263 to 306 K. The negative value of (ΔG^o) indicates spontaneous nature of adsorption. It also suggests that it is a feasible process. The positive value of (ΔH^O) describes the endothermic nature of adsorption. The positive value of (ΔS^O) indicates increase in randomness at liquid/ solid interface during the adsorption. The values of (ΔG^o) obtained for cobalt (II) ions are < *-6 KJmol^{-1}* which show that the predominant mechanism taking place during adsorption is physical in nature.
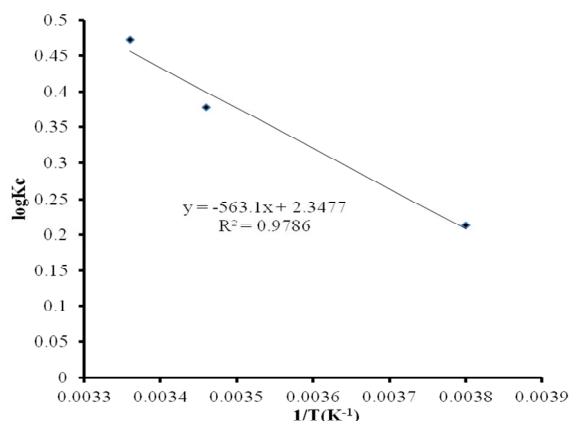

Figure 4: **Plot of log K$_c$ versus1/T**

Conclusion

The experimental study leads to the conclusion that alumina is an effective adsorbent for cobalt (II) ions. It showed excellent adsorptive characteristics for the removal of cobalt (II) ions from the aqueous medium. A higher percentage of cobalt removal from the solution was possible by alumina if the initial concentration of cobalt (II) ions is low. The optimum dose of adsorbent was found to be 20gl^{-1}. Results showed that equilibrium between adsorbent surface and adsorbate was achieved in 90 min. It was established that the equilibrium as well as kinetic data for adsorption for cobalt (II) ions on to alumina was best displayed by Langmuir pseudo-second-order kinetic model. Rise in the temperature of system significantly affects the adsorption of cobalt (II) ions onto alumina. Negative value of free energy (ΔG^O) shows the spontaneous adsorption of cobalt (II) ions onto alumina.

Acknowledgement

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