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Adsorption of Co(II) on nanobentonite surface: Kinetic and equilibrium studies

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The ability of selected adsorbents such as nano bentonite to remove Co (II) ions from wastewater at different conditions as contact time, amount of adsorbent, temperature, initial concentration, and *p*H has been studied and reported. In order to find out thermodynamic and kinetic parameters, equilibrium adsorption models have been applied. Although experimental data is confirmed with both Langmuir and Freundlich isotherm models. Adsorption rate constant has been determined from Lagergren Equation and pseudo-second order Equations.

Freundlich model has a better correlation coefficient (R^2) than the Langmuir model for the studied concentrations at 25°C also Tempkin isotherm is applied. Another important result withdrawn from the values of thermodynamic parameters can be stated as, negative value of $\Delta G°$ and positive value of the $\Delta S°$ show that the adsorption of Co(II) ions onto both adsorbents is a spontaneous process and positive value of $\Delta H°$ indicates that the adsorption is endothermic in nature. Finally, it can be seen that the pseudo-second order equation provide the best correlation coefficient (R^2) for the adsorption data.

Keywords: Nano bentonite, Cobalt, Wastewater, Thermodynamic parameter, Kinetic parameter, Adsorption models

Trace heavy metals play an important role as micronutrients in organisms. However, many metals have toxic effects in high concentration[1,2]. Cobalt has various applications in a variety of industrial processes and operations and is released through natural processes such as volcanic activities[3,4]. It directly meets water bodies through the effluent of industries causing a marked increase in its concentration. The major sources of cobalt release into the environment by waste streams are electroplating, smelting, alloy manufacturing, pigments, plastic, battery, mining and refining processes[5,6]. A number of treatment methods for the removal of metal ions from aqueous solutions have been reported are reduced, ion exchange, electro dialysis, electrochemical precipitation, evaporation, solvent extraction, reverse osmosis, chemical precipitation, ultra filtration and adsorption[7,8]. Most of these methods suffer from some drawbacks such as high capital and operational costs. Disposal of the residual metal sludge causes problem for the small-scale Industries. Also, these methods are inadequate when the permissible concentrations of the metal ions are low[9,10]. Cobalt has been recognized as one of toxic metals. Toxic effects of cobalt on humans include both chronic and acute disorders like testicular atrophy, hypertension, damage to kidneys and bones, anemia, itai-itai, etc.[11-15].

Cobalt has an extremely long biological half-life (>20 years) and it is listed by the US-EPA as one of the 126 priority contaminants and a known carcinogen by the International Agency for Research on Cancer[16]. Many of the researches are carried out on the development of technology for the removal of cobalt ions from the effluent before discharging into the water system. The use of platinum oriental leaves and other agricultural fibers have good efficiencies in adsorption of heavy metals[17,18]. Other process such as electro coagulation has also been used for the removal of heavy metals[19].

Adsorption is one of the methods for the removal of heavy metals from wastewater. Much work has been done on the removal of lead and cobalt by different adsorbents such as:

Adsorbent	% Removal
Clays[20-24]	44
Minerals such as goethite[25]	46
Hydroxyapatite[26]	52
Calcite[27-30]	55
Calcareous soils[31,32]	45
Sludges[33]	46
Modifedasphaltite ashes[34]	48
Bark, fly ash[35]	54%
Chitosan, dead biomass, modifed wool, moss, Peat, sea-weed, zeolite, humic acid[36]	~ 56
Sesquioxides (iron, alu-minium, or manganese oxides)[37]	60
Hydroxyapatite[24]	62
Nano bentonite[21]	74
Bone char[38]	76
Activated dolomite[39]	80

Experimental Section

Adsorbents

Nano bentonite is used as an adsorbent. The crystalline phases in the nano bentonite were characterized with an X-ray diffraction (XRD; Philips pw 1750), as shown in Table 1. The surface area measurement was carried out by the BET method using Nova 2000 (quanta chrome) instrument as shown in Table 1.

Method

Effect of initial concentration

Adsorbents (nano bentonite) (0.1 g) was added to 200 mL of Co^{2+} aqueous solutions with concentration 50, 100, 200 and 300 mg/L. The mixture was stirred using magnetically stirred for 1 h at 500 rpm. Over time (0, 5, 10, 15, 20, 30, 45 and 60 min). After any specified time the sorbents were separated from the solution by centrifuge and filtration through the filter paper (Whatman grade 6). The exact concentration of metal ions was determined by AAS (atomic absorption spectrophotometer). All experiments were carried out twice. (Filtered through Whatman No.1 filter paper and the residual Co^{2+} ion quantified using atomic absorption spectroscopy. Repeat this experiment using 0.3, 0.5, 0.7 and 1.0 g adsorbent (nano bentonite)

Table 1 — Adsorbent analysis of nano bentonite

Adsorbents	Nano bentonite
Surface area(BET) Nova 2000 Quanta chrome	119 m^2/g (dry)
Particle size (XRD) Philips pw 1750	

Table 2 — Elemental analysis for nano bentonite was evaluated using X-ray fluorescence (Philips pw 1390) as shown in Chemical composition of nano bentonite

Oxide (wt %)	Nano bentonite
SiO_2	55.89
Al_2O_3	16.03
Fe_2O_3	4.19
CaO	3.25
MgO	2.75
K_2O	0.49
Na_2O	0.34
TiO_2	0.15
P_2O_5	0.086
SO_3	0.23
L.O.I	17.2

Effect of *p*H of solution

Adsorbents (nano bentonite,) (0.1 g) was added to 200 mL of Co^{2+} aqueous solutions. The *p*H of the solution was adjusted to 1, 3, 5 and 7 by adding 0.1 N H_2SO_4 or 0.1 N NaOH. The mixture was stirred using magnetic stirrer for 1 h at 500 rpm. Over time (0, 5, 10, 15, 20, 30, 45 and 60 min). After any specified time the sorbents were separated from the solution by centrifuge and filtration through the filter paper (Whatman grade 6). The exact concentration of metal ions was determined by AAS (atomic absorption spectrophotometer). All experiments were carried out twice, filtered through Whatman No.1 filter paper and the residual Co^{2+} ion quantified using (atomic absorption spectroscopy). Repeat this experiment using 0.3, 0.5, 0.7 and 1.0 g adsorbent (nano bentonite,)

Effect of stirring speed

Adsorbents (nano bentonite) (0.1 g) was added to 200 mL of Co^{2+} aqueous solutions. The mixture was stirred using magnetically stirred for 1 h at 100, 300, 500, 700 and 900 rpm. Over time (0, 5, 10, 15, 20, 30, 45 and 60 min). After any specified time, the sorbents were separated from the solution by centrifuge and filtration through the filter paper (Whatman grade 6). The exact concentration of metal ions was determined by AAS (atomic absorption spectrophotometer). All experiments were carried out twice, filtered through Whatman No.1 filter paper and the residual Co^{2+} ion quantified using atomic absorption spectroscopy. Repeat this experiment using 0.3, 0.5, 0.7 and 1.0 g adsorbent (nano bentonite).

Effect of temperature

Adsorbents (nano bentonite) (0.5 g) was added to 200 mL of Co^{2+} aqueous solution with concentration 50, 100, 200 and 300 mg/L. The experiment was carried out at T=298 K. The mixture was stirred using magnetic stirrer for 1 h at 500 rpm. Over time (0, 5, 10, 15, 20, 30, 45 and 60 min). After any specified time the sorbents were separated from the solution by centrifuge and filtration through the filter paper (Whatman grade 6). The exact concentration of metal ions was determined by AAS atomic absorption spectrophotometer). All experiments were carried out twice. Filtered through Whatman No.1 filter paper and the residual Co^{2+} ion quantified using atomic absorption spectroscopy. Repeat this experiment at different temperature T=303, 308, 313 K.

Data analysis

The percentage of adsorption (%) is calculated using the following Equation:

% adsorption= $(C_o-C_t)/C_o \times 100$ … (1)

The adsorbed amount of $Co^{2+}(q_t)$ on nano bentonite at time t is given by the following Equation:

$q_t= (C_o-C_t)V/m$ … (2)

The Co^{2+} concentration retained in the adsorbed phase (q_e) nano bentonite:

$q_e= (C_o-C_e)V/m$ … (3)

where V is the volume (l); m is the weight (g) of adsorbent; C_o is the initial concentration of metal ions in the solution (mg/L), C_e is the equilibrium concentration or final concentration of metal ions in the solution (mg/L) and C_t is the concentration of metal ions in the solution at time t (mg/L), q_e is the sorption capacity at equilibrium (mg/g).

Result and Discussion

Kinetics of heavy metal adsorption

In order to investigate the controlling mechanism of adsorption processes, the pseudo-first order and pseudo- second order equations are applied to model the kinetics of cobalt adsorption onto nano bentonite. The kinetic parameters are useful in predicting the adsorption rate which can be used as important information in designing and modeling of the adsorption operation.

Pseudo-first order model

Lagergren proposed a pseudo-first order kinetic model.The integral form of the model is[40]:

$\ln(q_e-q_t)= \ln q_e- k_1t$ … (4)

where q_t is the adsorbed amount of ions on nano bentonite in time t(mg/g); t is the contact time(min); k_1 is the first-order rate constant (min^{-1}).

The plot of $\ln(q_e-q_t)$ versus t (Fig. 1) gives a linear relationship form which k_1 and q_e can be determined from the slope and intercept of the graph, respectively.

Pseudo-second order model

The adsorption kinetics may also be described by a pseudo-second order reaction. The linearized-integral form of the model is[41-48]:

$t/q_t = 1/(k_2q_e^2) + (1/q_e)t$ … (5)

where k_2 is the pseudo-second order rate constant of adsorption (mg g^{-1} min^{-1}).The plot of t/q_t versus t Figure 2 should be a linear relationship from which q_e and k_2 can be determined from the slope and intercept of the plot, respectively (q_e=1/slope and k_2 = $(slope)^2$/ intercept).

The applicability of the above two models can be examined by each linear plot and are presented in Figs 1 and 2. To quantify the applicability of each model, the correlation coefficient, R^2, was calculated from these plots. The kinetic rate constants obtained from first and second-order pseudo kinetic model are given in Table 3. The values of correlation coefficient, R^2, for the pseudo-second order adsorption model is relatively high (>0.9979), and the adsorption capacities calculated by the model are also close to those determined by experiments. However, the values of R^2 for the pseudo-first order are not

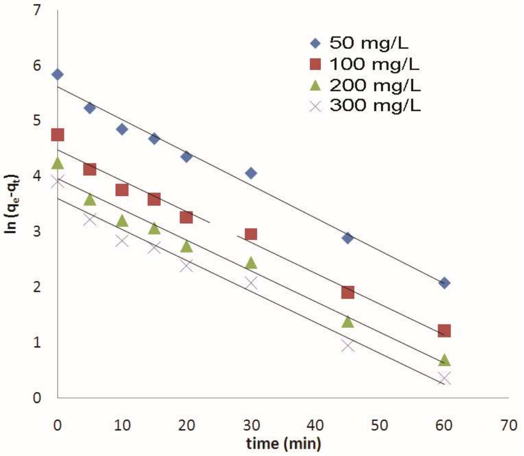

Fig. 1 — Pseudo first order Kinetics for the adsorption of cobalt on nano bentonite at different initial concentrations, m/V = 2.5 g/L, *p*H=7, stirring speed= 500 rpm, temperature=293K.

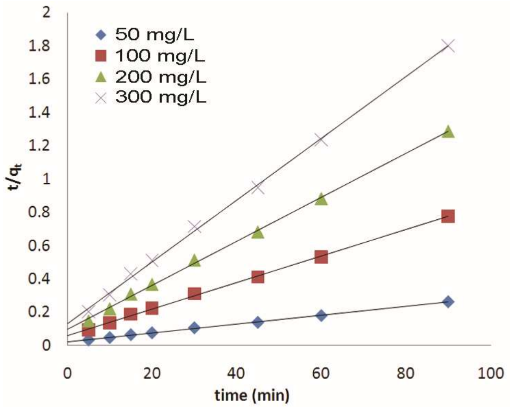

Fig. 2 — Pseudo second-order kinetics for the adsorption of cobalt on nano bentonite at different initial concentrations, m/V = 2.5 g/L, *p*H=7, stirring speed= 500 rpm, temperature=293K.

Table 3 — Adsorption rate constants, q_e estimated, and coefficient of correlation associated to the Lagerggren pseudo-first and second order adsorption for the nano bentonite

Adsorbent	Initial concentration (mg/L)	q_{eexp}(mg/g)	First-order model			Second-order model		
			10^3k_1(min $^{-1}$)	q_{ecal}(mg/g)	R^2	10^3k_2(g mg^{-1} min^{-1})	q_{ecal}(mg/g)	R^2
Nano bentonite	50	16.4	84.1	8.26	0.9476	22.87	16.98	0.9983
	100	33.2	72.2	7.80	0.9146	16.22	34.01	0.9998
	200	64.0	65.8	38.19	0.9333	2.55	69.93	0.9995
	300	100.8	55.8	68.75	0.9103	1.23	112.36	0.9981

satisfactory. Therefore, it has been concluded that the pseudo-second order adsorption model is more suitable for describing the adsorption kinetics of cobalt on nano bentonite.

In general, the adsorption reaction is known to proceed through the following three steps:

(i) Transfer of adsorbate from the bulk solution to adsorbent surface, which is usually mentioned as diffusion.

(ii) Migration of adsorbate into pores.

(iii) Interaction of adsorbate with available sites on the interior surface of pores[49].

It can be seen from the literatures that the rate-determining step for the adsorption of Co^{2+} ions depends on:

- The interaction of adsorbate with available sites on the interior surface of pores of the adsorbents.
- Migration of Co^{2+} ions into the pores of the nano bentonite[49].

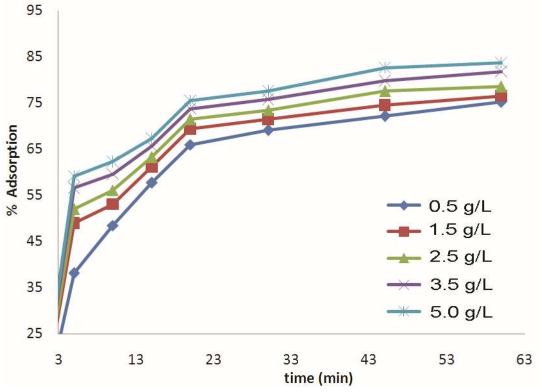

Fig. 3 — Effect of contact time on Co(II) removal at different doses of nano bentonite [Co(II) conc = 100 mg/L; *p*H = 7.0; stirring speed = 500 rpm; temperature = 293 K]

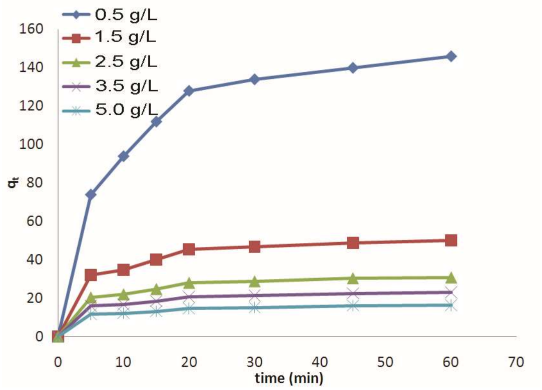

Fig. 4 — Effect of contact time on amount of cobalt adsorbed by nano bentonite at different doses of adsorbent [Co(II) conc = 100 mg/L; *p*H = 7.0; stirring speed = 500 rpm; temperature = 293K].

Effect of contact time

Various adsorption parameters for the effective removal of cobalt using nano bentonite as an adsorbent from aqueous solution were studied and optimized. The sorption of Co^{2+} ions has been investigated onto adsorbed as a function of time in the range of 5-60 min as shown in Fig. 3. The adsorption was very fast from the beginning to 20 min. Therefore, a 20 min contact time was found to be appropriate for maximum adsorption, with further increase of time the adsorption approached to equilibrium within 20 min in all the cases. The initial faster rate may be due to surface adsorption and in the initial stage, the surface is free and the reaction proceeds at a faster rate, then the adsorbate molecules penetrate through the pores and get adsorbed inside the pore, which is known as intra-particle diffusion. A great number of sites available for the sorption operation and adsorption equilibrium were then gradually achieved. Figure 4 represents a plot of amount of cobalt metal ion adsorbed (mg/g) versus contact time (min) for different initial metal ion concentrations of 50, 100, 200, 300 (mg/L) respectively. From these plots, it is found that the amount of adsorption increases with increasing contact time i.e. mg of adsorbate per gram of adsorbent increases with increasing contact time at all initial metal ion concentrations and equilibrium is attained within 20 min. Further, it is observed that the amount of metal ion uptake, q_t (mg/g) is increased with an increase in initial metal ion concentration (see appendix). This kinetic experiment clearly indicates that adsorption of cobalt metal ion (Co^{2+}) on nano bentonite is a more or less two-step process[50-54]; a very rapid adsorption of Co^{2+} to the external surface is followed by possible slow intra particle diffusion in the interior of the adsorbent. This two stage metal ion uptake can also be explained as adsorption occurring onto two different types of binding sites on the adsorbent particles[55].

Effect of adsorbent dose

Adsorbent dosage seemed to have great effect on adsorption process. The effect of adsorbent dose on the adsorption of heavy metal was studied at contact time of 60 min for initial heavy metal concentration of 100 mg/L at 293 K. The amount of nano bentonite adsorbents varied from 0.5 to 5.0 g/L. The adsorption (%) increased rapidly as more and more of the adsorbent was added. This can be explained by a greater availability of increasing the number of exchangeable sites or surface area ensured enhanced uptake of Co^{2+}. The maximum adsorption of heavy metal was obtained for the adsorbent dose of 3.5 g/L. However, it is observed that after a dosage of 3.5 g/L, there was not a significant change in the percentage adsorption of heavy metal. It may be due to the overlapping of active sites at higher dosages. There is a decrease in the effective surface area, resulting in the conglomeration of exchange particles. Therefore, 3.5 g/L was considered as an optimum dose[56]. The amount of Co^{2+} adsorbed per unit mass of the adsorbent (q_e) at its equilibrium decreased with an increase in the amount of nano bentonite Figs. (5,6).

Effect of Initial concentration

The effect of Co^{2+} concentration on adsorption was studied under the optimized conditions of time (60 min), *p*H (7),stirring speed (500 rpm), different adsorbent doses (0.5-5.0 g/L) and concentration of $Co^{2+}$was varied from 50 to 300 mg/L. Figure 7 show the effect of initial adsorbate concentration versus the adsorption capacity, q_e (mg/g). It was observed that the adsorption capacity increased with the increase of adsorbate concentration. This may be due to the fact that at a fixed adsorbent dose, the number of active adsorption sites to accommodate the adsorbate ion remains unchanged while with higher adsorbate concentrations, the adsorbate ions to be accommodated increases. Thus, the adsorption capacity is faster with higher initial concentrations of adsorbate[57].

Effect of *p*H

The *p*H of the aqueous solution is an important controlling parameter in the adsorption process and particularly on the adsorption capacity. Thus, the effect of *p*H has been studied by varying it in the range of 1-7 as shown in Fig. 8. The results are presented in Tables 3,4 which reveals that the adsorption of cobalt increases with increasing *p*H. It can be seen from

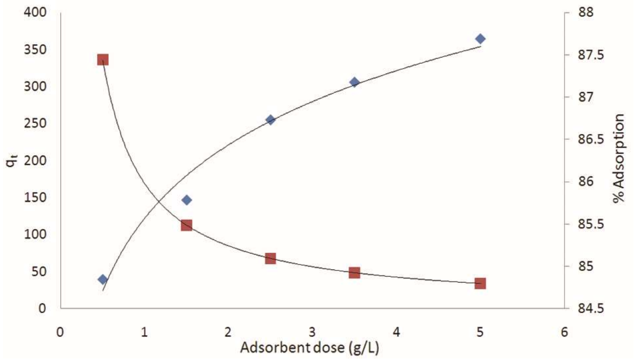

Fig. 5 — Effect of adsorbent dose of nano bentonite on % Adsorption and q_e, initial concentration [Co^{2+}] =200 mg/L, *p*H=7, stirring speed= 500 rpm, temperature=293K.

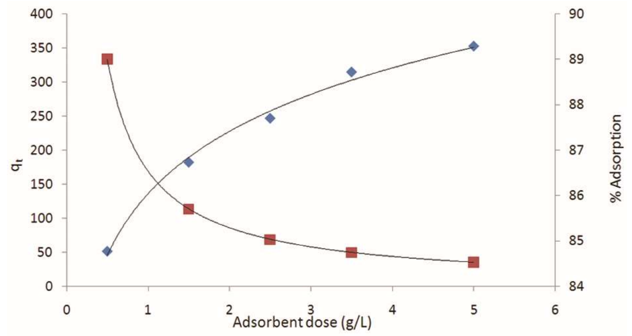

Fig. 6 — Effect of adsorbent dose of activated carbon on % Adsorption and q_e, initial concentration [Co^{2+}] =200 (mg/L), *p*H=7, stirring speed= 500 rpm, temperature=293K.

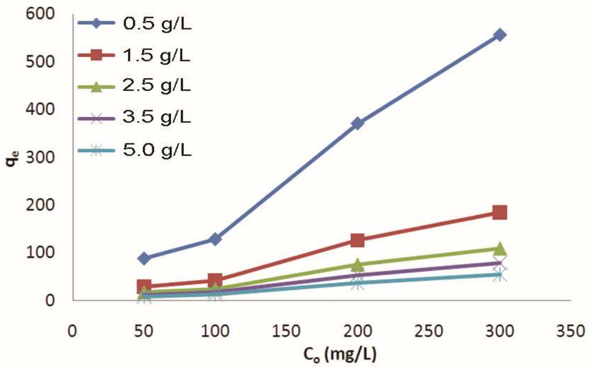

Fig. 7 — Effect of cobalt concentration on the amount of cobalt adsorbed on nano bentonite at equilibrium at different adsorbent doses (*p*H=7, stirring speed= 500 rpm, temperature=293K).

Table 4 — Values of thermodynamics parameters for the adsorption of Co^{2+} on nano bentonite

			ΔG°($KJmol^{-1}$)			
Concentration of Co^{2+}	ΔH°($KJmol^{-1}$)	ΔS°($Jmol^{-1}K^{-1}$)	298 K	303 K	308 K	313 K
50 mg/L	26.05	93.52	-1.86	-2.26	-2.66	-3.29
100 mg/L	17.73	64.74	-2.20	-1.87	-2.26	-2.51
200 mg/L	12.75	48.31	-1.65	-1.89	-2.15	-2.36
300 mg/L	19.16	71.83	-2.21	-2.70	-2.80	-3.38

Figures 8,9 that by decreasing the acidity of the solution, the adsorption (%) as well as the amount of adsorbed per unit of mass (q_e), showed a positive variation. The adsorption capacity of nano bentonite increased when the initial *p*H of the solution was increased from 1 to 7. The mechanisms that affect the adsorption characteristics can be explained by dissolution, ion exchange, adsorption and precipitation[57,58]. From Fig. 8 the lowest Co^{2+} sorption rates were obtained at *p*H 1. This could be due to the increase in competition for adsorption sites. The maximum adsorption percentage of Co^{2+} at *p*H 7.0 was determined at about 90 %. Therefore, at higher *p*H, there is more interaction between the negatively charged and positively charged cobalt species.

The *p*H of the system controls the adsorption capacity due to its influence on the surface properties of the adsorbent and ionic forms of the cobalt in solutions. The cobalt uptake reached the maximum at *p*H 7.0. Therefore, *p*H 7.0 was selected for further experiments Fig. 9.

Effect of speed of rotation on uptake of cobalt

Experimental results for the effect of speed of rotation (100, 300, 500, 700, 900 rpm) are presented in Fig. 10. The removal of Co^{2+} using activated carbon reaches 87% at 900 rpm. On the other hand, the higher removal level reached by nano bentonite is found to be at 94% (and other examples see Tables-5,6. It is obvious that speed of rotation helps cobalt removal from aqueous solutions. This is because cobalt ions, through their transportation to a solid phase, meet resistance at the liquid phase, through the boundary layer. Rotation during experiments has led to a decrease of the boundary layer and a decrease to the resistance of transport of cobalt ions. This increases the transfer rate of the ions.

Effect of temperature

Different sets of experiments are conducted at 100 mg/L concentration at different temperatures at 298, 303, 308, 313 K and it is evident in the Fig. 11 that adsorption of cobalt increases with increase in the

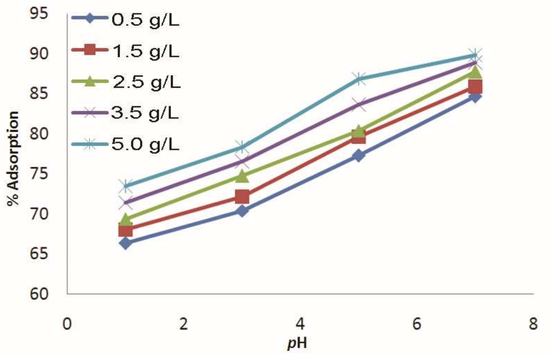

Fig. 8 — Effect of *p*H on the removal of cobalt by nano bentonite at different adsorbent doses (initial concentration =100 mg/L; stirring speed= 500 rpm, temperature=293K).

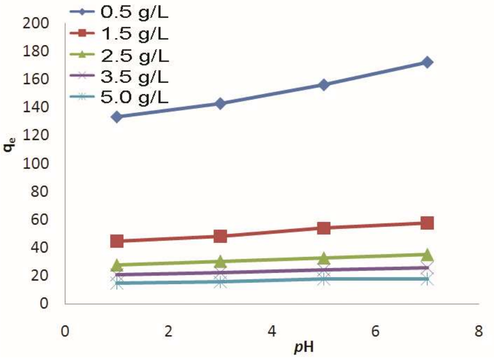

Fig. 9 — Effect of *p*H on the amount of cobalt adsorbed on nano bentonite at equilibrium at different adsorbent doses (initial concentration=100 mg/L, stirring speed= 500 rpm, temperature=293K).

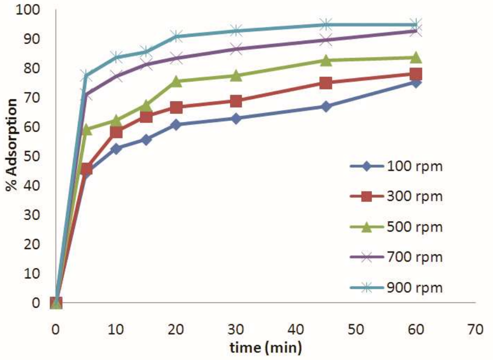

Fig. 10 — Percentage adsorption of cobalt with agitation using nano bentonite adsorbent [Co(II) conc = 100 mg/L; *p*H = 7.0;m/V = 2.5 g/L; temperature = 293K].

temperature. In presence of nano bentonite, % adsorption increases from 86.7 to 89.8% and for activated carbon from 81.6 to 85.7 % .The figures show that the removal efficiency increases by increasing the temperature where the maximum adsorption (90%, 87% approx.) is achieved at 313 K in case of nano bentonite and activated carbon respectively. The augmentation of the removal efficiency by stepping up the temperature are due to:

- The higher temperature activates the metal ions for enhancing adsorption at the coordinating sets of the adsorbent, and the metal cation move faster[59,60].
- Acceleration of some originally slow step (s) and creation of some new activation sites on the adsorbent surface[61].
- The increase in adsorption with temperature may be attributed to either increase the number of active surface sites available for adsorption on the adsorbent or the desolvation of the adsorbent with temperature, so that the mass transfer resistance of the adsorbate in the boundary layer decreases.

Table 5 — Parameters of Freundlich and Langmuir Isotherm models
(adsorption cobalt on nano bentonite at different temperatures)

Temperature	Freundlich constants			Langmuir constsnts		
(K)	1/n	K_F	R^2	b	q_{max}	R^2
308 K	0.87	2.76	0.9775	0.18	20.28	0.9247
313 K	0.79	3.67	0.9422	0.41	13.94	0.9199

Table 6 — Parameters of Freundlich and Langmuir Isotherm models

Temperature	Freundlich constants			Langmuir constants		
(K)	1/n	k_F	R^2	b	q_{max}	R^2
308 K	0.89	4.34	0.9999	0.012	322.58	0.9325
313 K	0.86	4.10	0.9659	0.0078	476.19	0.9222

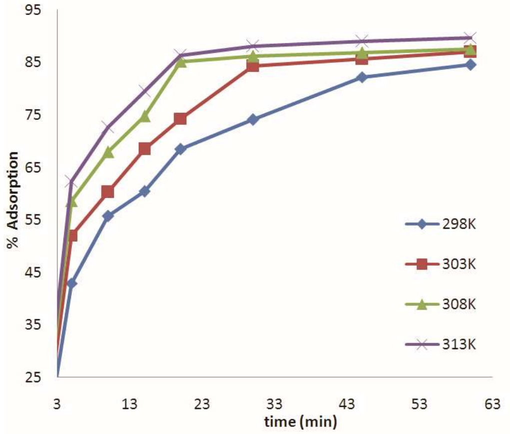

Fig. 11 — Percentage adsorption of cobalt on nano bentonite at different temperatures [Co(II) conc = 300 mg/L; m/V =2.5 g/L; *p*H = 7.0;stirring speed = 500 rpm].

Thermodynamics of adsorption

The influence of temperature variation was examined on the sorption of Co^{2+} nano bentonite from solution using 60 min, different initial concentrations of Co^{2+}. The adsorbent dose 2.5 g/L and temperature varied from 298 to 313 K. Thermodynamic parameters of the adsorption process can be determined from the experimental data:

$$k_d = q_e/C_e \qquad \dots (6)$$

$$\ln k_d = \Delta S°/R - \Delta H°/RT \qquad \dots (7)$$

$$\Delta G° = \Delta H° - T\Delta S° \qquad \dots (8)$$

where k_d is the distribution coefficient for the adsorption ΔS°, ΔH°, and ΔG° are the change of entropy, enthalpy, and the Gibbs energy, q_e is the equilibrium concentration of Co^{2+} on the adsorbent (mg/g), T(K) is the temperature, and R ($J\ mol^{-1}K^{-1}$) is the gas constant.

The values of ΔH° and ΔS° were determined from the slopes and intercepts of the plots of ln k_d Vs. 1/T Fig. 12, Gibbs free energy was calculated by using the following well-known Eq. (8).

The values of the thermodynamic parameters for the sorption of Co^{2+} on activated carbon and nano bentonite are given in Table 4. The positive values of ΔH° obtained indicated the endothermic nature of the process. Also the positive entropy favors complexation and stability of sorption and the negative ΔG° value confirmed the feasibility of the sorption process and the spontaneous nature of

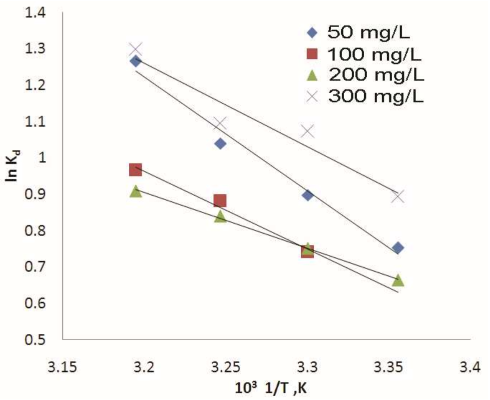

Fig. 12 — Vant Hoff plot for the adsorption of Co^{2+} onto nano bentonite at different initial concentration.

adsorption, and the degree of spontaneity of the reaction increases with increasing temperature.

Isotherms models

The study of adsorption isotherm is fundamental, and plays an important role in the determination of the maximal capacity of adsorbents. The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models (Langmuir, Freundlich, and Temkin) is an important step to find the suitable model that can be used for designing purpose. The Langmuir adsorption isotherm and the Freundlich isotherm are two common isotherms used to describe equilibrium[62]. The solid phase heavy metal concentrations, q_e (mg/g), were determined by analyzing the corresponding heavy metal concentration before and after the adsorption using the Equation below:

$$q_e = (C_o-C_e)/M \quad \ldots (9)$$

where C_o and C_e are the initial and equilibrium heavy metal concentrations in the solution (mg/L), and M is the sorbent dosage (g/L). The sorption data have been subjected to different sorption isotherms, namely, Langmuir, Freundlich, and Tempkin.

Langmuir isotherm model

Adsorption isotherm data are quantified to describe the interactions between the adsorbate and adsorbent and are critical in optimizing the use of adsorbent[58]. The Langmuir equation is the most popular of all the nonlinear isotherm expressions; it is a two-parameter Equation:

$$C_e/q_e = 1/q_{max}b + C_e/q_{max} \quad \ldots (10)$$

where q_{max} is the maximum metal ions uptake per unit mass of adsorbent (mg/g), which is related to adsorption capacity and b is Langmuir constant (L/mol) which is exponentially proportional to the heat of adsorption and related to the adsorption intensity. Therefore, a plot of C_e/q_e versus C_e, gives a straight line of slope $(1/q_{max})$ and intercept $(1/q_{max}b)$ as shown in Figs.-13,14 for temperature 308, 313 K. The linear nature of the plot shows the adsorption follows the Langmuir isotherm and in temperature 308 and 313 K.

The Langmuir adsorption constant and the regression, correlation coefficient obtained are given in Tables (5 and 6). The values of regression coefficients obtained from this model were used as the fitting criteria to find out this isotherm. Maximum sorption capacity q_{max} represents monolayer coverage of sorbent with sorbate and b represents enthalpy of sorption and should vary with temperature. The essential characteristic of the Langmuir isotherms can be expressed in terms of dimensionless constant separation factor or equilibrium parameter, R_L, which is defined as[59]:

$$R_L = 1/(1+bC_o) \quad \ldots (11)$$

where b is the Langmuir constant and C_o is the initial concentration of the metals ions (mg/L). R_L value indicates the shape of the isotherm. R_L values between 0 and 1 indicate favorable adsorption. R_L equal to 0 indicate irreversible adsorption, $R_L = 1$ is linear and $R_L>1$ is unfavorable. From our study, R_L values for Co^{2+} ions adsorption ranged from 0.018 to 0.1 for nano bentonite, therefore the adsorption process is favourable[60], from 0.018 to 0.1 for nano bentonite.

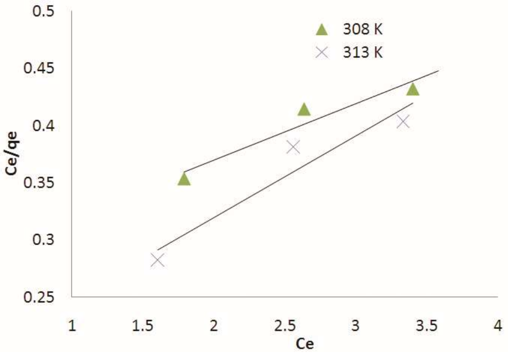

Fig. 13 — The linearized Langmuir adsorption isotherm for Co^{2+} by nano bentonite at different temperatures

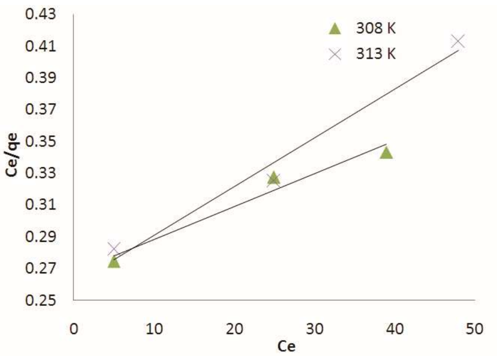

Fig. 14 — The linearized Langmuir adsorption isotherm for Co^{2+} by activated carbon at different temperatures.

Freundlich isotherm model

The Freundlich Equation is an empirical model allowing for multilayer adsorption on sorbent. The non-linear form of Freundlich model Eq. (12) is[61]:

$$q_e = K_F (C_e)^n \quad \dots (12)$$

The linear form of Freundlich model can be expressed as Eq. (13).

$$\ln q_e = \ln K_F + 1/n \ln C_e \quad \dots (13)$$

where q_e is loading adsorbate on adsorbent at equilibrium (mg/g), K_F is indicator of sorption capacity, C_e is an aqueous concentration of adsorbate at equilibrium (mg/L) and n is adsorption intensity.

The cobalt sorption isotherm followed the linearized Freundlich model as shown in Fig. 15. The relation between the metal uptake capacity q_e (mg/g) of adsorbent and the residual metal ion concentration C_e(mg/L) at equilibrium is given by Eq. (13).

The correlation coefficient and other parameters obtained for adsorbent is shown in Table 5. Correlation coefficient (R^2) of the adsorption isotherm data showed that adsorption of Co^{2+} ions on activated carbon and nano bentonite was better fitted to Freundlich isotherm model. The 1/n value is less than 1, it indicates a favorable adsorption and confirmed the heterogeneity of the adsorbent and it indicates that the bond between heavy metal ions and nano bentonite is strong[63].

Tempkin isotherm

Tempkin isotherm is given as:

$$q_e = B\ln(K_T C_e) \quad \dots (14)$$

It can be expressed in the linear form as:

$$q_e = B\ln K_T + B\ln C_e \quad \dots (15)$$

where B=RT/b

A plot of q_e versus ln C_e Fig.-16 enables the determination of the isotherm constants B and K_T from the slope and the intercept respectively[64].Tempkin constants are given in Table 7. K_T is the equilibrium binding constant corresponding to the maximum binding energy and constant B is related to the heat of adsorption[65].

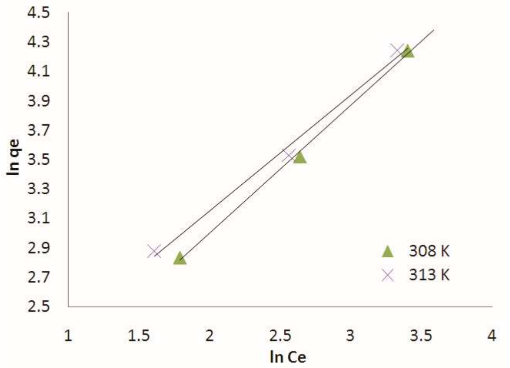

Fig. 15 — The linearized Freundlich adsorption isotherm for cobalt by nano bentonite at different temperatures.

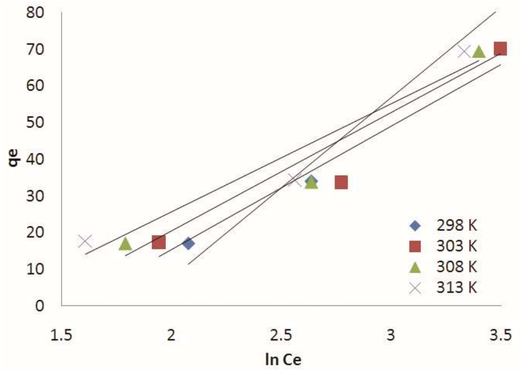

Fig. 16 — The linearized Tempkin adsorption isotherm for cobalt by nano

Table 7 — Parameters of Tempkin Isotherm models(adsorption cobalt on nano bentonite and activated carbon at different temperatures)

	Nano bentonite Tempkin constants		
Temperature (K)	B	K_T	R^2
298 K	49.18	0.16	0.9035
303 K	33.68	0.21	0.937
308 K	32.36	0.25	0.9457
313 K	29.50	0.32	0.9283

Conclusion

This thesis deals with studying the removal of toxic heavy metal ions, such as cobalt (II) from wastewater using nano bentonite as adsorbents

It is found that, both of activated carbon and nano bentonite capable of removing Co(II) ions from wastewater. The adsorption was dependent on contact time, initial Co(II) ion concentration, adsorbent dosage and temperature. The sorption of Co(II) onto activated carbon and nano bentonite is strongly dependent on *p*H value. The sorption increased with increasing the *p*H value at *p*H < 6.5, and then maintains a high level of *p*H > 6.5.

Freundlich model has a better correlation coefficient (R^2) than the Langmuir model for the studied concentrations at 25°C also tempkin isotherm is applied.

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