Removal of Co^{2+} ions from aqueous solution by cation exchange sorption onto NiO

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ABSTRACT

Batch adsorption technique was used to study the adsorption of cobalt on NiO. The aim of this work was to examine the effect of pH, concentration and temperature on the ion exchange removal of Co^{2+} from aqueous solution by the NiO surface. We used Langmuir model to interpret the adsorption data. The Kurbatov-type plots were tested to determine the adsorption mechanism. The kinetics of Co^{2+} adsorption on NiO was best described by film diffusion model. A well-known thermodynamic equation was used to assess the enthalpy and entropy of the system. The thermodynamic data were indicative of the spontaneous nature of the endothermic sorption process of Co^{2+} onto the NiO.

1. Introduction

Cobalt is released into the atmosphere from coal-fired power plants, incinerators, vehicular exhaust, mining, glass ceramics and paint industries, etc. [1]. One may be exposed to cobalt through breathing air, drinking water and eating cobalt-containing food. Cobalt may be easily transferred from pregnant mother to the infant through the breast milk. Beyond the permissible limit, cobalt causes chronic diseases in human beings such as vomiting, nausea, diarrhea, asthma, pneumonia, kidney congestion, skin degeneration, and weight loss [1,2].

Industrialization has a tremendous impact on the distribution of heavy metals in the environment. Industrial wastewaters generally contain different types of heavy metals. Most of the toxic metals enter into the water bodies from industrial discharges [3]. Various processes including electrolysis, reverse osmosis, evaporation, precipitation and sorption for the removal of metals from wastewater have been frequently studied [4]. Adsorption of metals on metal oxides/hydroxides plays a significant role in both natural and technological processes. Various conventional and non-conventional low cost adsorbents including metal oxides [5,6], resin [7], bacteria [8], algae [9] and fungi [10] have been frequently tested for the removal of metals from aqueous solution. The usefulness of the adsorbents depends upon their affinity, versatility and cost effectiveness. However, no data regarding to adsorption of Co^{2+} onto NiO has been reported elsewhere [11]. This work dealt with a series of

experiments to assess the feasibility of NiO for the removal of cobalt from aqueous solution under batch conditions. Effects of solution temperature, pH, initial cobalt concentration, and equilibrium time on the sorption performance of NiO were evaluated. This study is the first of its nature to be reported in the literature.

2. Materials and methods

2.1. Reagents and equipments

All the reagents used in this study were prepared of the chemicals of analytical grade. Cobalt nitrate $[Co(NO_3)_2]$ and nickel oxide [NiO] were purchased from Merck and BDH, respectively. Stock solutions of test reagents were prepared in deionized water. The cobalt and nickel in solution were analyzed using a Perkin Elmer atomic absorption spectrophotometer AAnalyst 800 with a graphite furnace atomizer, Zeeman background correction and an autosampler.

2.2. Characterization of NiO

The sample (NiO) was characterized by using the following methods [4]. Fourier transform infrared (FTIR) spectra of NiO mixed with KBr crystals were recorded in the range 400–4000 cm^{-1} with a Perkin Elmer 16 PC Fourier transform infrared spectrophotometer. X-ray patterns of the NiO were determined using JEOL X-ray diffractometer, model JDX-7E with Mn-filtered $CuK\alpha$ radiation. The surface area of the sample was calculated by the nitrogen adsorption using the surface area and pore size analyzer, Quantachrome Nova 2200e. The salt addition method [11] was applied for the

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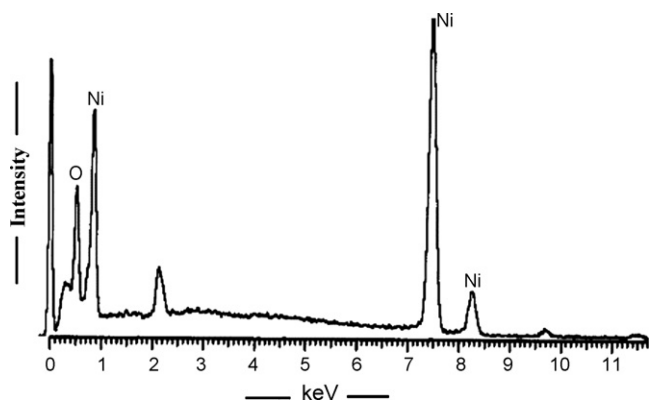*E-mail address:* naeeem64@yahoo.com (A. Naeem).

Fig. 1. EDX of virgin sample of NiO.

Fig. 2. Kinetics of Co^{2+} adsorption from its 20 mg L^{-1} solution onto NiO at pH 7.50.

determination of the point of zero charge (PZC). The dissolution method for NiO is the same as we reported earlier [12].

2.3. Adsorption experiment

The adsorption experiments of Co^{2+} ions were conducted in polypropylene batch reaction vessels using 5 g L^{-1} NiO suspension, which was prepared by suspending NiO powder (0.20 g) in 40 mL deionized water. Initial pH of the suspension was adjusted to 7.50 ± 0.10. The reaction vessels were placed on rotating rack that provided gentle end-over-end rotation for 24 h to attain a true equilibrium and final pH of the suspension was noted [10]. The suspension was centrifuged, filtered through a 0.45 µm nylon filter and the filtrate was analyzed for Ni^{2+} released and Co^{2+} ions adsorbed on NiO using atomic absorption spectrophotometer model AAnalyst 800. Similar adsorption experiments of Co^{2+} ions were conducted at different pH and temperatures. Some preliminary adsorption kinetics experiments were performed at 303, 313 and 323 K at pH 7.50 ± 0.10 to elucidate the sorption mechanism.

3. Results and discussion

3.1. Characterization of NiO

The characteristics of adsorbent play a significant role in the adsorption of metal ions from aqueous solution. It is, therefore, necessary to determine the surface properties of the adsorbent for proper interpretation of adsorption data.

The surface area of NiO determined by nitrogen gas adsorption is observed to be $23 \pm 2 \, m^2 \, g^{-1}$ which is comparable to the value reported by Tewari and Campbell [13] and Micale et al. [14]. The point of zero charge determined by salt addition method is observed to lie at pH 8.45 [12]. The powder diffraction patterns of sample correspond to the NiO according to the joint committee for powder diffraction (JCPDS) card 01-1239 [15]. No element other than the Ni and O was detected in the energy dispersive X-ray (EDX) spectrum of NiO (Fig. 1). As was reported in our previous paper [11], the FTIR spectrum displayed the peaks at 520, 1000, 1640 and 3400 cm^{-1} which are the characteristic peaks of NiO. The FTIR spectrum demonstrates that the sample is hydrated NiO. The dissolution of NiO decreases with increase in pH. No dissolution of NiO occurs at pH 7 and above. These findings are in fair agreement with results reported elsewhere [12,16].

3.2. Sorption kinetics

Simple batch adsorption kinetics experiments of NiO for Co^{2+} ions were conducted in the temperature range $303–323 \pm 1$ K. The

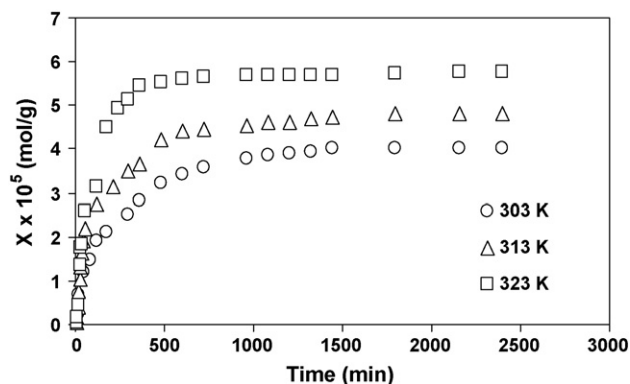adsorption kinetics is shown in Fig. 2, which shows that the adsorption (X) of cobalt ion reaches equilibrium in about 960 min. The equilibrium adsorption of Co^{2+} ions is observed to be 3.40, 4.16 and 5.63 mol g^{-1} at 303, 313 and 323 K, respectively. The equilibrium time is an important parameter for economical wastewater treatment. Therefore, 1440 min (24 h) was selected as an optimum agitation period to attain a true equilibrium condition for subsequent batch experiments.

The diffusion of ions within the adsorbent particle is termed as particle diffusion. Respective kinetic film diffusion equation can be written as follows [17]:

$$-\ln(1 - F) = K_{fd}t \tag{1}$$

where F ($F = q_t/q_e$) refers to the ratio of metal adsorbed at time t (q_t) to the metal adsorbed at equilibrium time (q_e) and K_{fd} is the film diffusion rate constant. The plots of $-\ln(1 - F)$ versus time (t) should pass through the origin with no intercept.

The diffusion of ions from liquid to the NiO surface might be important to interpret the kinetic of the adsorption process. The plots of $-\ln(1 - F)$ versus t fit the data over the entire course of experiment having coefficient of correlation greater than 0.98 (Fig. 3). The data in figure show a straight line having a slope with no intercept that indicates the mechanism of cobalt adsorption can be described by the film diffusion equation. Thus, the film diffusion is the mechanism controlling the rate of Co^{2+} adsorption onto the NiO. The values of film diffusion constant (K_{fd}) obtained from the slopes are found to be 4.00×10^{-3}, 5.60×10^{-3} and 8.60×10^{-3} min^{-1} at 303, 313 and 323 K, respectively.

The values of rate constants obtained from film diffusion (K_{fd}) increase with the increase in temperature indicating the stronger interaction of Co^{2+} with NiO at higher temperature. This infers that the adsorption reaction between cobalt and substrate is likely to
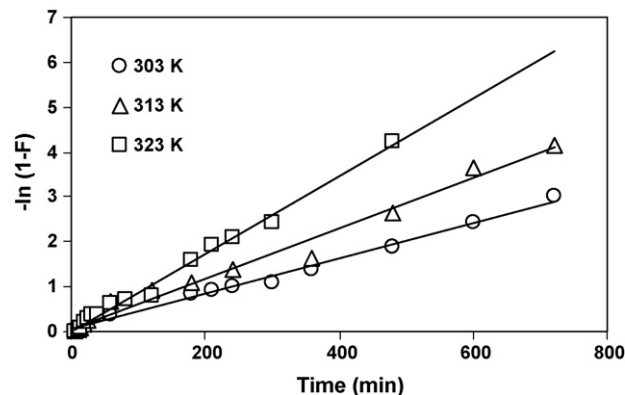

Fig. 3. Film diffusion plots for Co^{2+} adsorption of NiO at pH 7.50.
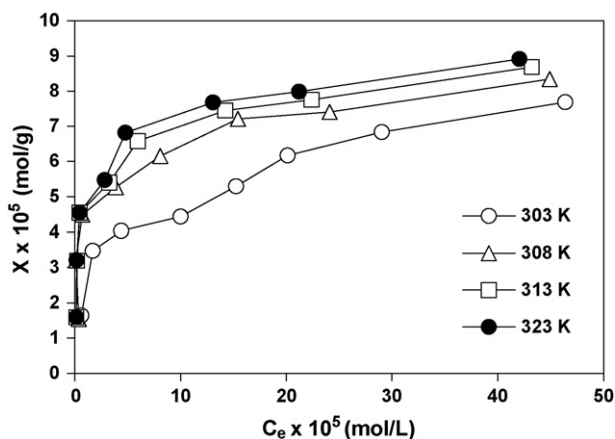
Fig. 4. Temperature effect on adsorption of Co^{2+} onto NiO at pH 7.50.

be film diffusion controlled process. Similar kinetics behaviour was observed elsewhere for the uptake of metal ions on zirconium oxide [17].

3.3. Adsorption studies

3.3.1. Effect of temperature

The effect of temperature on cobalt adsorption was investigated by measuring the adsorption isotherms in the temperature range 303–323 ± 1 K. The results are given in Fig. 4. The increase in the amount of cobalt adsorbed per unit mass of adsorbent is more obvious at higher surface coverage where the uptake of cobalt increases from 7.69×10^{-5} to 8.68×10^{-5} mol g^{-1} when the temperature is raised from 303 to 313 K. Further increase in temperature to 323 K leads to increase in adsorption from 8.68×10^{-5} to 8.91×10^{-5} mol g^{-1}. Thus, the adsorption does not change significantly when the temperature changes from 313 to 323 K suggesting that the adsorption behaviour is almost insensitive to the changes in the temperature in this range. Though, the overall temperature effect is weak on the cobalt adsorption, but yet the adsorption seems to be endothermic in nature. Several authors [18–20] have reported the endothermic nature of metal adsorption onto metal oxides/hydroxides and activated phosphate rock.

We observed that the adsorption capacity of NiO for Co^{2+} increases when the initial concentration of Co^{2+} is increased indicating that the uptake of Co^{2+} is concentration dependent. The increase in initial concentration provides an important driving force to overcome all mass transfer resistance of Co^{2+} ions between the aqueous and solid phases [21]. Similar results were reported for the ion exchange removal of metal ion by kaolinite [22].

3.3.2. Effect of pH

The pH of aqueous solution is an important controlling parameter in the adsorption of metal ions onto metal oxides/hydrous oxides. We studied the adsorption of cobalt on the NiO by varying the concentration from 5 to 50 mg L^{-1} over the pH range of 7.00–8.50 for a constant adsorbent amount of 5 g L^{-1}.

We noted that pH of the suspension is playing an important role in the ion exchange removal of cobalt from aqueous into the solid phase. The experimental results (shown in Fig. 5) indicate that the uptake of Co^{2+} onto the NiO surface increases sharply and reaching the higher value within a pH range of 1–2 pH units. Kanungo et al. [23] observed similar edges for Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} adsorption onto δ-MnO_2.

The increase in the adsorption capacity of NiO with the increase in pH is expected, as the increase in hydroxyl ions would dissociate more protons from the available surface group (NiOH) of the
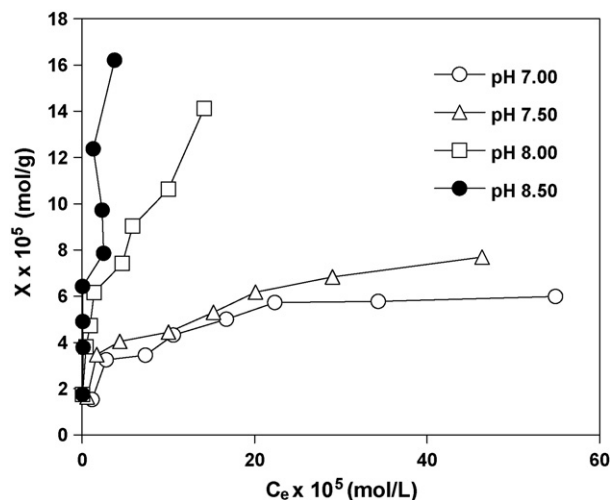

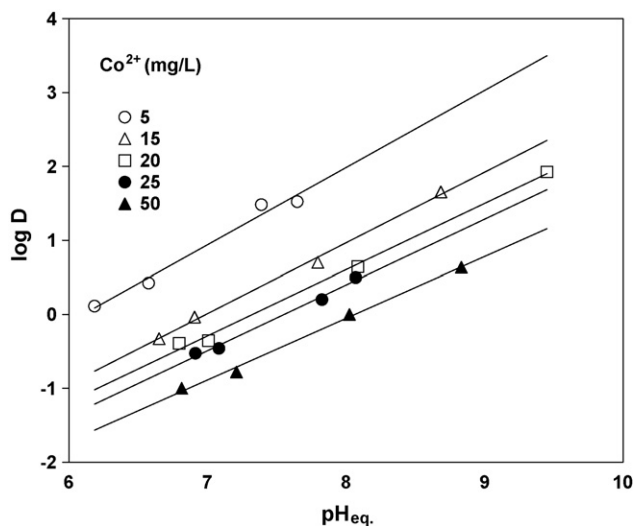**Fig. 5.** pH effect on the adsorption of Co^{2+} onto NiO at 303 ± 1 K.

Fig. 6. Plots between $\log D$ and pH_{eq} for Co^{2+} adsorption onto NiO at 303 ± 1 K.

NiO. Consequently, the surface becomes negatively charged which are neutralized by the Co^{2+} ions present in the solution [24]. The number of replaceable protons by the adsorbed metal ions can be estimated from the decrease in equilibrium pH of the suspension.

The ratio of the H$^+$ ions released to cobalt adsorbed can be determined by using a well-known Kurbatov equation in the form [25,26]

$$\log D = K + n pH_{eq} \tag{2}$$

where D (L g^{-1}) is the distribution coefficient, n is the stoichiometric ratio and K is the exchange constant.

The plots of $\log D$ versus pH_{eq} of the suspension (Fig. 6) give a linear relation with correlation coefficient (R^2) >0.98. The molar stoichiometry (n) of H$^+$/Co^{2+} (Table 1) is found to be in the range 0.83–1.04. This shows that the surface of NiO prefers to adsorb the

Table 1
Stoichiometric (n) values for Co^{2+} adsorption onto NiO at 303 ± 1 K.

Cobalt conc. (mg L^{-1})	Stoichiometry (n) (H$^+_{rel}$/Co^{2+}_{adsorb})	R^2
5	1.04	0.980
15	0.96	0.997
20	0.89	0.996
25	0.88	0.991
50	0.83	0.996
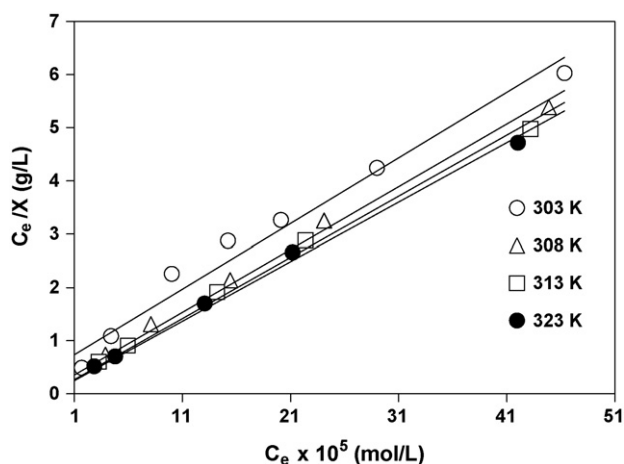
Fig. 7. Langmuir plots for adsorption of Co^{2+} onto NiO at pH 7.50.

Fig. 8. Plot of $\ln K_b$ versus T^{-1} for Co^{2+} adsorption onto NiO at pH 7.50.

singly charged $CoOH^+$ from aqueous electrolyte solution. Thus, the mechanism for Co^{2+} sorption onto the solid surface can be proposed as follows:

$$NiOH + CoOH \rightleftarrows NiOCoOH + H^+ \qquad (3)$$

where NiOH represents the available surface groups for the adsorption. Kanungo et al. [23] also support the proposed mechanism by mentioning that the singly charged $M(OH)^+$ ions are more easily exchanged than the doubly charged M^{2+} ions.

We used the linear form of conventional Langmuir model to calculate the Langmuir parameters. This model is explained with the help of following equation [25].

$$\frac{C_e}{X} = \frac{1}{K_b X_m} + \frac{C_e}{X_m} \qquad (4)$$

where C_e (mol L^{-1}) is the equilibrium concentration of Co in the bulk solution, X (mol g^{-1}) is the amount of Co^{2+} sorbed per mass of NiO, X_m and K_b are the sorption maxima and the binding energy constant, respectively.

The coefficient of correlation (R^2) for all plots in Fig. 7 is found to be higher than 0.976 indicating that the experimental data is best fitted to Eq. (4). The similar values of X_m represent the good fit of Langmuir model to the present experimental data (Table 2). Moreover, the X_m values are found to increase with the increase in initial pH of the suspension (Table 3), which augments the conclusion drawn from the adsorption isotherms.

The magnitude of the adsorption maxima is in agreement with sorption maxima of ZnO [27] and is comparable in magnitude with the other metal oxides/hydroxides [28]. The increase in X_m and K_b values shows that binding strength between Co^{2+} and NiO becomes more favourable at higher temperatures.

3.4. Thermodynamic parameters

The temperature dependence of Co^{2+} adsorption was studied by conducting batch experiments at different temperatures. The standard enthalpy (ΔH) and entropy (ΔS) changes for Co^{2+} adsorption were assessed by using the relationship [6,18]:

$$\ln K_b = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (5)$$

The data in Fig. 8 show a linear relation between $\ln K_b$ versus T^{-1} according to Eq. (5). The values of the thermodynamic parameters are listed in Table 4. The standard enthalpy change (ΔH) computed from the slope was assessed to be 72.34 kJ mol^{-1} which shows the increased supply of heat would lead to enhance the adsorption of cobalt onto the NiO. Similar positive values of ΔH have been reported elsewhere for the adsorption of metal on Na-rectorite [29] and divalent and trivalent oxides/hydrous oxides of metal [27,28].

The positive value of ΔS shown in Table 4 indicates the increase randomness at solid solution interface during the adsorption of Co^{2+} on NiO. The spontaneity of the Co^{2+} adsorption onto the NiO has been justified thermodynamically by the decrease in Gibbs free energy with increase in temperature [29]. To our knowledge, no data on metal ions adsorption onto NiO is reported, elsewhere. Thus, the magnitude of the thermodynamic parameters cannot be compared directly with the literature. However, present findings are consistent with the results observed by Angove et al. [22,30] on the Co^{2+} adsorption by koalinite and goethite in the temperature range of 303–323 K with the ΔG values decreasing from −25.56 to −32.02 kJ mol^{-1}.

Table 2
Langmuir parameters X_m and K for Co^{2+} adsorption on NiO as a function of temperature at pH 7.50.

Temp. (K)	X_m ($\times 10^5$ mol g^{-1})	K (L g^{-1})	Experimental X_m ($\times 10^5$ mol g^{-1})	R^2
303	8.13	20065.45	7.69	0.976
308	8.48	50424.83	8.34	0.994
313	8.69	74672.34	8.68	0.995
323	8.93	82958.98	8.91	0.996

Table 3
Langmuir parameters X_m and K for Co^{2+} adsorption onto NiO as a function of pH at 303 ± 1 K.

pH	X_m ($\times 10^5$ mol g^{-1})	K (L g^{-1})	Experimental X_m ($\times 10^5$ mol g^{-1})	R^2
7.00	6.41	17550.38	5.99	0.995
7.50	8.13	20048.90	7.69	0.976
8.00	11.27	2634.52	14.13	0.976
8.50	17.61	260550.50	16.21	0.988

Table 4
Enthalpy, entropy and free energy changes for Co^{2+} adsorption on NiO at pH 7.50.

S. No	Temp. (K)	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J/mol K)
1	303	−25.56	72.34	323.10
2	308	−27.17		
2	313	−28.79		
3	323	−32.02		

4. Conclusions

The Co^{2+} adsorption onto NiO increases with the increase in concentration, temperature and pH of the system. The solution pH plays a decisive role in the surface dissolution and adsorption of metal ions onto the NiO. The uptake of Co^{2+} by NiO is achieved neither by its precipitation nor due to the replacement of Ni from NiO. The adsorption process is found to be the cation exchange between protons from the solid and Co^{2+} from aqueous solution. The film diffusion mechanism is responsible for the uptake of Co^{2+} by the NiO. The thermodynamic parameters are indicative of the spontaneous nature of the cobalt adsorption process on to the NiO.

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