



## Cation exchange removal of Cd from aqueous solution by NiO

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### ABSTRACT

Detailed adsorption experiments of Cd from aqueous solution on NiO were conducted under batch process with different concentrations of Cd, time and temperature of the suspension. The solution pH is found to play a decisive role in the metal ions precipitation, surface dissolution and adsorption of metal ions onto the NiO. Preliminary adsorption experiments show that the selectivity of NiO towards different divalent metal ions follows the trend  $Pb > Zn > Co > Cd$ , which is related to their first hydrolysis equilibrium constant. The exchange between the proton from the NiO surface and the metal from solution is responsible for the adsorption. The cation/exchange mechanism essentially remains the same for Pb, Zn, Co and Cd ions. The sorption of Cd on NiO particles is described by the modified Langmuir adsorption isotherms. The isosteric heat of adsorption ( $\Delta H$ ) indicates the endothermic nature of the cation exchange process. Spectroscopic analyses provide evidence that Cd is chemisorbed onto the surface of NiO.

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### 1. Introduction

Cadmium is an extremely toxic metal even in low concentrations. It naturally occurs in environment and is a major contaminant. Cadmium (Cd) toxicity contributes to diseases such as heart disease, cancer and diabetes. Cadmium intoxication also causes tracheo-bronchitis, pneumonitis, pulmonary edema, brain damage, bone diseases, anemia, skin and lung cancer [1–4]. Cadmium concentrates in the kidney, liver and bone and is considered more toxic than either lead or mercury. Ingestion of any significant amount of cadmium causes immediate poisoning and damage to the liver and the kidney [3,4].

Exposure to cadmium is also on the increase due to its use as a coating for iron, steel and copper. It is also used in phosphate fertilizer, cadmium batteries, copper alloys, cosmetics and fungicides and in many other products [5,6]. Cigarettes are also an important source of cadmium exposure. Even though there is usually smaller amount of cadmium in tobacco than in food, the lungs take up cadmium more efficiently than the stomach [6,7].

The main source of cadmium contact by the general population is drinking water. Environmental pollution and contamination are major problems and have become key focus of concern. It is essential to reduce the metal load of an effluent before its release into water body [8,9].

Metal removal from industrial wastewater has been accomplished by several techniques [10–14]. Considerable work [15–18] has been done on the metal removal through adsorption because the system is simple to operate, accurate and cost-effective. We recently studied the cation exchange properties of NiO [19–21]. The current study regarding the adsorption of Cd by NiO is a reasonable extension of the work being carried out in our lab. This study presents new and interesting results and it also confirms the potential use of NiO for the effective removal of cadmium from water.

### 2. Materials and methods

All the required solutions were prepared in polypropylene bottles to prevent contamination. Cadmium nitrate [ $Cd(NO_3)_2$ ] salt was used to prepare cadmium solutions. The determination of metals concentrations was performed using a Perkin Elmer atomic absorption spectrophotometer (model AAnalyst 800, graphite furnace mode). The purity of the sample NiO supplied by the manufacturer is >99.9%.

#### 2.1. Characterization of NiO

The BDH sample of NiO was characterized by X-ray diffractometry (XRD), infrared spectroscopy (IR), scanning electron microscopy (SEM) coupled with energy dispersive X-ray analyses (EDX), surface area and point of zero charge (PZC). The methods of characterization and dissolution are given in our earlier papers [7,19–21].

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## 2.2. Adsorption experiments

The adsorption experiments of Cd on NiO were conducted in polypropylene batch reaction vessels using  $5 \text{ g L}^{-1}$  NiO suspension, which was prepared by suspending NiO powder (0.20 g) in 40 mL deionized water. In most of the sorption studies initial pH of the suspension was adjusted to 7.50 to minimize the potential experimental complication resulting from the precipitation of the metal cation and dissolution of the adsorbent. The reaction vessels were equilibrated in a temperature controlled shaker bath for 24 h at desired temperature. The suspension was centrifuged, filtered through a  $0.45 \mu\text{m}$  nylon filter. The filtrate was acidified and analyzed by a Perkin Elmer atomic absorption spectrophotometer (model AAnalyst 800, graphite furnace mode) to determine the concentrations of metal remaining in the solution. Detailed adsorption experiments were performed at 298, 303, 308 and 313 K at pH 7.50. The effect of pH on metal adsorption was studied by varying the pH in the range of 7.50–9.50.

The adsorption kinetics experiments were conducted separately at pH 7.50 for NiO using  $20 \text{ mg L}^{-1}$  Cd suspension and 0.20 g dry mass of media in 40 mL at different temperatures. Solid residues were subjected to XRD and SEM/EDX analyses to probe the adsorption mechanism.

## 3. Results and discussion

### 3.1. Characterization of NiO

The surface area of NiO was determined by nitrogen gas adsorption after 24 h degassing at 77.4 K. The BET equation was used to calculate the surface area ( $23 \pm 2 \text{ m}^2 \text{ g}^{-1}$ ) of NiO which is comparable to the values reported by Tewari and Campbell [22] and Micalé et al. [23]. The average pore width and micropore volume of NiO were found to be  $1.98 \times 10^2 \text{ \AA}$  and  $2.52 \times 10^{-2} \text{ cm}^3 \text{ g}^{-1}$ , respectively. The PZC of NiO determined by the method of Kinniburgh et al. [24] is found to be 8.45 at 303 K which decreases to 8.09 at 323 K. This value of PZC is similar to the one reported for ZnO [25].

X-ray patterns of the powder sample were recorded over a range of  $2\theta$  angle from  $30^\circ$  to  $65^\circ$  using a JEOL X-ray diffractometer, model JDX-7E with Mn-filtered Cu-K $\alpha$  radiation. The crystalline phases of the NiO were identified using the joint committee on powder diffraction standards (JCPDS) file. The XRD measurement shows that the virgin sample of NiO is single-phase with a cubic structure (see supporting information Fig. S1). The observed diffraction data are in good agreement [26] with JCPDS card no: 01-1239 of NiO. The current results of XRD are also similar to the one reported for NiO by Tao and Wei [27]. Moreover, the XRD analyses of the sample supported the conclusion that the particles were composed of nickel oxide only and no evidence of impurity was obtained. Scanning electron microscopy (SEM) model JSM5910 (JEOL Japan) revealed that the NiO is porous in nature. In this study, the EDX analyses were also employed to analyze the elemental composition of the virgin sample by using the EDX microanalyzer model INCA 200 (UK). In addition to Ni and O, a peak for carbon was also detected in the EDX spectrum of NiO (Fig. S2). The observed peak for carbon is due to the coating of the sample with carbon coater, model no. 11428, SPI Supplies USA. The IR spectrum of NiO has been discussed in detail in our previous work [19–21].

### 3.2. Dissolution

We observed that the dissolution of the NiO decreases with the increase in pH from 2.00 to 11.00 (Fig. S3). However, the release of Ni from NiO becomes negligible at pH 7.00 and above. These findings are in agreement with results reported for the dissolution of

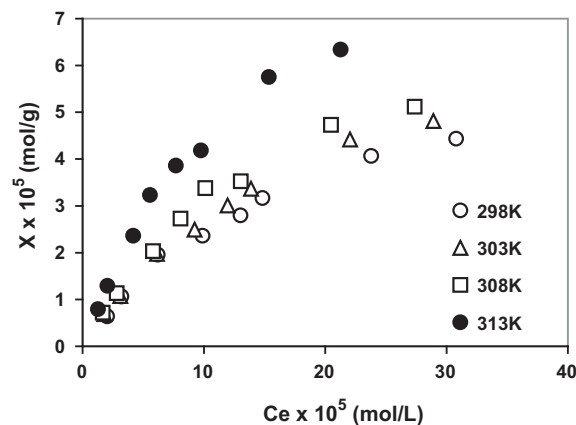


Fig. 1. Temperature effect on the adsorption of Cd on NiO at pH  $7.50 \pm 0.10$ .

NiO [28], ZnO [25] and BeO [29]. We also studied the dissolution of NiO activated (heat treated) at 523, 823 and 1223 K under vacuum. The dissolution of NiO decreases significantly with the heat treatment and no dissolution of Ni was detected in the pH range 2–11 for sample heated at 1223 K. Thus, NiO was activated at higher temperature in order to prevent the dissolution of NiO and to clean up the environment without creating harmful byproduct.

### 3.3. Adsorption equilibrium

Simple batch adsorption kinetics experiments of NiO for Cd were carried out in the temperature range of 303–323 K. The preliminary experimental data showed that the adsorption of Cd onto NiO reaches equilibrium in about 16 h. However, we selected 24 h as an optimum agitation period to attain a true equilibrium condition for subsequent batch experiments.

The temperature dependence of Cd adsorption data at pH 7.50 is displayed in Fig. 1. As can be seen, the temperature has a substantial effect on the extent of Cd adsorption onto the nickel oxide. The adsorbate–adsorbent complex becomes more significant at higher temperature, which indicates that the interaction between Cd and solid surface to be endothermic. The increase in the Cd adsorption with temperature may also be correlated with a decrease in the positive surface charge on account of the lowering of its PZC and the subsequent increase in the number of neutral surface OH group [30].

We observed that the adsorption capacity of NiO for Cd increases (Fig. 1) when the concentration of Cd is increased indicating that the uptake of Cd is concentration dependent. This increase in the equilibrium sorption capacity of the NiO with the initial concentration of Cd may be due to high driving force for mass transfer. Similar results were reported for the ion exchange removal of metal ion by different metal oxides [31,32].

### 3.4. Selectivity of NiO

The selectivity of NiO towards the studied metal ions is found to be in the order  $\text{Pb} > \text{Zn} > \text{Co} > \text{Cd}$  (Fig. 2). The selectivity sequence of metal is generally explained on the basis of ionic radii, atomic weight, softness, electronegativity and hydrolysis constants of metal cations. As was observed elsewhere [33], the present selectivity sequence is in a line with the first hydrolysis constant values of these metal ions. Several investigators are of the opinion that the hydrolysed metal ( $\text{MOH}^+$ ) is strongly sorbed than free metal cations. The preferential uptake of Pb by NiO is assigned to its lowest pH of hydrolysis. The uptake of Cd is lowest in the series because of its higher pH values at which Cd hydrolysis begins to occur. The cur-

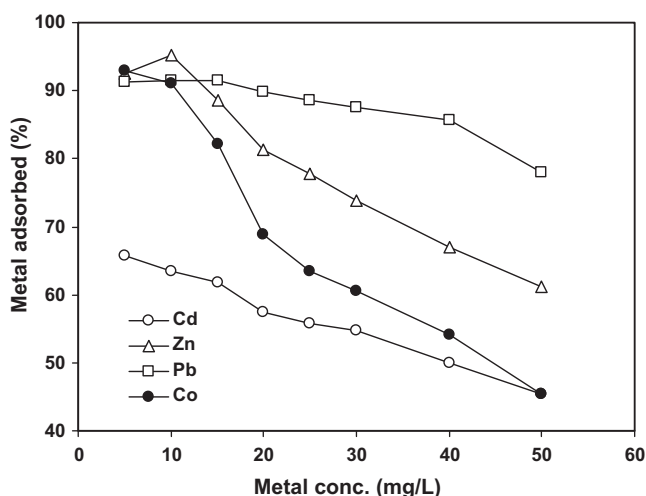


Fig. 2. Adsorption affinity of NiO toward different divalent metal ions at  $303 \pm 1$  K.

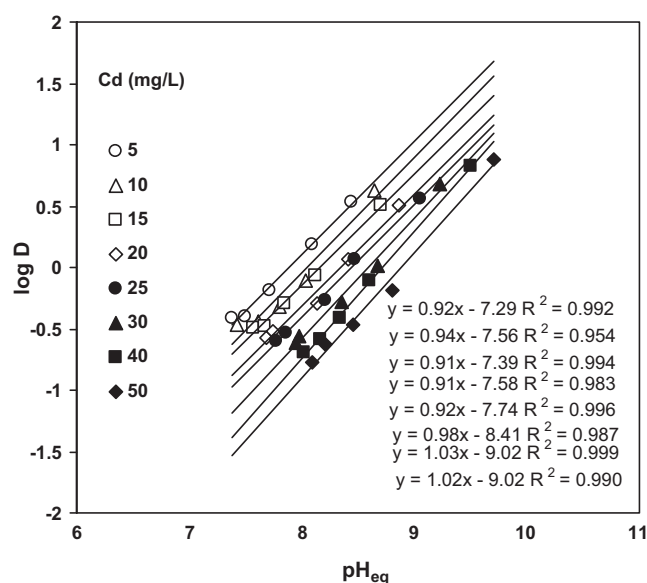


Fig. 4.  $\log D$  vs.  $\text{pH}_{\text{eq}}$  for Cd adsorption on NiO at  $303 \pm 1$  K

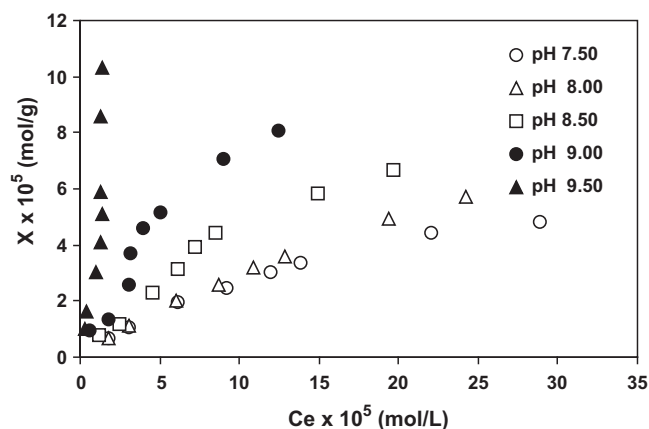


Fig. 3. pH effect on the adsorption of Cd on NiO at  $303 \pm 1$  K.

rent selectivity sequence is consistent with one reported for other metal oxides/hydroxides [34].

### 3.5. pH effect

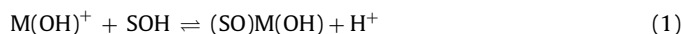
Adsorption of Cd on the NiO was observed to increase with the increase in pH of the system (Fig. 3). The surface is more protonated at lower pH values because of the high concentration of protons, which prevents the adsorption of Cd due to electrostatic repulsion. However, the converse is true at higher pH values due to electrostatic attraction [35]. The almost complete removal of Cd at pH values  $\geq 9.00$  is due to onset of Cd precipitation at the solid surface as it is highly insoluble in alkaline medium.

Table 1

Langmuir parameters  $X_m$  and  $K$  for the adsorption of Cd on NiO as a function of temperature at  $\text{pH} 7.50 \pm 0.10$ .

Temp. (K)	Experimental value $X_m$ ( $\times 10^5$ mol/g)	Modified Langmuir equation			
		$X_m$ ( $\times 10^5$ mol/g)	Binding constant, $K$ (L/g)	Separation factor ( $R_L$ )	Correlation coefficient ( $R^2$ )
298	4.44	5.21	–	–	0.993
303	4.81	5.87	11.96	0.999	0.999
308	5.12	8.62	18.91	0.999	0.995
313	6.34	9.09	47.60	0.998	0.996

The pH of the suspension is observed to decrease with the increase in the adsorption of the divalent metal ions which is indicative of the replacement of surface protons by the adsorbed metal cations, according to the following tentative mechanisms:



The mechanism of divalent metal adsorption onto the substrate (SOH) was determined by testing a well-known Kurbatov equation [35] into the experimental data in the form:

$$\log D = C + n\text{pH}_{\text{eq}} \quad (3)$$

where  $D$  ( $\text{L g}^{-1}$ ) represents the distribution coefficient,  $C$  is the constant, and slopes  $n$  of the lines refer to the  $\text{H}^+/\text{M}^{2+}$  stoichiometry.

The experimental data is plotted in the form of  $\log D$  vs. equilibrium pH of the suspension (Fig. 4). As can be seen, the values of  $n$  ( $\text{H}^+/\text{M}^{2+}$ ) determined from the slopes of the straight lines are almost equal to one (Table S1). These values of  $n$  ( $n \cong 1$ ) show a one-to-one correspondence between metal loading and the hydrogen ion release from the solid, according to reaction (1). Thus, one mole of hydrogen is released for one mole of divalent metal adsorbed, indicating that  $\text{M}^{2+}$  is adsorbed in its hydrolyzed ( $\text{MOH}^+$ ) form. It is concluded from above discussion that the singly charged  $\text{MOH}^+$  ions are easily exchanged (reaction (1)) than the doubly charged  $\text{M}^{2+}$  ions (reaction (2)). James and Healy [36] also reported that the adsorption mechanism which occurs through the formation of hydroxo complex is thermodynamically more stable than the free metal cations.

One can also predict from  $n$  values that the adsorption mechanism for Zn, Co, Cd and Pb essentially remains the same except

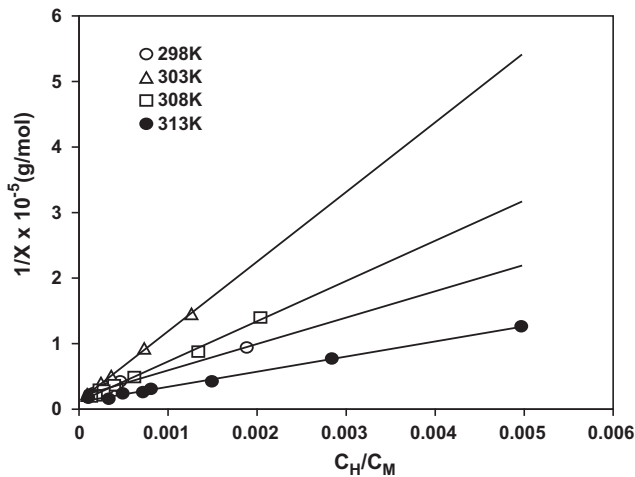


Fig. 5.  $1/X$  vs.  $C_H/C_M$  for Cd adsorption onto NiO at pH  $7.50 \pm 0.10$ .

for the highest concentration of Pb where the value of  $n$  decreases from unity to 0.68 (Table S1). The low value of  $n$  indicates the precipitation of Pb in the form of  $Pb(OH)_2$ .

We reached the following general adsorption mechanism on the basis of proton released from the surface into the aqueous phase:



where R stands for the solid surface of NiO.

Conventional Langmuir model [15,37] was applied in the present case. However, the values of sorption maxima ( $X_m$ ) were found to be sufficiently higher than the values experimentally observed (Table 1). Generally, the adsorption of metal cations leads to decrease in equilibrium pH of the solution [15], which substantially changes the sorption capacity of the metal oxides/hydroxides. In the present study the modified Langmuir equation is used which is basically derived for solid–liquid interface and takes into account the  $H^+$  of the aqueous solution. Applying the law of mass action to the general form of ion exchange reaction (4), the equilibrium constant can be written as:

$$K = \frac{[R_nM^{z-1}][H^+]^n}{[RH]^n[M^{z+}]} \quad (5)$$

Eq. (5) can be re-written in the form:

$$K = \frac{[X]}{[X_m - X]} \frac{[C_H]}{[C_M]} \quad (6)$$

where  $X$  is the amount of Cd sorbed per unit mass of NiO,  $C_H$  and  $C_M$  are the equilibrium concentrations of  $H^+$  and  $Cd^{2+}$  ions in aqueous solutions, respectively,  $K$  is the binding energy constant and  $X_m$  is the exchange capacity in the metal oxide. On re-arrangement, Eq. (6) can be transformed into:

$$\frac{1}{X} = \frac{1}{X_m} + \left(\frac{C_H}{C_M}\right) \frac{1}{KX_m} \quad (7)$$

The plots of  $1/X$  vs.  $C_H/C_M$  should be a straight line with slope of  $1/KX_m$  and intercept of  $1/X_m$ . The coefficient of correlation ( $R^2$ ) for all the plots in Fig. 5 are found to be higher than 0.992 indicating that the data is best fitted to Eq. (7). The values of sorption maxima ( $X_m$ ) are similar to those determined from the experimental data. The  $X_m$  values are found to increase with the increase in temperature (Table 1), which augments the conclusion drawn from the adsorption isotherms. Like  $X_m$ , the values of  $K$  increase with increase in temperature. The values of the adsorption maxima are in agreement with sorption maxima of ZnO [25] and are comparable in magnitude with the other metal oxides/hydroxides [15].

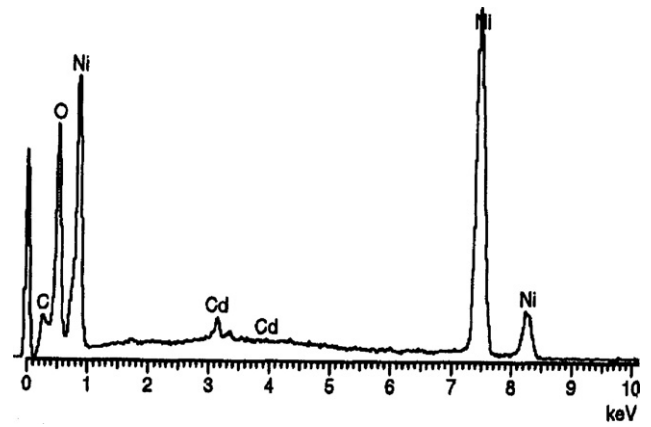


Fig. 6. EDX of Cd impregnated NiO at 303 K.

### 3.6. Spectroscopic evidence

The solid residues of the adsorbent before and after adsorption of Cd were subjected to XRD and SEM/EDX analyses. We did not observe any change in the X-ray diffraction pattern of the substrate before and after adsorption of Cd. This is probably due to the limitation of the XRD. As reported elsewhere [18], the XRD can normally detect phases at concentration higher than 1% of the sample matrix.

In this study, the EDX analyses were employed to analyze the elemental composition of the solid samples. The data given in Fig. 6 display a spectrum of NiO after reacting with Cd ions. The EDX spectrum shows the presence of Cd in the sample which confirms the cadmium adsorption onto the surface of the NiO. Lai et al. [38] have reported similar results for the uptake of Cd, Pb and Cu adsorption on the goethite-coated sand.

### 3.7. Isothermic heats of adsorption

We conducted adsorption experiments at different temperatures to calculate the isothermic heats of adsorption ( $\Delta H$ ) by applying the Clausius–Clapeyron equation [39] in the form:

$$\ln[C_e]_\theta = \frac{\Delta H}{RT} + \text{constant} \quad (8)$$

where  $C_e$  is the remaining concentration of the Cd ions in solution after equilibration, the relative amount of Cd sorbed [ $\theta$ ] is maintained constant,  $R$  is the molar gas constant and  $T$  is the absolute temperature.

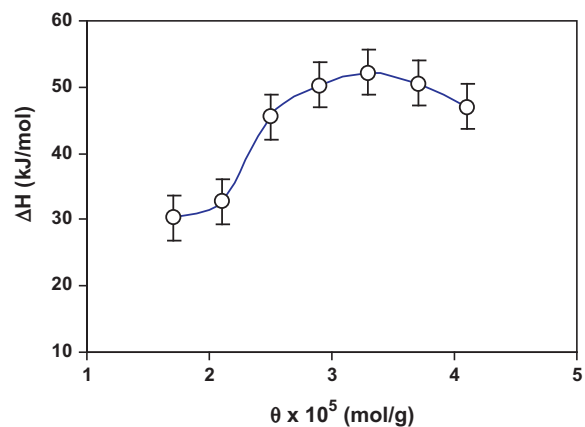


Fig. 7. Isothermic heat of adsorption ( $\Delta H$ ) as a function of surface coverage ( $\theta$ ) of Cd on NiO at pH  $7.50 \pm 0.10$ .

The plots of  $\ln[C_e]_\theta$  vs.  $T^{-1}$  are shown in [supplementary Fig. S4](#) with the coefficient of correlation ( $R^2$ ) > 0.90. The isosteric heats of adsorption ( $\Delta H$ ) obtained from the slopes of the adsorption isostere are given in [Fig. 7](#).

The values of  $\Delta H$  shown in [Fig. 7](#) vary with surface loading  $[\theta]$  which indicates that the surface of NiO is energetically heterogeneous. The adsorption enthalpy also shows that adsorption of Cd on NiO is endothermic [40] which becomes more endothermic as the surface coverage increases. Bruemmer et al. [41] observed similar positive enthalpy values for Cd, Zn and Pb sorption onto hematite surface. The enthalpy–surface coverage curve exhibits that at lower surface coverage region the enthalpy is lower and the temperature has insignificant role in adsorption process when the surface coverage is low. However, at high surface coverage the adsorption enthalpy gradually increases indicating the more dependency of adsorption process on temperature at high surface coverage, which augments the conclusion drawn from the adsorption isotherms.

#### 4. Conclusions

The dissolution of the NiO becomes negligible at pH 7 and above at all the temperatures of the system. NiO has an appreciable adsorptive capability for Cd dissolved in water. The Cd adsorption onto NiO is observed to increase with the increase in concentration, temperature and pH of the system. The affinity of NiO towards the divalent metals is observed to be  $Pb > Zn > Co > Cd$ . The removal of Pb, Zn, Co and Cd from aqueous solution onto NiO takes place through an ion exchange process. The solution pH is found to play a decisive role in the metal ions precipitation, surface dissolution and adsorption of metal ions onto the NiO. The uptake of Cd by NiO is achieved neither by the replacement of Ni from NiO nor due to precipitation of Cd at pH 7.50. However, the cation exchange process of Cd is partially accompanied by the precipitation of Cd ions at  $pH \geq 9.00$ . The spectroscopic analyses of the solid media also give strong support to the conclusion that cadmium ions were chemisorbed onto the surface of nickel oxide. The isosteric heats of adsorption ( $\Delta H$ ) showed that the adsorption process was endothermic in nature.

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jhazmat.2010.09.094](https://doi.org/10.1016/j.jhazmat.2010.09.094).

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