

Cation exchange removal of Pb from aqueous solution by sorption onto NiO

A. Naeem^{a,*}, M.T. Saddique^a, S. Mustafa^a, Y. Kim^b, B. Dilara^a

^a National Center of Excellence in Physical Chemistry, University of Peshawar, Peshawar-25120, Pakistan

^b Chungcheongnamdo Watershed Management Research Center, Chungnam Development Institute (CDI), 101 Geumheung-dong, Gongju, Chungcheongnam-Do 314-140, Republic of Korea

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ABSTRACT

This paper reports NiO as a novel and an efficient adsorbent for the removal of Pb from aqueous solutions. In the present investigation, Pb adsorption experiments on NiO were conducted on aqueous solution at different initial Pb concentration, pH of the solution and adsorption temperature. The mechanism of adsorption was observed to be an ion exchange between the surface proton and Pb in aqueous solution. Experimental data were best described by the Langmuir isotherms. The surface structure of the NiO before and after adsorption of Pb was analyzed by using FTIR spectroscopy, scanning electron microscopy (SEM) coupled with energy dispersive X-ray analyses (EDX).

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1. Introduction

Heavy metals and their compounds are widely used in industrial applications such as metallurgy, battery, paper and paint manufacturing [1]. The excessive use of the metal cations is increasing their amounts in the aquatic systems. Heavy metals are among the most important pollutants in waters. They are non-degradable and, therefore, continue to accumulate in water bodies [2,3]. Because of their toxic properties and the tendency for bio-accumulation in the food chain, it is necessary to take effective measures to reduce the concentration levels of heavy metals in waters.

Various methods including precipitation, ion exchange and adsorption [4–7] have been frequently practiced for the removal of heavy metals from water. Among these methods, precipitation is a simple, easily automated and widely applied process. However, this method fails to reduce the metal concentration to low level required by water quality standards [8].

Lead (Pb) is also one of the potentially toxic trace metal whose physiochemical cycle has been substantially affected by human activities. Lead is highly toxic when its concentration exceeds the threshold limit value (15 ppb) in drinking water. The environmental chemistry of Pb has probably stimulated more scientific interest than all other metallic elements combined [9,10].

Lead enters into water from mining, metallurgical processes, metal plating, phosphate fertilizer, lead storage batteries,

electrodes, cables, ceramics, oil refinery, plumbing, building construction, leaded gasoline, ammunition, lead based paints, pigments and alloy industries [1]. The major source of Pb exposure by the general population is drinking water [4]. The entrance of Pb ion at elevated levels into the blood causes anemia, paralysis, coma, kidney dysfunctions, brain damage, bone diseases, skin and lung cancer, convulsion and even death. High blood lead levels are associated with delayed puberty in girls and lead is also harmful for women's ability to reproduce. It is, therefore, necessary to reduce the level of Pb in effluent before it is discharged into the water body. Various processes for the separation of Pb from water have been practiced [9,11]. This study was chosen because NiO is an important material for several applications [12,13] and has a greater tendency to remove the Pb ions from aqueous solution. This study is first of its nature and has not been reported earlier.

2. Materials and methods

2.1. Analytical methods

All the reagents used in this study were of analytical grade. Merck and BDH supplied lead nitrate and nickel oxide respectively. Stock solutions of test reagents were prepared by dissolving lead nitrate [Pb(NO₃)₂] in deionized water. The lead and nickel in aqueous solution were determined by using a Perkin Elmer atomic absorption spectrophotometer model AAAnalyst 800 with a graphite furnace tube atomizer, Zeeman background correction and an auto-sampler.

* Corresponding author. Tel.: +92 91 9218480; fax: +92 91 9216671.

E-mail address: naeem64@yahoo.com (A. Naeem).

Table 1
Dissolution of NiO as a function of pH at 303 ± 1K.

pH	Ni _(released) × 10 ⁵ (mol g ⁻¹)
2	64.70
3	27.24
4	3.05
5	2.61
6	0.58
7	0.00
8	0.00
9	0.00
10	0.00
11	0.00

2.2. Dissolution of NiO

Dried sample of NiO (0.20 g) and 0.1 M NaNO₃ solutions (40 mL) were mixed in different flasks. The initial pH of each solution was adjusted to 2, 3, 4, 5, 6, 7, 8, 9, 10 and 11 ± 0.10 using either 0.1 M HNO₃ or NaOH. The suspensions were agitated in a shaker bath for 24 h at 303 K. The suspensions were filtered and filtrates were analyzed for determination of Ni released from the NiO as a function of pH.

2.3. Adsorption experiments

The adsorption experiments of Pb on NiO were conducted at different temperatures in polypropylene batch reaction vessels using 5 g L⁻¹ NiO suspension. In most of the sorption studies initial pH of the suspension was adjusted to 7.00 ± 0.10 to minimize the potential experimental complication resulting from the precipitation of the metal cation and dissolution of the adsorbent. The reaction vessels were placed on rotating rack that provided gentle (30 rpm) end-over-end rotation for 24 h to attain a true equilibrium and final pH of the suspension was recorded. The suspension was centrifuged, filtered through a 0.45 μm nylon filter and filtrate was analyzed for Ni ions released and Pb adsorbed on NiO using atomic absorption spectrophotometer. Similar adsorption experiments were also conducted at different pH and temperatures of the system. The system was purged with nitrogen gas to bubble out CO₂ from the suspension. Solid residues were subjected to FTIR and SEM/EDX analyses to probe the adsorption mechanism.

3. Results and discussion

3.1. Characterization of NiO

The point of zero charge (PZC) and surface area of NiO determined by the salt addition and BET method are observed to be 8.45 and 23 ± 2 m² g⁻¹ respectively. The PZC of NiO was observed to decrease from 8.45 to 8.09 in between 303 and 333 K. Both the values of surface area and PZC are reasonably good compared to the available data in the literature [14]. The dissolution study of NiO in the aqueous electrolyte solution was conducted at different pH values at 303 K (Table 1). As can be seen the dissolution of NiO decreases with the increase in pH of the system. However, we did not detect the release of Ni from NiO at pH 7.00 and above. Almost similar behaviors were observed for the dissolution of the oxides of zinc [14] and titanium [15].

3.2. Adsorption of Pb

Preliminary adsorption kinetics experiments of NiO for Pb were carried out in the temperature range of 298–323 K. The adsorption equilibrium was established in 16 h. We used 24 h as an optimum

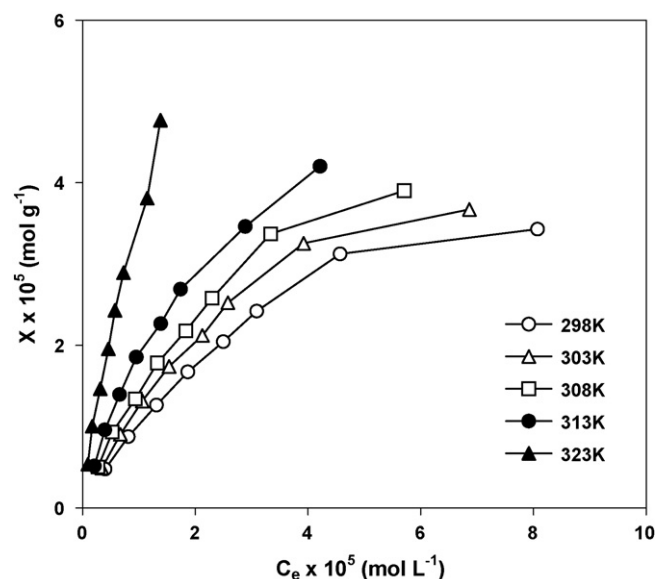


Fig. 1. Temperature effect on the adsorption of Pb²⁺ on NiO at pH 7.00 ± 0.10.

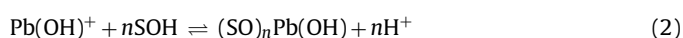
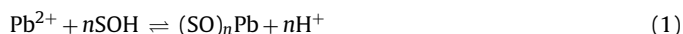
agitation period to attain a true equilibrium condition for all the subsequent batch adsorption experiments [16].

Adsorption isotherms were developed for NiO by measuring Pb ion partitioning between the substrate and solution phase over a wide range of concentration and temperature. The effect of temperature on Pb adsorption at pH 7.00 is shown in Fig. 1. The extent of Pb adsorption increases with the increase in temperature, which may 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 [13,17]. It indicates that adsorbate–adsorbent complex becomes more significant at higher temperature [18,19].

We observed that the uptake of Pb increases with the increase in initial concentration of Pb in aqueous solutions [20]. The increase in initial concentration provides an important driving force to overcome all mass transfer resistance of metal ions between the aqueous and solid surface. Similar results were reported [18,21] for the ion exchange removal of lead and other metal ions.

The pH of the suspension affects the degree of ionization, precipitation and the surface charge of adsorbent. Some experiments of Pb adsorption on NiO were conducted by varying the initial pH of the suspension (Fig. 2). The increase in the removal of Pb from aqueous solution at high pH values is probably due to electrostatic attraction as the solid surface acquires a negative charge because of deprotonation [17,22]. The maximum removal of Pb from aqueous solution at pH 8.00 is probably due to its precipitation [Pb(OH)₂] on the solid surface as the Pb has low solubility in the alkaline medium. The equilibrium pH of the suspension decreases with the increase in adsorption indicating the release of surface protons by the adsorbed Pb ions.

From the preceding discussion, we propose the following tentative mechanisms for the removal of Pb from aqueous solution



where S refers to the solid surface. To validate the proposed mechanisms for the removal of Pb from aqueous solution, we used Eq. (4) to the experimental data in the form

$$\log K_d = n\text{pH}_{\text{eq}} + \text{constant} \quad (4)$$

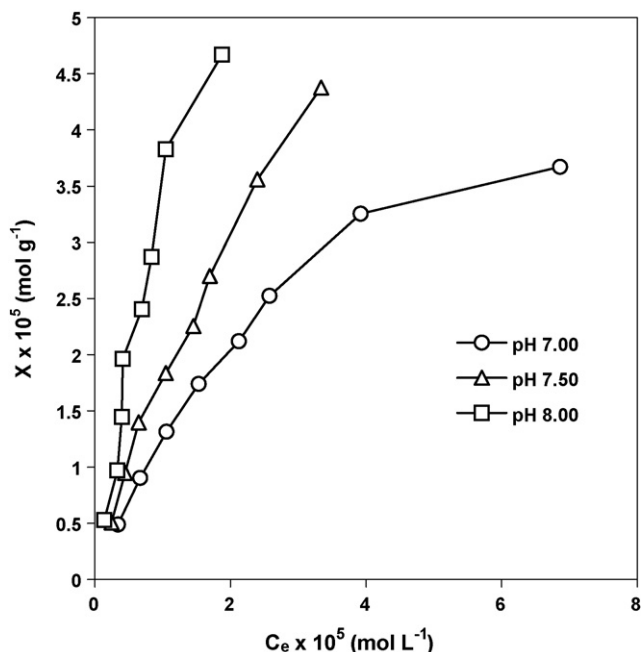


Fig. 2. pH effect on the adsorption of Pb^{2+} on NiO at $303 \pm 1K$.

where $K_d (X/C_e)$ is the distribution coefficient, n represents the number of replaceable protons from the solid surface.

The log–log plots of K_d vs pH given in Fig. 3 show a linear behavior, with coefficient of correlation ≥ 0.97 . One can observe from this figure that the values of K_d increase with increase in pH indicating the more uptake of Pb at higher pH values. The values of n determined from the slopes are nearly equal to one suggesting the cation exchange removal of Pb from aqueous solution according to reaction (2). Thus, the singly charged ($PbOH^+$) ion is easily adsorbed than the doubly charged M^{2+} because of steric hindrance. The decrease in the value of n from almost unity to 0.68 (Table 2) for the highest concentration indicating the onset of Pb precipitation in the form of $Pb(OH)_2$ as suggested by reaction (3). Thus, the cation exchange process changes into the precipitation when the initial concentration of Pb is reached to 50 mg L^{-1} . Similar adsorption mechanism was reported elsewhere [18,23].

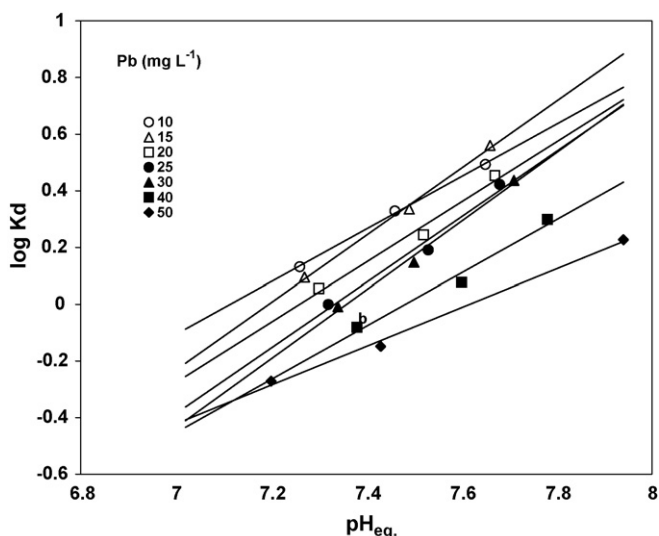


Fig. 3. Plots between $\log K_d$ and pH for Pb^{2+} adsorption on NiO at $303 \pm 1K$.

Table 2

The values of replaceable proton (n) for Pb^{2+} adsorption onto NiO at $303 \pm 1K$.

Pb^{2+} conc. (mg L^{-1})	n -Values	R^2
10	0.93	0.999
15	1.19	0.997
20	1.06	0.981
25	1.16	0.978
30	1.21	0.991
40	0.94	0.977
50	0.68	0.996

Table 3

Langmuir and Freundlich parameters for Pb^{2+} adsorption by NiO at $pH 7.00 \pm 0.10$.

Temp (K)	Langmuir isotherm			Freundlich isotherm			Separation factor (R_L)
	$X_m \times 10^5$ (mol g^{-1})	K (L g^{-1})	R^2	$\log K$	$1/n$	R^2	
298	5.28	25461.16	0.98	1.56	0.69	0.97	0.58–0.13
303	5.52	29732.39	0.99	1.46	0.69	0.97	0.54–0.11
308	6.12	32077.69	0.99	1.40	0.69	0.98	0.53–0.11
313	6.46	41887.51	0.99	1.34	0.68	0.98	0.46–0.08
323	6.62	78076.53	0.98	1.22	0.67	0.98	0.29–0.04

3.2.1. Langmuir model

The Langmuir model [13,17] assumes that the adsorption results in monolayer coverage and all the adsorption sites are equivalent and solute immobilization occurs without mutual interaction between the neighboring adsorbed molecules. The linear version of the Langmuir model mathematically can be described as

$$\frac{C_e}{X} = \frac{1}{KX_m} + \frac{C_e}{X_m} \quad (5)$$

where C_e is the Pb equilibrium concentration in aqueous phase, X is the amount of Pb adsorbed per unit mass of the NiO, K and X_m are the Langmuir constants. The Langmuir plots (Fig. 4) appear to be the best fitting model with correlation coefficient (R^2) ≥ 0.98 .

The values of sorption maxima (X_m) and binding energy constant (K) indicating that the values of K increase with the corresponding increase in sorption maxima (Table 3). The values of both the parameters (X_m and K) increase with the rise in temperature, which reveal endothermic behavior of the adsorption process. The values of X_m are in nice agreement with the results obtained from the adsorption isotherm. The adsorption capacity (X_m) of NiO given in Table 3 is comparable in magnitude with the sorption capacity ($3.9 \times 10^{-5} \text{ mol g}^{-1}$) of silica [24]. Moreover, the values of binding constant are in the same range as reported for other metal oxides/hydroxides [14,17].

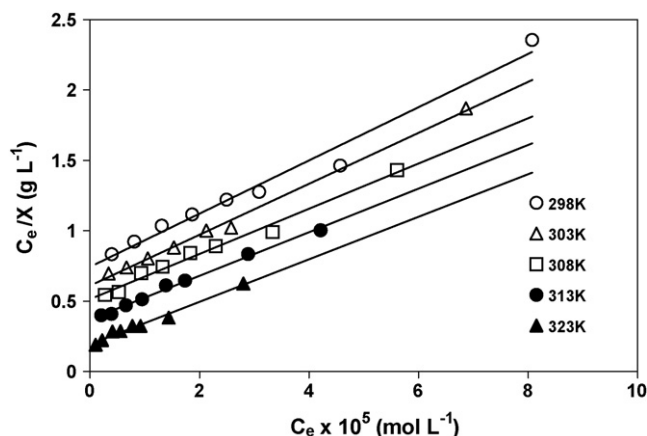


Fig. 4. Langmuir plots of Pb^{2+} adsorption on NiO at $pH 7.00 \pm 0.10$.

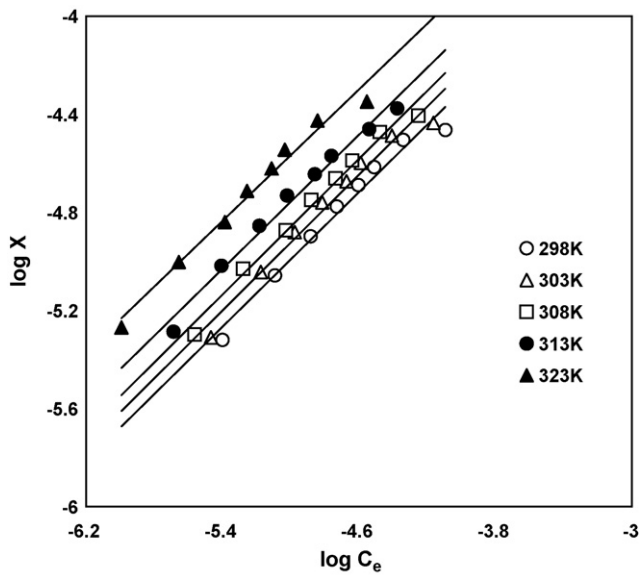


Fig. 5. Freundlich plots of Pb²⁺ adsorption on NiO at pH 7.00 ± 0.10.

3.2.2. Freundlich model

The Freundlich model [13] is frequently used for the energetically heterogeneous adsorption sites. The logarithmic form of Freundlich isotherm is represented as follows

$$\log X = \log K_F + \frac{1}{n} \log C_e \quad (6)$$

where K_F is the Freundlich adsorption capacity and $1/n$ refers to the Freundlich adsorption intensity parameter. The rest of the terms have their usual meanings as described in Langmuir isotherm.

The plots of $\log X$ vs $\log C_e$ for adsorption of Pb onto NiO (Fig. 5) were employed to determine the intercept values of $\log K_F$ and the slope of $1/n$. The values of Freundlich constant ($\log K_F$) change from 1.56 to 1.22 when the temperature is changed from 298 to 323 K (Table 3). Moreover, the values of $1/n$ at equilibrium are found to be 0.67–0.69, which indicate that the Pb has good adsorption onto NiO. As reported elsewhere [17] the values of $1/n < 1$ reflecting the favorable adsorption.

The dimensionless separation factor (R_L) for the adsorption isotherms was calculated from the following relationship [25–27]:

$$R_L = \frac{1}{(1 + KC_i)} \quad (7)$$

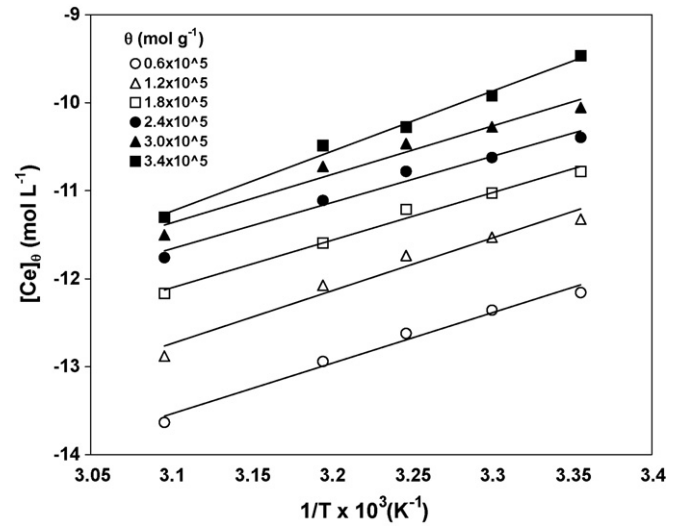


Fig. 7. Plots of $(C_e)_\theta$ vs $1/T$ for Pb²⁺ adsorption on NiO at pH 7.00 ± 0.10.

where K ($L \cdot mol^{-1}$) is the Langmuir binding constant; C_i ($mol \cdot L^{-1}$) is the initial metal concentration in the solution and R_L indicates the shape of isotherm. If the process is irreversible $R_L > 0$, favorable $0 < R_L < 1$, linear $R_L = 1$, unfavorable $R_L > 1$ [25].

In the present case, the values of R_L are greater than 0 and lesser than 1 at different temperatures indicating the favorable adsorption of Pb²⁺ onto NiO in aqueous solution. The correlation coefficients (R^2) given in Table 3 indicate that the Langmuir model exhibits relatively better fit to the experimental data compared to the Freundlich isotherms.

3.3. Spectroscopic studies

The solid residues of the adsorbent before and after adsorption of Pb²⁺ were subjected to SEM/DX and FTIR analyses. The IR spectrum of NiO (Fig. 6) shows the peaks at 480, 1350, 1640, 2450, 2920 and 3630 cm^{-1} , which are the characteristic peaks of NiO. We observed that the IR spectrum of NiO before and after adsorption of Pb were almost the same except the appearance of a new peak at 670 cm^{-1} after Pb adsorption. This new peak may be assignable to the Pb-O stretching vibration. The EDX analysis showed the presence of Pb in the Pb impregnated NiO which corroborates the results obtained from the adsorption studies. Thus, the spectroscopic techniques val-

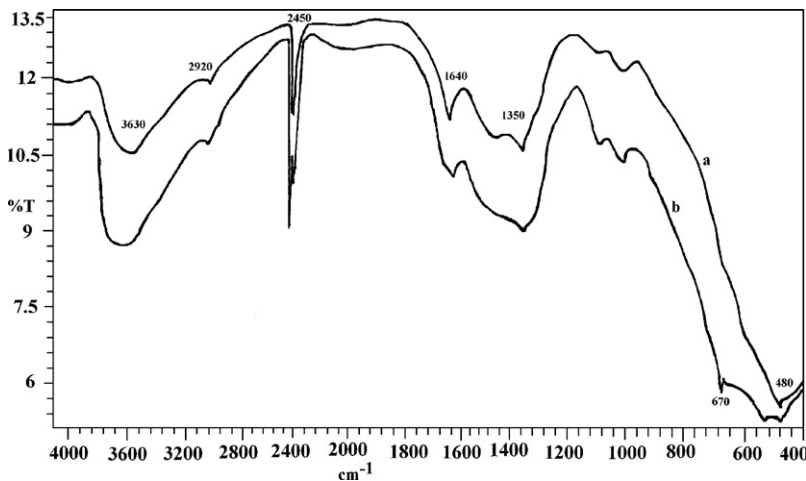


Fig. 6. FTIR spectrum of NiO (a) before and (b) after Pb adsorption.

Table 4
Isothermic heats of adsorption (ΔH) at different surface coverages (θ).

$\theta \times 10^5$ (mol g ⁻¹)	ΔH (kJ mol ⁻¹)
1.7	30.34
2.1	32.73
2.5	45.48
2.9	50.32
3.3	52.18
3.7	50.61
4.1	47.04

idate the evidence that the Pb is chemisorbed onto the surface of NiO.

3.4. Isothermic heats of adsorption

The isothermic heats of adsorption (ΔH) were determined from the adsorption experiments conducted at different temperatures. A well-known Eq. (8) is applied to the adsorption data to calculate the isothermic heat of adsorption (ΔH)

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

where C_e is the remaining concentration of Pb corresponding to the constant amount (θ) of Pb adsorbed.

The isothermic heats of adsorption (ΔH) derived from the slopes of the $\ln(C_e)_{\theta}$ vs $1/T$ (Fig. 7) are given in Table 4. The variation in the ΔH values (Table 4) with surface loading indicates that the NiO surface is energetically heterogeneous. It is inferred from the adsorption enthalpy data that Pb adsorption by NiO is endothermic suggesting that more heat is required to shift the Pb ions from aqueous solution into the solid phase [19].

4. Conclusions

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 mechanism of Pb adsorption changes from simple cation exchange to precipitation with the increase in pH and Pb concentration in the system. The Langmuir model fitted the experimental equilibrium data reasonably well. The positive values of the isothermic heats of adsorption confirm the endothermic behavior of the adsorption reaction. The spectroscopic results augment the conclusions drawn from the adsorption isotherms.

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