

Cation Exchange Behaviour of NiO

¹ABDUL NAEEM*, ¹MUHAMMAD TAHIR SADDIQUE, ¹SYED MUSTAFA, ²SYED TASLEEM,
³MUHAMMAD SAFDAR AND ⁴HAMIDULLAH MARWAT

¹National Centre of Excellence in Physical Chemistry, University of Peshawar, Peshawar, Pakistan.

²Chemistry Department, KUST, Kohat, Pakistan.

³Chemistry Department, AJK University.

⁴Chemistry Department, Agriculture University, Peshawar, Pakistan.

(Received 4th March 2008, revised 14th June 2008)

Summary: The surface characterization of nickel oxide was performed using various physicochemical methods. Batch adsorption technique was used to measure the adsorption of calcium onto NiO. The adsorption experiments of Ca by NiO were conducted at different temperatures and concentrations of the metal ion. The effect of pH on Ca removal from aqueous solution was also studied to observe the sorption behavior of NiO at different pH values. Langmuir model was used to interpret the cation exchange sorption of Ca onto NiO. The proton stoichiometry was derived from Kurbatov-type plot. The isosteric heat of adsorption (ΔH) revealed that adsorption process was endothermic.

Introduction

Pollution and contamination of water with metals is a major ecological problem and has become a key focus of concern. It is, therefore, necessary to alleviate metal load of an effluent before its discharge into water body [1-3].

Generally, the techniques used for the removal of metals from industrial wastewater consist of precipitation/coagulation, ultra-filtration, reverse osmosis, electrode-deposition, solvent extraction and evaporation [1, 4-7]. As reported by Bhattacharyya and Gupta [8], these techniques add to costs of water treatment, generating secondary pollutants, and generally their performance is poor at low metal concentration. A viable alternative to this techniques is the adsorption which is applicable at very low concentration of the adsorbate, simple to operate, produce little sludge, possibility of regeneration and reuse and cost-effective. It also regulates the mobility of chemical species and their geochemical cycles in the environment [7-9].

The efficiency of the adsorption process depends mainly on the adsorbent used. Most of the metal oxides/ hydroxides [10-15] have been studied for the removal of metal ions from aqueous solutions. This study was selected because NiO is an important material for several applications [16, 17] and to our knowledge no report on the adsorption of alkaline earth metals onto NiO is available in the literature.

The aim of the current study is to explore the cation exchange behavior of NiO towards calcium ions.

Results and Discussion

Characterization of NiO

The PZC and surface area of NiO are found to be 8.45 and $23 \pm 2 \text{ m}^2/\text{g}$ respectively. These values are consistent with the data reported in the literature [18, 19]. The XRD analysis showed the crystalline nature of the NiO while the EDX results revealed no evidence of impurity in the sample.

Adsorption Studies

Temperature Effect

We studied the ion exchange sorption of Ca on NiO at different temperatures, pH and concentration. The experimental data for Ca are shown in Fig. 1. As can be seen, the adsorption increases with the increase in temperature indicating the adsorption of Ca onto the NiO is endothermic in nature like other divalent transition metal cations [1, 15, 20].

The increase in the Ca adsorption with temperature may be correlated with the increase in the negative surface charge on the NiO on account of

*To whom all correspondence should be addressed.

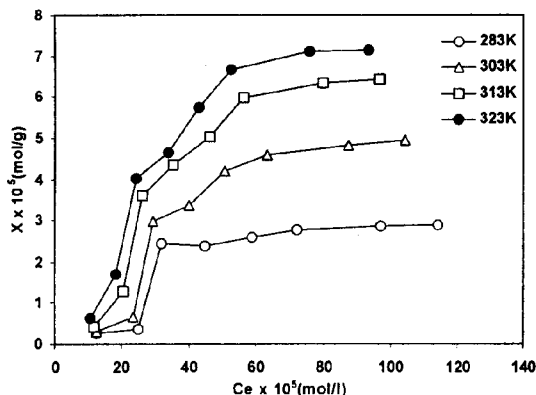


Fig. 1: Adsorption isotherms of Ca ions on NiO at pH 8.00 ± 0.20.

the lowering of its PZC [1, 3]. This results in increase in the adsorption capacity of NiO due to electrostatic attraction.

Concentration Effect

The data in Fig. 1 depict and the effect of concentration on the Ca adsorption. One can observe that the adsorption strongly depends on the concentration of metal ion. The increase in the sorption capacity of the NiO with the initial concentration of Ca is probably due to high driving force for mass transfer. As reported elsewhere [1, 4, 15] the higher initial concentration of solution results in the greater adsorption. Similar findings were reported for the ion exchange removal of alkaline earth metal ion by other metal oxides [1, 4].

pH Effect

The adsorption of Ca was also investigated by varying the initial pH 7.50 to 9.00. The experimental data are presented in the form of pH uptake curves. The pH uptake data in Fig. 2 reveal that the adsorption increases with the increase in initial pH of the solutions. The low adsorption capacity of NiO at lower pH value (pH 7.50) may be attributed to the electrostatic repulsion. However, at a solution pH > p*H*_{zpc}, the solid surface of NiO acquires a negative charge, and more surface sites are available for the adsorption of Ca (II) onto the NiO due to electrostatic attraction. We noted that the pH of the suspension decreases with the increase in the adsorption of the Ca ions. As suggested elsewhere [1,

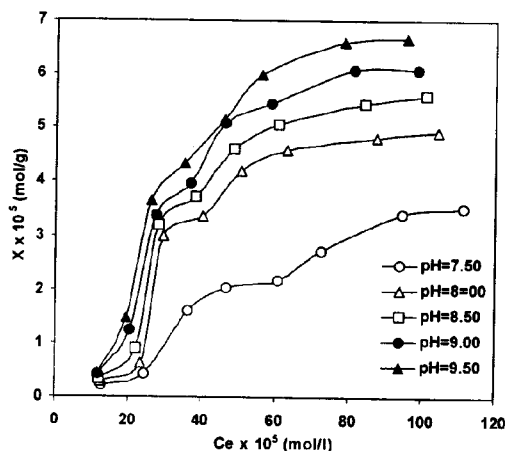


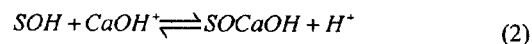
Fig. 2: Adsorption isotherms of Ca adsorption on NiO at 303 ± 1K.

+) the Ca adsorption onto the oxide surface releases one or two hydrogen atoms from surface hydroxyl groups. This change in pH is indicative of the replacement of surface protons by the adsorbed metal cation. The mechanism of metal ions sorption was determined by using the equation in the form:

$$\log D = K + npH_{eq} \quad (1)$$

where p*H*_{eq} is the equilibrium pH of the suspension, D (l.g⁻¹) represents the distribution coefficient, K is the cation exchange constant, and slopes n of the lines correspond to the number of replaceable protons from the solid phase.

The plots of log D vs. equilibrium pH of the suspension are shown in Fig. 3. The values of n obtained from the slopes of straight lines are found to be 1.00 ± 0.30. This shows that on the average one mole of H⁺ released per mole of Ca²⁺ ions sorbed. Thus, the alkaline earth metal cation is going to be sorbed in the form of CaOH⁺ according to the following proposed mechanism:



where S stands for matrix of the solid surface. Kanungo *et al.* [14] projected similar mechanism for the adsorption of metal ions by metal oxides.

We used (Fig. 4) the linear form of conventional Langmuir model [1] to interpret the

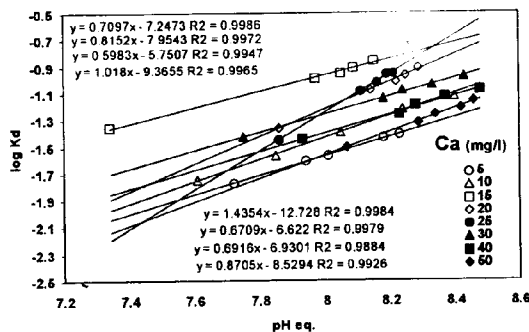


Fig. 3: Plot of log K_d vs pH eq. for Ca adsorption on NiO at $303 \pm 1K$.

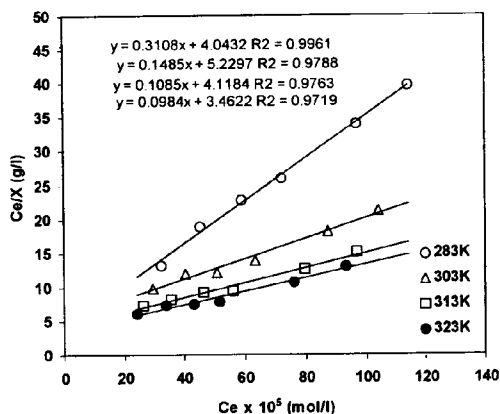


Fig. 4: Langmuir Plots for the Ca adsorption onto NiO at pH 8.00 ± 0.20 .

cation exchange sorption of Ca onto the NiO, which is given in the form:

$$C_e/X = 1/KX_m + C_e/X_m \quad (3)$$

where C_e (mol/l) is the equilibrium concentration, X (mol/g) is the amount adsorbed, K and X_m are the Langmuir parameters.

The values of both the sorption maxima (X_m) and binding energy constant (K) increased with the increase in temperature and pH of the system (Table-1). This further substantiated the results obtained from the adsorption isotherms. The values of the sorption maxima (X_m) were reasonably good compared to the sorption maxima of ZnO [21]. Moreover, these values of X_m were comparable in magnitude with the other metal oxides/hydroxides [1].

Table-1: Langmuir parameters X_m and K for the adsorption of Ca^{2+} ion on NiO as a function of temperature at pH 8.00 ± 0.20 .

S. No	Temperature (K)	$(X_m) \times 10^5$ [mol/g]	K [l/g]	R^2	Separation factor (R_L)
1	283	3.218	7686.98	0.996	0.48-0.09
2	303	6.734	2839.55	0.979	0.71-0.21
3	313	9.217	2634.52	0.976	0.73-0.23
4	323	10.163	2842.12	0.972	0.72-0.21

The dimensionless separation factor, R_L , was determined by using the relationship [22]:

$$R_L = 1/(1 + KC_0) \quad (4)$$

where K (l/mg) is the Langmuir constant, C_0 (mol/l) is the initial concentration, and R_L indicates the shape of the isotherm. The values of R_L at different temperatures are found to be greater than 0 and lesser than 1, indicating the favorable adsorption of Ca on NiO in aqueous solution.

Thermodynamic Parameters

The adsorption experiments were carried out at different temperatures to calculate the isosteric heat of adsorption (ΔH) by applying a well-known equation in the form:

$$\ln [C_e]_{\theta} = \frac{\Delta H}{RT} + \text{const} \ln t \quad (5)$$

where C_e is remaining concentration of metal ions in solutions, the relative amount of Ca ions sorbed [θ] is maintained constant, R is the molar gas constant and T is the absolute temperature.

The isosteric heat of adsorption (ΔH) resulting from the slopes of the adsorption isostere (Fig. 5) is given in Fig. 6. The correlation coefficient (R^2) is found to be ≥ 0.93 . The positive values of ΔH illustrate that adsorption of Ca from aqueous solution into the solid phase is more favourable at higher temperatures. As is obvious from the Figure, the isosteric heat of adsorption (ΔH) first decreases gradually from 14.49 to 8.58 kJ/mol with surface coverage and then increases to 12.87 kJ/mol at high surface coverage. This range of (ΔH) illustrates that the removal of Ca from aqueous solution onto the solid surface takes place through the cation exchange process.

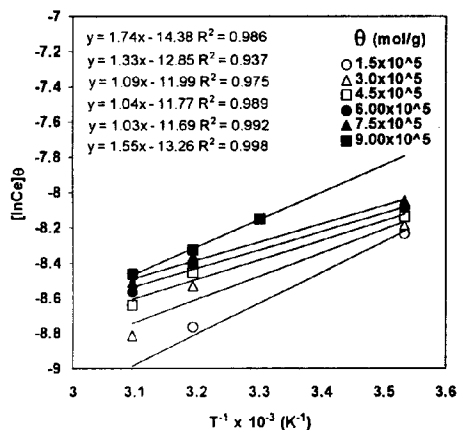


Fig. 5: Plots of $\ln[Ce]_0$ vs T^{-1} for Ca adsorption on NiO at pH 8.00 ± 0.20 .

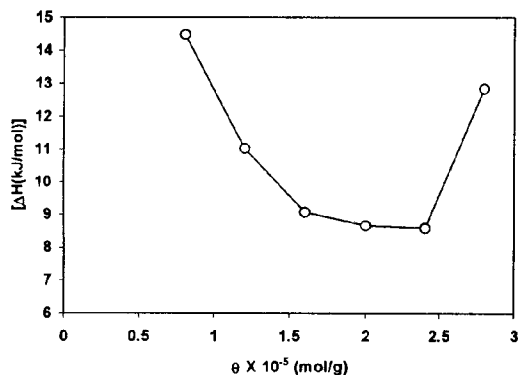


Fig. 6: Isothermic heat of adsorption (ΔH) as a function of surface coverage of Ca adsorption on NiO at pH 8.00 ± 0.20 .

The variation in the ΔH values (Fig. 6) with surface loading indicates that the surface is energetically heterogeneous in nature. Adsorption enthalpy data further suggest that Ca adsorption on NiO is endothermic and becomes more endothermic as the surface coverage increases. This shows the more dependency of the alkaline earth metal ion adsorption process on temperature at high surface coverage, which favours the conclusion drawn from the adsorption isotherms (Fig. 1).

Similarly, the standard Gibbs free energy (ΔG) changes for the Ca adsorption were assessed by using the relationship:

$$\Delta G = -RT \ln K \quad (6)$$

The value of ΔG computed from the Langmuir constant (K) is found to be -21.05 ± 0.4 kJ/mol. The spontaneity of the Ca adsorption onto the NiO is exemplified by the decrease in Gibbs free energy which is responsible for imparting stability to adsorption complexes formed between Ca and NiO surface.

No thermodynamic data on metal ions adsorption by NiO is available in the literature and the magnitude of the thermodynamic parameters cannot be compared directly with the literature.

Experimental

Analytical Methods

Analytical grade reagents were used. Nitrate of calcium [$Ca(NO_3)_2$] was used to prepare calcium solutions. The concentration of calcium and nickel remaining in solution were analyzed using a Varian atomic absorption spectrophotometer with a Varian graphite furnace tube atomizer, Zeeman background correction and an auto-sampler. Sample of NiO provided by BDH was characterized by X-ray diffractometry (XRD), scanning electron microscopy (SEM) coupled with energy dispersive X-ray analyses (EDX), surface area and point of zero charge (PZC).

Adsorption Experiment

The adsorption experiments of Ca on NiO were conducted in polypropylene batch reaction vessels using 5 g/L NiO suspension, which was prepared by suspending NiO powder (0.20 g) in 40 ml deionized water. The same measurements were also carried out without NiO. Initial pH of the suspension was adjusted to desired pH values. The reaction vessels were placed on rotating rack that provided gentle (30 rpm) end-over-end rotation for 24 hr to attain a true equilibrium and final pH of the suspension was recorded. The suspension was then centrifuged, filtered through a $0.45 \mu m$ nylon filter and filtrate was analyzed for Ni ions released and Ca adsorbed on NiO using atomic absorption spectrophotometer. Preliminary adsorption kinetics experiments demonstrated that 16 hr was sufficient for adsorption equilibrium to be attained.

Conclusions

NiO appreciably removes the Ca from aqueous solution. The adsorption of Ca increases

with the increase in pH till it begins to precipitate. The sorption data are best fitted to Langmuir model. The positive values of ΔH indicate that the metal ions have a tendency to escape from the aqueous phase to the solid surface with the rise in temperature, which promotes the adsorption of Ca onto the NiO. The spontaneity of the adsorption process is supported by the decrease in Gibbs free energy.

References

1. M. A. Anderson and A. J. Robin, Adsorption of Inorganic at Solid Liquid Interfaces, *Ann. Arbor Sci. Pub. Ann. Arbor*, MI, 212 (1981).
2. M. J. Angove, B. B. Johnson and J. D. Wells, *J. Colloid Interface Sci.*, **204**, 93 (1998).
3. A. Corami, S. Mignardi and V. Ferrini, *J. Colloid Interface Sci.*, **317**, 402 (2008).
4. B. Dilara, Ph.D Thesis, Univ. Pesh. Peshawar, Pakistan, (2001).
5. J. Goel, K. Kadirvein, R. Rajagopal, V. K. Garg, *Ind. Eng. Chem. Res.*, **45**, 6531 (2006).
6. V. K. Gupta and S. Sharma, *Environ. Sci. Technol.*, **36**, 3612 (2002).
7. S. Mustafa, A. Hamid, and A. Naeem, *J. Chem. Soc. Pak.*, **27**, 115 (2005).
8. K. G. Bhattacharyya and S. S. Gupta, *Colloids Surf. A.*, **317**, 71 (2007).
9. B. E. J. Bodmann, D. P. Dick and Y. P. Dick, *Adsorption*, **10**, 277 (2004).
10. A. Naeem, P. Westerhoff and S. Mustafa, *Water Res.*, **41**, 1596 (2007).
11. S. Mustafa, S. Murtaza, and A. Naeem, *Environ. Technol.*, **26**, 353 (2005).
12. D. G. Kinniburgh, J. K. Styres and M. L. Jackson, *Soil Sci. Soc. Am. J.*, **40**, 796 (1976).
13. A. Naeem, J. B. Fein and J. R. Woertz, *Environ. Sci. Technol.*, **40**, 5724 (2006).
14. S. B. Kanungo, S. S. Tripathy, S. S. Mishra, S. K. Sashoo and B. Rajeev, *J. Colloid Interface Sci.*, **269**, 11 (2004).
15. B. B. Johnson, *Environ. Sci. Technol.*, **24**, 112 (1990).
16. Z. J. Yan, L. F. Bai, J. B. Chang and P. X. Yan, *Rare Metal Mat. Engg.*, **36**, 484 (2007).
17. G. J. Li, R. M. Ren, X. X. Huang and J. K. Guo, *Chinese J. Inorg. Chem.*, **20**, 287 (2004).
18. F. J. Micale, M. Topic, C. L. Cronan, H. Leidheiser and A. C. Zettlemyer, *J. Colloid Interface Sci.*, **55**, 540 (1976).
19. P. H. Tewari and A. B. Campbell, *J. Colloid Interface Sci.*, **55**, 531 (1976).
20. A. Naeem, S. Mustafa and B. Dilara, *J. Chem. Soc. Pak.*, **29**, 1 (2007)
21. S. Mustafa, P. Shahida, A. Naeem and B. Dilara, *Langmuir*, **18**, 2254 (2002).
22. D. Mohan, K. P. Singh and V. K. Singh, *Ind. Eng. Chem. Res.*, **44**, 1027 (2005).