



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 (ΔH) 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 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 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 2θ angle from 30° to 65° using a JEOL X-ray diffractometer, model JDX-7E with Mn-filtered Cu-K α 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

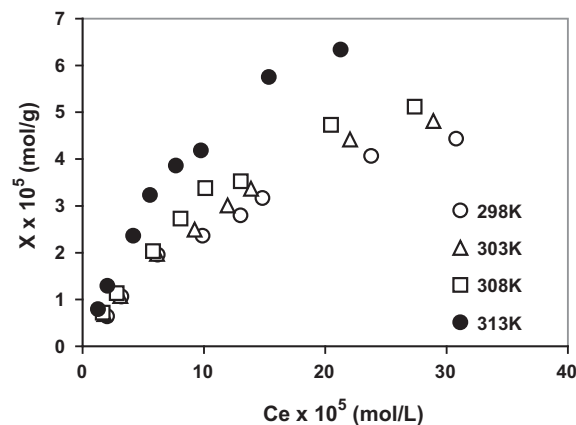


Fig. 1. Temperature effect on the adsorption of Cd on NiO at pH 7.50 ± 0.10 .

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 (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-

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