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Properties of a novel adsorbent produced by calcination of nickel hydroxide and its capability for phosphate ion adsorption

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ABSTRACT

Nickel hydroxide (Ni) was calcined at 270 and 400 °C (denoted Ni270 and Ni400), and the properties of Ni, Ni270, and Ni400 were investigated. In addition, the phosphate adsorption capabilities of Ni, Ni270, and Ni400 were evaluated by examination of the effects of contact time and solution pH, analysis of an adsorption isotherm, and study of desorption. The amounts of phosphate ion adsorbed by the different samples showed the order Ni < Ni400 < Ni270. Finally, phosphate ions adsorbed onto Ni270 could be desorbed using sodium hydroxide, indicating that Ni270 can be used as a renewable adsorbent.

Introduction

Phosphate is an essential macronutrient for biomass growth and the normal functioning of ecosystems [1,2]. Apart from the weathering of rocks and the decomposition of organic materials, phosphate can enter water bodies through runoff or discharge from various human activities, including urban sewage discharge, industrial wastewater disposal, and use of agricultural fertilizers [3]. However, an overloading of phosphorus in aquatic environments is often responsible for algal blooms and eutrophication [4,5], especially in lakes, coastal areas, and reservoirs, and may cause environmental damage such as esthetic problems [6], decreases in dissolved oxygen (DO), and destruction of aquatic ecosystems leading to the death of aquatic animals [7]. It is believed that once the concentration of phosphate ions in lakes or seas rises above 0.03 mg/L, algal blooms or red tides will occur [8]. Therefore, the removal of phosphate ions from wastewater prior to its discharge into aquatic environments is critical [9]. To date, various techniques have been developed for phosphate ion removal, such as adsorption, precipitation, ion exchange, reverse osmosis, and biological methods [3,10–13]. Of these, adsorption is considered a promising method because of its high efficiency and low cost [14]. In recent years, the development of composite adsorbents containing two (or more) metal oxides for phosphate ion removal has gained increasing attention [15–17]. For instance, Al–Fe hydroxide [18], Fe–Mn binary oxide [19], Fe–Zr binary oxide [20], and Fe–Al–Mn trimetal oxide [21] have been reported for phosphate ion removal.

On the other hand, nickel hydroxide and nickel oxide materials have received much attention in recent years for applications in alkaline secondary batteries, fuel cells, electrochemical capacitors, electrolyzers, electro-synthetic cells, and electrochromic devices [22–27]. At present, however, nickel hydroxide and nickel oxide are not extensively used. Moreover, the purification of wastewater (adsorption of phosphate ions from aqueous solutions) by nickel hydroxide and nickel oxide has received little attention. Thus, if methods for the purification of wastewater based on nickel hydroxide and nickel oxide could be developed, the value and application range of these materials would dramatically increase. Although nickel is expensive compared to another materials, if techniques that allow recycling of nickel materials are developed, they could be environmentally friendly [20].

In our previous study, we showed that nickel materials are capable of adsorbing phosphate ions from aqueous solution, but did not evaluate the mechanism of phosphate ion adsorption in

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detail. In this study, we prepared calcined nickel hydroxide (nickel oxide) and used it as an adsorbent for phosphate ion adsorption from aqueous solution. The properties of the adsorbents, adsorption kinetics, adsorption isotherms, effects of pH and temperature, and desorption ability were investigated. Moreover, the mechanism of phosphate ion adsorption was elucidated. The results provide new insights into the development of high-performance adsorbents for phosphate ion adsorption.

Experimental

Materials

Nickel hydroxide (Ni) was purchased from Kansai Catalyst Co., Ltd (Japan). Calcined nickel hydroxide samples were prepared by treating nickel hydroxide in a muffle furnace at temperatures of 270 or 400 °C for 2 h (calcined samples are denoted Ni270 and Ni400). Potassium dihydrogen phosphate and sodium hydroxide were purchased from Wako Pure Chemical Industries, Ltd (Japan). The specific surface area and thermogravimetric-differential thermal analysis (TG-DTA) were measured by a NOVA4200*e* specific surface analyzer (Yuasa Ionics, Japan) and TG8120 (Rigaku, Japan), respectively. X-ray diffraction (XRD) analysis was performed using a Mini Flex II (Rigaku, Japan). The amount of hydroxyl group was measured by the fluoride ion adsorption method [28]. In this procedure, the adsorbent (0.125 g) was added to 0.01 mol/L NaF solution (50 mL) at pH 4.6. The pH was adjusted using 0.2 mol/L acetic acid solution and 0.2 mol/L acetate buffer solution. The solution was shaken at 25 °C for 24 h at 100 rpm and was then filtered using a 0.45 μm membrane filter. The concentration of fluoride ion in the filtered solution was measured by absorption spectrophotometry (DR890, HACH, USA), and the amount of fluoride ion adsorbed on the adsorbent was calculated (the ratio of the concentration of fluoride ion and the concentration of hydroxyl group is 1:1) [20]. The distribution of phosphorus and nickel on the adsorbent was measured using an electron microanalyzer (EPMA, JXA-8530F, JEOL, Japan), at an accelerating voltage of 15.0 kV and a beam diameter of 5 μm.

Amount of phosphate ion adsorbed

The adsorbent (0.1 g) was added to a solution (50 mL) containing phosphate ion (50 mg/L initial concentration). The suspension was shaken at 100 rpm for 24 h at 25 °C. The sample was then filtered through a 0.45 μm membrane filter, and the filtrate was analyzed using absorption spectrophotometry (DR/890, HACH, USA). The concentration of phosphate ion was determined by the ascorbic acid reduction method. The amount of phosphate ion adsorbed onto the adsorbent was calculated using Eq. (1):

$$q = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where q is the amount of adsorbed phosphate (mg/g), C_0 is the initial concentration (mg/L), C_e is the equilibrium concentration (mg/L), V is the solvent volume (L), and W is the weight of the adsorbent sample (g).

Effect of contact time on the adsorption of phosphate ions

The adsorbent (0.1 g) was added to the phosphate ion solution (50 mL, 100 mg/L initial concentration). The sample solution was shaken at 25 °C for 0.5, 1, 3, 6, 9, 12, 15, and 24 h at 100 rpm. The amount of phosphate adsorbed was calculated using Eq. (1).

Effect of pH in solution on the adsorption of phosphate ions

The adsorbent (0.1 g) was added to the phosphate ion solution (50 mL, 50 mg/L initial concentration) with an initial pH controlled in the 2.0–10 range by addition of sodium hydroxide or hydrochloric acid. The sample solution was shaken at 25 °C for 24 h at 100 rpm. The amount of phosphate adsorbed was calculated using Eq. (1).

Effect of temperature on the adsorption of phosphate ions

The adsorbent (0.1 g) was added to the phosphate ion solution (50 mL, 10–100 mg/L initial concentration). The sample solution was shaken at 5, 25, and 45 °C for 24 h at 100 rpm. The amount of phosphate adsorbed was calculated using Eq. (1).

Adsorption or desorption capability of phosphate ion

The adsorbent (2 g) was added to the phosphate ion solution (300 mL, 500 mg/L initial concentration). The sample solution was shaken at 25 °C for 24 h at 100 rpm. Subsequently, the suspension was filtered through a 0.45 μm membrane filter, and the sample solution was measured by the absorption spectrophotometry (DR/890, HACH, USA). The amount of phosphate ion adsorbed was calculated using Eq. (1). After adsorption, the adsorbent was collected, dried, and then used for the desorption experiment. The collected adsorbent was added to a 100 mL solution of 1, 10 or 100 mmol/L sodium hydroxide. The suspension was shaken at 100 rpm for 24 h at 25 °C. The suspension was then filtered through a 0.45 μm membrane filter. The concentration of phosphate ion in the sample solution was measured by absorption spectrophotometry (DR/890, HACH, USA). The amount desorbed was calculated using Eq. (2).

$$d = \frac{C_e V}{W} \tag{2}$$

where d is the amount of phosphate desorbed (mg/g), C_e is the concentration after the desorption (mg/L), V is the solvent volume (L), and W is the weight of the adsorbent sample (g).

Results and discussion

Properties of adsorbents

Fig. 1 shows XRD patterns of Ni, Ni270, and Ni400. These demonstrate that the Ni sample has a nickel hydroxide structure. A

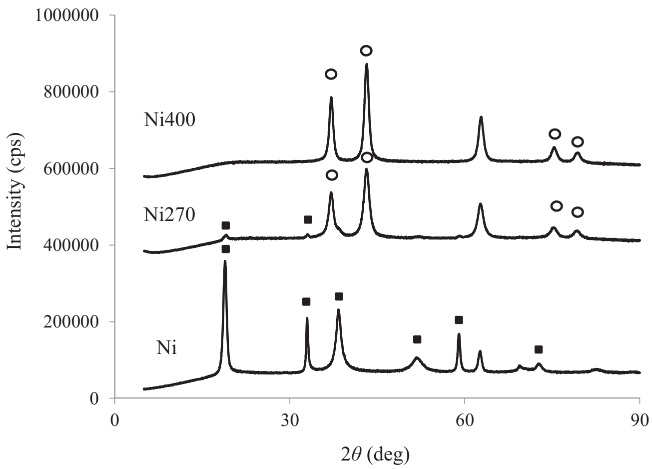

Fig. 1. XRD patterns of adsorbents. (■) Nickel hydroxide; (○) nickel oxide.