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Removal of Arsenic Using Nickel-Zinc Hydroxy Double Salts

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Abstract

Arsenic with high toxicity is harmful to the environment and the human body. It is known that As(III) has higher toxicity than As(V). It is necessary to develop adsorbent to effectively remove arsenic from wastewater and environmental water. NiZn hydroxyl double salt (NiZn) with acetate anion in interlayer was prepared by hydrothermal method. The effects of arsenic concentration on arsenic adsorption were investigated using the NiZn. Maximum adsorption capacities of As(III) and As(V) are 1.24 and 0.44 mmol/g, respectively. At pH 10.5 As(III) was more effectively removed than As(V) using NiZn. From resulting data by XRD and FT-IR it was found that As(III) and As(V) was exchange with acetate anion in interlayer keeping the layer structure.

Keywords: Arsenic, Hydroxy Double Salts, NiZn, Intercalation, Anion Exchange

1. Introduction

Arsenic widely distributed as arsenic sulfide in soil is released to groundwater by environmental change. Wastewater including arsenic might discharge to environment by industrial activities such as metal refining, thermal power generation and waste disposal. In the World Health Organization (WHO) guideline, arsenic concentration in drinking water was limited to less than 10 μ g/dm^3. Arsenic contamination to aquatic environment is a serious problem in many countries because chronical arsenic poisoning and cancer of liver, skin, blood and lung are caused by long-term uptake of drinking water including arsenic. Therefore the issue should be resolved immediately.

Inorganic arsenic is higher toxic than organic arsenic. The chemical species of inorganic arsenic in aqueous solution are arsenite (As(III), H_3AsO_3) and arsenate (As(V), H_3AsO_4). The acid dissociation constants (pK_{an}(n=1-3)) of As(III) are pK_{a1}=9.23, pK_{a2}=12.13 and pK_{a3}=13.4, and those of As(V) are pK_{a1}=2.24, pK_{a2}=6.96 and pK_{a3}=11.5. The main chemical species of As(III) in groundwater is H_3AsO_3 and those of As(V) are $H_2AsO_4^-$ and $HAsO_4^{2-}$. Since As(III) removal is more difficult than As(V), As(III) is usually treated using adsorbent after oxidation.

There are layered double hydroxides (LDHs) and hydroxyl double salts (HDSs) as layered metal hydroxides anion exchange. They have positively charged host layers and anions located in interlayer space. Their positively charged host layers are different. The host layers of LDHs include a mixture of divalent and trivalent metal cations, while those of HDSs consist of divalent metal cations.

In this work, Ni^{2+}-Zn^{2+} HDS (NiZn, $Ni_{1-x}Zn_{2x}(OH)_2(OCOCH_3)_{2x}\cdot nH_2O$) was used as arsenic adsorbent. The structure is nickel hydroxide host layer with vacancies, and Zn^{2+} ions located above and below the vacant sites outside the host layers. Acetate anions are weakly bound to the Zn^{2+} ions and easily exchanged. NiZn was prepared by hydrothermal method, and its adsorption behaviors of As(III) and As(V) were

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investigated.

2. Experimental

2.1 Preparation of NiZn

NiZn basic hydroxyl salt (NiZn) was prepared by hydrothermal synthesis method according to literature [1]. A mixed solution of 2 M $Ni(CH_3COO)_2$ solution and 1 M $Zn(CH_3COO)_2$ solution in Teflon™ lined hydrothermal synthesis autoclave reactor was heated at 423 K for 24h .The resulting precipitate was separated by centrifuge, washed with deionized water and dried under vacuum. The chemical formula of product analyzed using XRD, FT-IR, TG/DTA and AAS was determined as $Ni_{0.63}Zn_{0.37}(OH)_2(CH_3COO)_{0.37}\cdot 1.93H_2O$.

2.2 Adsorption tests

Adsorption experiments were carried out by batch method. Twenty mg of the NiZn was added to 15 cm^3 of arsenic solution adjusted various pH with 0.01 M NaOH. Then the suspensions were shaken at 303 K for 24 h. After adsorption, the suspensions were filtered with a 0.45 μ m membrane filter. The concentration of arsenic in filtrate was determined using ICP-AES and AAS.

3. Results and Discussion

The adsorption isotherms of As(III) and As(V) using the NiZn were conducted at initial pH 11.2. Langmuir isotherm model (Eq.(1)) was used to analyze the equilibrium data.

$$C_{eq}/q = C_{eq}/q_{max} + 1/K_L q_{max} \quad (1)$$

Where C_e (mmol/dm^3), q(mmol/g), q_{max}(mmol/g) and K_L(dm^3/mmol) were the equilibrium concentration, the amount of adsorption, the maximum amount of adsorption and the adsorption equilibrium constant, respectively. The q_{max} and K_L were calculated from the slope and the intercept of the linear plot of C_e/q versus C_e, respectively.

The adsorption isotherms of As(III) and As(V) adsorption were shown in Fig. 1. The parameters of Langmuir adsorption isotherm were summarized in Table 1.

Table 1 Parameters of Langmuir adsorption isotherm for As(III) and As(V) on NiZn at 303 K

	q_{max}[mmol/g]	K_L[dm^3/mmol]	R^2
As(III)	1.24	3.48	0.958
As(V)	0.446	287	0.998

Because the correlation coefficients (R^2) were larger than 0.95, the adsorption behaviors were described by

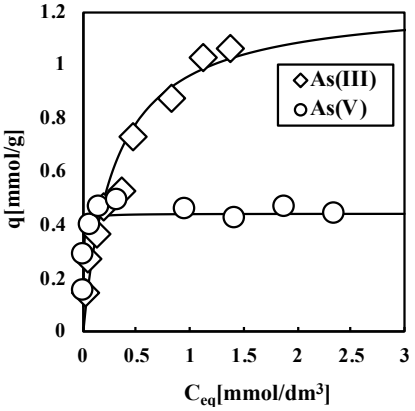

Fig. 1 Adsorption isotherms of As(III) and As(V) on NiZn at 303 K. Conditions: initial concentration 0.2-3.0 mM; weight of adsorbent, 20 mg; initial pH 11.2

Langmuir model. The q_{max} of As(III) was 2.8 times as high as that of As(V). Therefore it was found that the NiZn has high adsorption performance for As(III) at alkaline pH.

As(III)- and As(V)-loading NiZn were analyzed by XRD. The results are shown in Figs. 2 and 3, respectively.

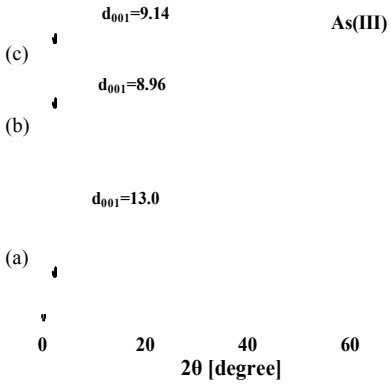

Fig. 2 XRD patterns of NiZn: (a) before adsorption, absorbed with As(III) (b) 0.27 mmol/g and (c) 1.06 mmol/g.

The d_{001} of the NiZn sifted to lower values due to the adsorption of As(III) and As(V) in the interlayers. Diffraction peaks derived from the NiZn decreased with increasing the amount of As(III) and As(V) adsorption. No diffraction peaks of As(III)-loading NiZn was observed when the amount of As(III) adsorption is 1.06 mmol/g. These results indicate that the adsorption mechanism of As(III) and As(V) on the NiZn is anion exchange.

The FT-IR spectra of the NiZn after As(III) and As(V) adsorption were shown in Figs. 4 and 5, respectively.

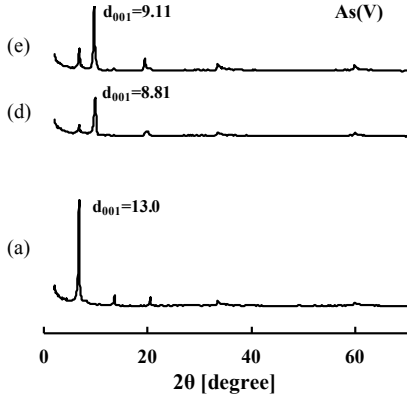

Fig. 3 XRD patterns of NiZn: (a) before adsorption, adsorbed with As(III) (d) 0.29 mmol/g and (e) 0.50 mmol/g.

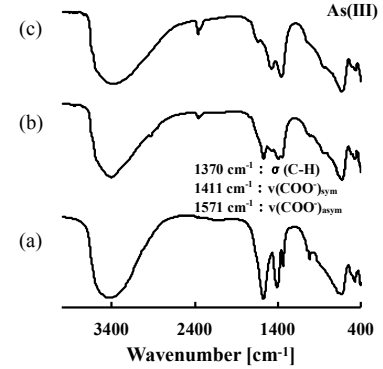

Fig. 4 FT-IR spectra of NiZn: (a) before adsorption, adsorbed with As(III) (b) 0.27 mmol/g and (c) 1.06 mmol/g.

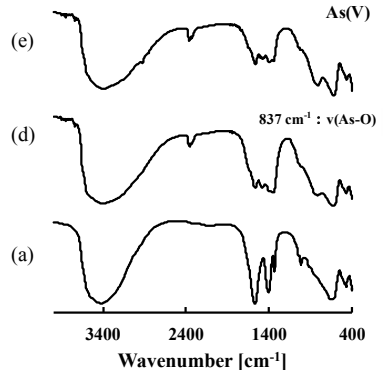

Fig. 5 FT-IR spectra of NiZn: (a) before adsorption, adsorbed with As(III) (d) 0.29 mmol/g and (e) 0.50 mmol/g.

The absorption peaks corresponding to the intercalated acetate ion were detected. The antisymmetric and the symmetric stretching vibrations of carboxylate anion, and the deformation vibration peak of alkane were observed at 1571, 1411 and 1370 cm^{-1}, respectively. These absorption peaks decreased with increasing the amount of arsenic adsorbed. The weak absorption peak attributed to stretching vibration of As(V)-O was appeared at 837 cm^{-1}. Therefore it was found that As(III) and As(V) were removed by anion exchange with acetate anion intercalated in NiZn.

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