

## Research Article

# Effect of Interlayer Anions with NiZn Hydroxy Double Salts on Adsorption of Selenite, Selenate and Arsenate

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## ABSTRACT

Development of adsorbents for selenium and arsenic, which are particularly toxic, is urgently needed. Arsenic was prepared for adsorption and removal. The experimental data of adsorption isotherms of As and Se oxyanions by NiZn adsorbents were well fitted to the Langmuir adsorption model, which is characteristic of monolayer adsorption, with a coefficient of determination of  $R^2 > 0.94$ . The maximum adsorption ( $q_{max}$ ) of Se(IV) by NiZn-Cl and NiZn-NO<sub>3</sub> was similar to that of NiZn-AcO, and no difference in adsorption due to interlayer ions was indicated. On the other hand, NiZn-Cl had the highest  $q_{max}$  for Se(VI) and As(V).  $q_{max}$  for As(V) by NiZn-Cl was about twice that of NiZn-AcO. As(V) and Se(VI) adsorption performance was greatly improved.

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## 1. Introduction

Arsenic and selenium are used as superior materials for semiconductor lasers ((Ga, In)As) and solar batteries (Cu(In, Ga)(Se, S)<sub>2</sub>), but are known to be damaging to the human body even in tiny amounts. In WHO guidelines, the standard value of arsenic [1] and selenium [2] is less than 0.01 mg/dm<sup>3</sup>. The International Agency for Research classifies arsenic and selenium compounds on Cancer (IARC) as Group 1 and 3, respectively, and cause cancer and other health damage. The main oxidation states of arsenic in aqueous solution are +3 and +5, and they exist as oxyanions arsenite, As(III) and arsenate, As(V). As(III) exists as H<sub>n</sub>AsO<sub>3</sub><sup>-(3-n)</sup> (n = 0-3), and their acid dissociation constants are 9.23 (pK<sub>a1</sub>), 12.13 (pK<sub>a2</sub>) and 13.4 (pK<sub>a3</sub>) [3]. As(V) exists as H<sub>n</sub>AsO<sub>4</sub><sup>-(3-n)</sup> (n = 0-3), and their acid dissociation constants are 2.24 (pK<sub>a1</sub>), 6.96 (pK<sub>a2</sub>) and 11.5 (pK<sub>a3</sub>) [3]. The main oxidation states of selenium in aqueous solution are +4 and +6, and they exist as oxyanions selenite, Se(IV), and selenate, Se(VI). The acid dissociation constants of Se(IV) are pK<sub>a1</sub> = 2.62 and pK<sub>a2</sub> = 8.23 and the chemical species of Se(IV), H<sub>n</sub>SeO<sub>3</sub><sup>-(2-n)</sup> (n = 0-2). The acid dissociation constant of Se(VI) is pK<sub>a</sub> = 1.7 [4], and chemical species are H<sub>n</sub>SeO<sub>4</sub><sup>-(1-n)</sup> (n = 0, 1).

Anion exchangeable layered compounds are mainly two type layered double hydroxides (LDHs) and hydroxyl double salts (HDSs). General formula of LDHs is [M<sup>II</sup><sub>(1-x)</sub>M<sup>III</sup><sub>x</sub>(OH)<sub>2</sub>]<sup>x+</sup>Y<sup>z-</sup><sub>x/z</sub>nH<sub>2</sub>O, where M<sup>II</sup> and M<sup>III</sup> are cations and Y<sup>z-</sup> is anion. The most investigated anion exchangeable layered compounds are LDHs. On the other hand, hydroxyl double salts, HDSs are inorganic anion exchangers with general formula [M<sup>A</sup><sub>(1-x)</sub>M<sup>B</sup><sub>2x</sub>(OH)<sub>2</sub>(Y<sup>z-</sup>)<sub>2x/z</sub>nH<sub>2</sub>O. In detail, NiZn double basic salt with acetate anion Ni<sub>1-x</sub>Zn<sub>2x</sub>(OH)<sub>2</sub>(OCOCH<sub>3</sub>)<sub>2x</sub>nH<sub>2</sub>O (NiZn-AcO) is an inorganic anion exchanger that has a structure in which 1/4 of Ni<sup>2+</sup> in a brucite-like layer of Ni(OH)<sub>2</sub> is removed from the brucite-like layer, and two Zn<sup>2+</sup> are located outside the layers, just above and below the Ni<sup>2+</sup> vacancy [5], [6]. The layers have positive charges in excess, balanced by intercalation of acetate anion. The acetate anions bind directly to the tetrahedral sites along with three OH<sup>-</sup> groups from the layer to satisfy the coordination number of Zn<sup>2+</sup>. The acetate anions are exchanged with guest ions in aqueous solution. Most of research on HDS is in the field of catalysis [7], and to my knowledge, there are few applications in the aqueous environment. The NiZn-AcO is a more effective arsenic removal adsorbent than MgAl Layered double hydroxide (LDH) with carbonate ion [8]. Using selectivity coefficients, Kozai *et al.* showed that NiZn hydroxyl double salts are more effective than LDH for selenium

removal [9]. However, adsorption isotherms and adsorbent evaluation after selenium adsorption have not been investigated in detail.

In this study, NiZn adsorbents were prepared by adding chloride (NiZn-Cl), nitrate (NiZn-NO<sub>3</sub>), and sulfate (NiZn-SO<sub>4</sub>) to the acetate ion of NiZn-AcO to improve the adsorption and removal performance of arsenic and selenium. The effect of interlayer anions of NiZn adsorbents on the adsorption of arsenic and selenium was investigated.

## 2. Experimental

### 2.1. Preparation of NiZn adsorbents

NiZn-AcO, NiZn hydroxide double salt with acetate anion (AcO) was prepared by a modified hydrothermal synthetic method reported by Rojas *et al.* [5], [8]. NiZn-Cl adsorbent was prepared using an ion exchange method using NiZn-AcO. 50 cm<sup>3</sup> of 1 M NaCl solution and 1 g of NiZn-AcO were placed in a glass vessel and stirred at 333 K for 24 h. The supernatant was then discarded and the sample was stirred in a new 1 M NaCl solution, which was repeated three times. NiZn-NO<sub>3</sub> and NiZn-SO<sub>4</sub> were prepared in the same method as NiZn-Cl using aqueous solutions of NaNO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub>, respectively. The NiZn adsorbents were washed several times using deionized water and dried in a vacuum oven. XRD, FT-IR, and CHN elemental analysis characterized the adsorbents.

### 2.2. Adsorption test of arsenic and selenium

The adsorption experiments of Se(IV), Se(VI) and As(V) were carried out by batch method. 1.0 × 10<sup>-4</sup> M aqueous metal solution was adjusted to a given pH using HCl solution or an aqueous NaOH solution in the pH-dependent adsorption test. In the adsorption isotherm experiments, metal concentrations were prepared at 2.0 × 10<sup>-4</sup> - 4.0 × 10<sup>-3</sup> M and adjusted to the prescribed pH with the aqueous NaOH solution. Ten mg of NiZn adsorbent and 15 cm<sup>3</sup> of metal solution were added to a sample tube and shaken at 303 K, 120 rpm for 24 h. pH of the filtrate was measured. The metal concentrations of the solutions before and after adsorption equilibrium were measured using atomic absorption spectrophotometer and ICP emission spectrometer. The amount of adsorption ( $q$ ) and the adsorption percentage ( $A\%$ ) were calculated according to the following equations, respectively:

$$q = (C_{\text{int}} - C_{\text{eq}}) v/w \quad (1)$$

$$A = (C_{\text{int}} - C_{\text{eq}}) / C_{\text{int}} \quad (2)$$

where  $C_{\text{int}}$  and  $C_{\text{eq}}$  are initial and equilibrium concentration, respectively [mM],  $v$  is the volume of solution,  $w$  is the weight of adsorbent [g],  $q$  is the amount of arsenic or selenium adsorbed,  $A$  is the adsorption percentage [%]

Langmuir equation and its variant equation are given in Eq.(3) and (4), respectively.

$$q = K_L q_{\text{max}} C_{\text{eq}} / (1 + K_L C_{\text{eq}}) \quad (3)$$

$$C_{\text{eq}} / q = C_{\text{eq}} / q_{\text{max}} + 1 / K_L q_{\text{max}} \quad (4)$$

where  $q_{\text{max}}$  is the maximum adsorption capacity [mmol/g] and  $K_L$  is the adsorption equilibrium constant [dm<sup>3</sup>/mmol]

## 3. Results and Discussion

### 3.1. Characterization of NiZn adsorbents

Four NiZn adsorbents prepared were identified by XRD and FT-IR analysis. XRD diffraction pattern of NiZn-AcO is shown in Fig. 1. In the XRD pattern of NiZn-AcO, diffraction peaks specific to the layer structure were

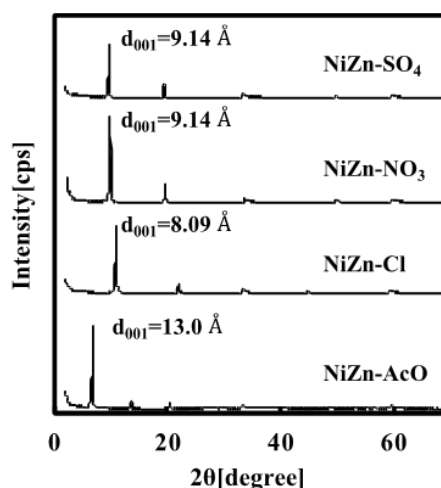


Fig. 1 XRD patterns of NiZn-AcO, NiZn-Cl, NiZn-NO<sub>3</sub> and NiZn-SO<sub>4</sub>.

detected. The lattice plane spacing ( $d$ ) of the diffraction peaks were 13.0 Å, 6.49 Å, and 4.33 Å for  $d_{001}$ ,  $d_{002}$ , and  $d_{003}$ , respectively, from the low angle side, which is consistent with the literature values [5]. Diffraction patterns of NiZn-Cl, NiZn-NO<sub>3</sub>, and NiZn-SO<sub>4</sub> also detected peaks originating from layered compounds, similar to NiZn-AcO. As shown in Fig. 1, their  $d_{001}$  values decreased to 8.09 Å (NiZn-Cl), 9.14 Å (NiZn-NO<sub>3</sub>), and 9.14 Å (NiZn-SO<sub>4</sub>) After inorganic anions replace organic anions between the LDH layers, the space within the LDH layers increases significantly [12]. The results indicate that inorganic ions replace the acetate ions in the NiZn adsorbent. from the  $d_{001}$  of NiZn-AcO. FT-IR spectrum of NiZn-AcO with the absorption bands at 1572 cm<sup>-1</sup> for the carboxylate (COO<sup>-</sup>) and 1407 cm<sup>-1</sup> for the symmetric stretching, and an absorption peak at 1339 cm<sup>-1</sup> for the C-H symmetric angular vibration. The interlayer ions of absorption peaks of NO stretching vibration at 1385 cm<sup>-1</sup> for NiZn-NO<sub>3</sub> and SO asymmetric stretching vibration at 963 cm<sup>-1</sup> and SO symmetric stretching vibration at 1061 cm<sup>-1</sup> for NiZn-SO<sub>4</sub> were confirmed [10].

The chemical formula of NiZn adsorbents was determined using atomic absorption analysis (Ni/Zn mole ratio), CNH elemental analysis (amount of acetate) and TG/DTA (amount of adsorption water) [11], and is shown in Table 1. The ion exchange capacity of NiZn-

AcO is 2.45 meq/g (= acetate anion content); the Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> amounts in NiZn-Cl, NiZn-NO<sub>3</sub> and NiZn-SO<sub>4</sub> are 2.22 meq/g, 1.57 meq/g and 2.09 meq/g respectively.

Table 1. Chemical fomula of NiZn adsorbents

NiZn adsorbents	Chemical formula
AcO	Ni <sub>0.67</sub> Zn <sub>0.34</sub> (OH) <sub>2</sub> (CH <sub>3</sub> COO) <sub>0.34</sub> 0.65H <sub>2</sub> O
Cl	Ni <sub>0.67</sub> Zn <sub>0.34</sub> (OH) <sub>2</sub> (CH <sub>3</sub> COO) <sub>0.03</sub> (Cl) <sub>0.31</sub> nH <sub>2</sub> O
NO <sub>3</sub>	Ni <sub>0.67</sub> Zn <sub>0.34</sub> (OH) <sub>2</sub> (CH <sub>3</sub> COO) <sub>0.12</sub> (NO <sub>3</sub> ) <sub>0.22</sub> nH <sub>2</sub> O
SO <sub>4</sub>	Ni <sub>0.67</sub> Zn <sub>0.34</sub> (OH) <sub>2</sub> (CH <sub>3</sub> COO) <sub>0.05</sub> (SO <sub>4</sub> ) <sub>0.15</sub> nH <sub>2</sub> O

### 3.2. Adsorption isotherms of arsenic and selenium

Adsorption isotherms of Se(IV), Se(VI), and As(V) at 303 K were conducted. The adsorption isotherms for Se(IV), Se(VI), and As(V) increased with increasing metal ion concentration and approached a constant value at high concentrations, which the Langmuir adsorption model characteristic of monolayer adsorption is applied. The experimental data for Se(VI) adsorption fitted the Langmuir plot well (Fig. 2), with coefficient of determination  $R^2 > 0.988$ . Se(IV) and As(V) adsorption also fit the Langmuir plot well ( $R^2 > 0.94$ ). The maximum adsorption capacity ( $q_{max}$ ) for Se(IV), Se(VI) and As(V) and adsorption equilibrium constants ( $K_L$ ) were calculated using Langmuir's equations (equations (3) and (4)) and are listed in Table 2.

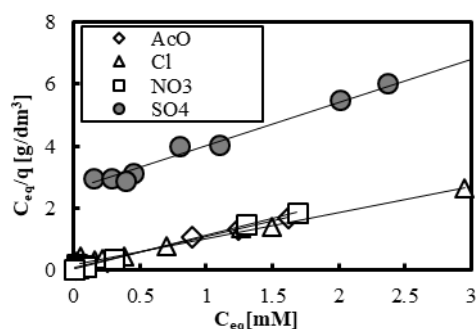


Fig. 2 Langmuir plots of Se(VI) on NiZn-AcO, -Cl, -NO<sub>3</sub> and -SO<sub>4</sub>...

The maximum adsorption capacities ( $q_{max}$ ) of Se(IV), Se(VI), and As(V) by NiZn-Cl and NiZn-NO<sub>3</sub> were almost the same or increased compared to that of NiZn-AcO, except for NiZn-SO<sub>4</sub>. Since the dissolved species of Se(VI) or As(V) have a significant effect on  $q_{max}$ , the saturated adsorbed amount of Se(VI) or As(V) was converted to an equivalent unit by considering the mole fractions of the main dissolved species at each pH, which were obtained from the acid dissociation constants. As shown in Table 2, Se(VI) species are SeO<sub>4</sub><sup>2-</sup> from pH, the  $q_{max}$  of NiZn-AcO and NiZn-Cl are calculated to be 1.96 meq/g and 2.38 meq/g, respectively. Acetate in NiZn-

Table 2. Parameters of the Langmuir adsorption isotherms for Se(IV), Se(VI) and As(V) at 303 K.

Adsorbates	Adsorbents	pH <sub>eq</sub>	$q_{max}$ [mmol/g]	$K_L$ [dm <sup>3</sup> /mmol]	$R^2$
Se(IV)	NiZn-AcO	8.54±0.33	1.48	7.10	0.94
	NiZn-Cl	7.88±0.39	1.44	9.98	0.994
	NiZn-NO <sub>3</sub>	7.67±0.59	1.54	7.47	0.971
	NiZn-SO <sub>4</sub>	7.35±0.39	0.909	4.09	0.965
Se(VI)	NiZn-AcO	6.85±0.15	0.979	14.2	0.989
	NiZn-Cl	6.72±0.54	1.19	4.31	0.988
	NiZn-NO <sub>3</sub>	6.60±0.42	0.983	12.8	0.997
	NiZn-SO <sub>4</sub>	6.77±0.21	0.718	0.531	0.99
As(V)	NiZn-AcO	10.3±0.32	0.446	287	0.998
	NiZn-Cl	9.67±0.43	0.947	14.3	0.997
	NiZn-NO <sub>3</sub>	10.0±0.36	0.524	77.6	0.999
	NiZn-SO <sub>4</sub>	9.59±0.49	0.564	11.1	0.988

AcO and NiZn-Cl The Se(VI) exchange percentage was estimated to be 80.0% and 107% by comparing the amount of acetate anion and Cl<sup>-</sup> (meq/g) in NiZn-AcO and NiZn-Cl, respectively, as shown in section 3.1.

When Se(IV) was examined similarly, the exchange rate of Se(IV) by NiZn-Cl (82.7%) was slightly lower than that of NiZn-AcO (96.7%) From the pH given in Table 2, the  $q_{max}$  of NiZn-AcO and NiZn-Cl were calculated to be 0.918 meq/g and 1.91 meq/g, respectively, considering the mole fraction of As(V) chemical species, and the exchange percentage of As(V) was estimated to be 37.5% and 85.9%. These results indicate that NiZn-Cl can adsorb Se(VI) and As(V) more effectively than NiZn-AcO.

### 3.3. Effect of contact time of Se(VI) adsorption

Fig. 3 shows the effect of contact time on the Se(VI) adsorption by NiZn-AcO and NiZn-Cl. The time for the adsorption of Se(VI) by NiZn-AcO and NiZn-Cl to reach equilibrium was 5 min, which was extremely rapid. The result is the same as the ion exchange reaction with LDH [12], indicating that the Se(VI) adsorption is considered to be due to the ion exchange reaction.

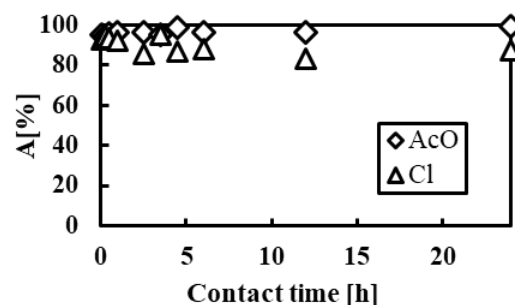


Fig. 3 Time course of Se(VI) adsorption on NiZn-AcO and NiZn-Cl.

### 3.4. XRD results of NiZn adsorbent after Se(IV) and Se(VI) adsorption

The  $d_{001}$  values of NiZn-AcO and NiZn-Cl changed before and after the adsorption of Se(IV) or Se(VI) (Fig. 1 and 4). The thickness of the basic brookite layers does not change much during the anion exchange process, but the interlayer distance varies with the configuration and size of the intercalated anions. After selenium adsorption, these interlayer distances were nearly equal, suggesting that the interlayer acetate anions and  $\text{Cl}^-$  are exchanged for anions by Se(IV) and Se(VI).

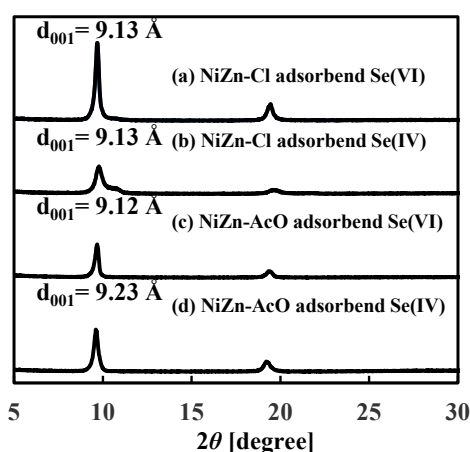


Fig. 4 XRD patterns of NiZn-AcO adsorbed (a) Se(IV) and (b) Se(VI), and NiZn-Cl adsorbed (c) Se(IV) and (d) Se(VI).

## 4. Conclusions

After hydrothermal synthesis preparation of NiZn-AcO, NiZn-Cl, NiZn- $\text{NO}_3$ , and NiZn- $\text{SO}_4$  were prepared from NiZn-AcO by ion exchange method to obtain NiZn layered basic salt adsorbents. These four NiZn adsorbents were found to be able to adsorb and remove Se(IV), Se(VI), and As(V) from the aqueous solution. NiZn-Cl was able to adsorb Se(IV), Se(VI), and As(V) according to Langmuir adsorption model. NiZn- $\text{NO}_3$  and NiZn- $\text{SO}_4$  adsorbed the same amount of Se(IV) as NiZn-Cl and NiZn- $\text{NO}_3$ . In contrast, the maximum amount of Se(VI) adsorbed by NiZn-Cl was slightly increased compared to NiZn- The adsorption performance of As(V) and Se(VI) was improved by ion exchange of the interlayer anions of NiZn adsorbent from acetate to chloride ions.

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## Authors Introduction

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