

# Adsorption Behavior of Arsenic and Selenium using NiZn Hydroxy Double Salts with Acetate, Chloride, Nitrate and Sulfate Anions

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## Abstract

Arsenic(As) and selenium(Se) has become an increasingly serious water contamination worldwide, so the development of adsorbents to improve the adsorption performance of As and Se oxyanions is desired. In this study, NiZn adsorbents intercalated acetate, chloride, nitrate, and sulfate anions to interlayers of NiZn hydroxy double salts were prepared and their adsorption behavior of As and Se oxyanions was investigated. The Langmuir isotherm model, characteristic of monolayer adsorption, fit the experimental data well with  $R^2 > 0.94$ . The adsorption capacity ( $q_{max}$ ) of Se(IV) was the other NiZn-AcO  $\approx$  NiZn-Cl  $>$  NiZn-NO<sub>3</sub>  $>$  NiZn-SO<sub>4</sub> and that of Se(VI) was the order of NiZn-Cl  $>$  NiZn-AcO  $>$  NiZn-NO<sub>3</sub>  $>$  NiZn-SO<sub>4</sub>. The  $q_{max}$  of as(V) on NiZn-Cl was about twice as large as that on NiZn-AcO, NiZn-NO<sub>3</sub> and NiZn-SO<sub>4</sub>. NiZn-Cl was found to adsorb As(V) and Se(VI) oxyanions more efficient than NiZn-AcO.

**Keywords:** NiZn hydroxy double salts, arsenic, selenium, adsorption, Langmuir isotherm model

## 1. Introduction

Arsenic and selenium are known to be harmful to human body even at low concentration. The environmental standard values for arsenic [1] and selenium [2] in drinking water are set by the WHO guidelines as less than 0.01 mg/dm<sup>3</sup>. Arsenic in nature has oxidation states of -3, 0, +3, and +5, and exists as inorganic and organic arsenic. Inorganic arsenic is known to more toxic than organic arsenic. Inorganic arsenic in natural water forms mainly oxyanions, arsenite (AsO<sub>3</sub><sup>3-</sup>, As(III)) and arsenate (AsO<sub>4</sub><sup>3-</sup>, As(V)). The acid dissociation constants of As(III) are  $pK_{a1}=9.23$ ,  $pK_{a2}=12.13$ , and  $pK_{a3}=13.4$ , and there are four chemical forms, H<sub>3</sub>AsO<sub>3</sub>, H<sub>2</sub>AsO<sub>3</sub><sup>-</sup>, HAsO<sub>3</sub><sup>2-</sup>, and AsO<sub>3</sub><sup>3-</sup> [3]. The acid dissociation constants of As(V) are  $pK_{a1}=2.24$ ,  $pK_{a2}=6.96$ , and  $pK_{a3}=11.5$ , and the chemical species are H<sub>3</sub>AsO<sub>4</sub>, H<sub>2</sub>AsO<sub>4</sub><sup>-</sup>, HAsO<sub>4</sub><sup>2-</sup>, and AsO<sub>4</sub><sup>3-</sup> [3]. Selenium solubilized and released into waste water exists in +4 and +6 oxidation states. Chemical species of selenium with these oxidation states are oxyanions selenite (SeO<sub>3</sub><sup>2-</sup>, Se(IV)) and selenate (SeO<sub>4</sub><sup>2-</sup>, Se(VI)) with high solubility and mobility in both aquatic and soil environment.. The acid dissociation constants of Se(IV) are  $pK_{a1}=2.62$ ,  $pK_{a2}=8.23$ , and there are three chemical forms, H<sub>2</sub>SeO<sub>3</sub>, HSeO<sub>3</sub><sup>-</sup>, and SeO<sub>3</sub><sup>2-</sup> [4]. The acid dissociation constants of Se(VI) are  $pK_{a1}=1.7$  and the chemical species are HSeO<sub>4</sub><sup>-</sup>, and SeO<sub>4</sub><sup>2-</sup> [4].

Hydroxyl double salts HDSs, one of inorganic anion-exchanger with a general formula  $[M_A^{II}(1-x)M_B^{II}(\text{OH})_2(Y^{z-})]_{2x/z} \cdot n\text{H}_2\text{O}$ . Specifically, the NiZn double basic salt with acetate anion (NiZn-AcO) Ni<sub>1-</sub>

<sub>x</sub>Zn<sub>2x</sub>(OH)<sub>2</sub>(OCOCH<sub>3</sub>)<sub>2x</sub>·nH<sub>2</sub>O has a structure in which 1/4 of Ni<sup>2+</sup> in 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, which are 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. We reported that NiZn-AcO is an effective adsorbent for arsenic removal than MgAl Layered double hydroxide [8]. Kozai *et al.* showed that NiZn hydroxyl double salts is more effective than LDH for selenium removal using selective coefficients [9], but adsorption isotherms and adsorbent evaluation after adsorption selenium were not studied.

In this study, NiZn adsorbents with chloride, nitrate and sulfate anions in the interlayer of NiZn were prepared to improve for arsenic and selenium removal performance and their adsorption behavior for arsenic and selenium was evaluated.

## 2. Experimental

### 2.1. Preparation of NiZn adsorbents

NiZn-AcO, NiZn hydroxide double salt intercalating acetate anion (AcO) was first prepared by modifying the synthetic method reported by Rojas *et al.* [5]. NiZn-Cl adsorbent was prepared by an ion-exchange method. One gram of NiZn-AcO was added to 50 cm<sup>3</sup> of 1 M NaCl solution and stirred at 333 K for 24h. The supernatant was then wasted and fresh 1 M NaCl solution was added and stirred. This procedure was repeated three times. NiZn-NO<sub>3</sub> and NiZn-SO<sub>4</sub> were prepared in the same procedure as NiZn-Cl using 1 M NaNO<sub>3</sub> and 1 M Na<sub>2</sub>SO<sub>4</sub>, respectively. The resulting adsorbents were washed several times with deionized water, dried in a vacuum drying oven and characterized by XRD, FT-IR, and CHN elemental analysis.

### 2.2. Adsorption test of arsenic and selenium

All adsorption test was carried out by batch method at 303 K. 1.0 × 10<sup>-4</sup> M 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 was added to a sample tube and shaken in 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:

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

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

where *C<sub>int</sub>* and *C<sub>eq</sub>* 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.

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

$$C_{eq} / q = C_{eq} / q_{max} + 1 / K_L q_{max} \tag{4}$$

where *q<sub>max</sub>* is the maximum adsorption capacity [mmol/g] and *K<sub>L</sub>* is the adsorption equilibrium constant [dm<sup>3</sup>/mmol]

## 3. Results and Discussion

### 3.1. Characterization of NiZn adsorbents

NiZn adsorbents prepared were identified by XRD and FT-IR analysis. XRD diffraction pattern of NiZn-AcO is shown in Fig. 1. The diffraction peaks of 001, 002 and 003 are at 2θ = 6.8, 13.6, 20.6, respectively, in agreement with the literature values [5]. The interlayer distance of

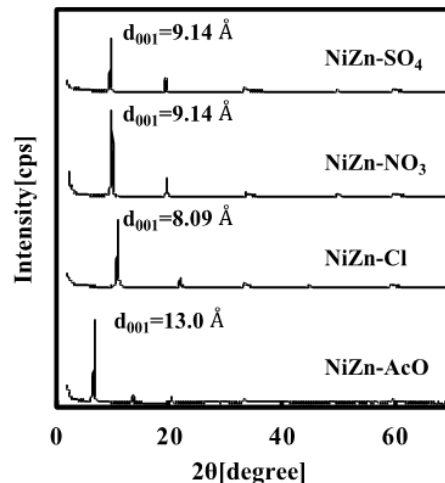


Fig. 1 XRD patterns of NiZn-AcO, NiZn-Cl, NiZn-NO<sub>3</sub> and NiZn-SO<sub>4</sub>.

NiZn-AcO was determined to be 8.40 Å by subtracting the thickness of the basic layer, Ni(OH)<sub>2</sub>, of 4.60 Å. Similarly, peaks derived from layered compounds were observed in the diffraction patterns of NiZn-Cl, NiZn-NO<sub>3</sub>, and NiZn-SO<sub>4</sub>, with *d<sub>001</sub>* values of 8.09 Å, 9.14 Å, and 9.14 Å, respectively, as shown in Fig. 1 [10].

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]. Table 1 shows the chemical formulas of the NiZn adsorbent, in which acetate anion in NiZn-AcO is ion-exchanged with Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>. The anion exchange capacity of NiZn-AcO is 2.45 meq/g. The amount of Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> exchanged were in the order of Cl<sup>-</sup> (2.22 meq/g) > SO<sub>4</sub><sup>2-</sup> (2.09 meq/g) > NO<sub>3</sub><sup>-</sup> (1.57 meq/g).

Table 1. Chemical formula 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

To evaluate the adsorption performance of NiZn adsorbents for As and Se oxyanions, adsorption isotherms of e and As oxyanions at 303 K were conducted. Langmuir isotherm model, characteristic of monolayer adsorption, since the amount increases with increasing concentration and approaches a constant value at high concentrations. The Experimental data for the adsorption of Se and As oxyanions using NiZn adsorbents fit Langmuir plot well with R<sup>2</sup> > 0.94 (Fig. 2). The maximum adsorption capacity (*q<sub>max</sub>*) and adsorption equilibrium constant (*K<sub>L</sub>*) for Se(IV), Se(VI) and As(V) were

calculated from the Langmuir equation (Eq. (3) and (4)) and are shown in Table 2.

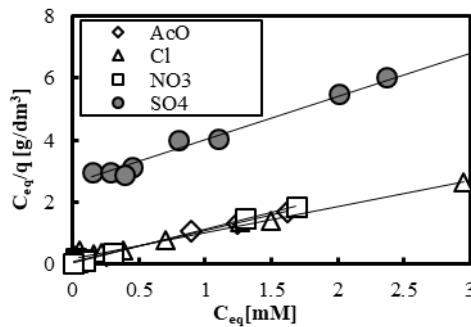


Fig. 2 Langmuir plots of Se(VI) on NiZn-AcO, -Cl, -NO<sub>3</sub> and -SO<sub>4</sub>...

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 <sub>max</sub> [mmol/g]	K <sub>L</sub> [dm <sup>3</sup> /mmol]	R <sup>2</sup>
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

The maximum adsorption capacity (q<sub>max</sub>) of Se(IV), Se(VI), and As(V) by NiZn-Cl, -NiZnNO<sub>3</sub>, and SO<sub>4</sub> was 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<sub>max</sub>, 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<sub>max</sub> of NiZn-AcO and NiZn-Cl are calculated to be 1.96 meq/g and 2.38 meq/g, respectively. Acetate in NiZn-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<sub>max</sub> 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

The effect of contact time on Se(VI) adsorption by NiZn-AcO and NiZn-Cl is shown in Fig. 3. The time to reach equilibrium for Se(VI) adsorptions was 5 min which was extremely rapid. During the first 5 min 95.2% of Se(VI) was adsorbed on NiZn-AcO, whereas NiZn-Cl adsorbed 92.7% of Se(VI). These fast adsorption process has been considered ion exchange reactions involving, which is similar to ion exchange in LDHs [12].

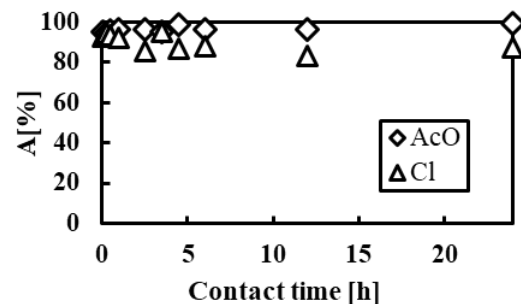


Fig. 3 Time course of Se(VI) adsorption on NiZn-AcO and NiZn-Cl...

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

The basic brookite layer thickness does not change much during the process of anion exchange, but the interlayer distance varies with the placement and size of the intercalated anions. When inorganic anions are replaced by organic anions in the LDH interlayer, the LDH layer space increases significantly [12]. In the present study, the (003) diffraction peaks observed in

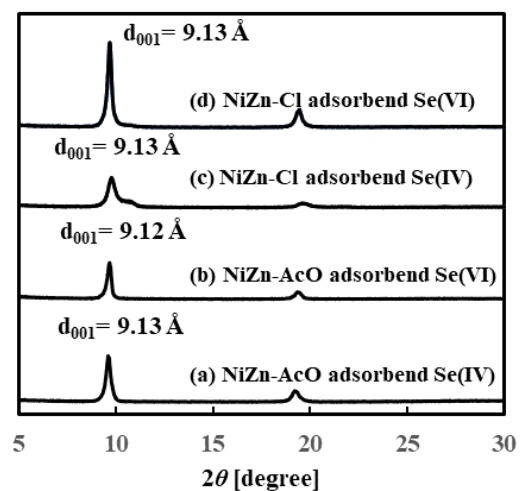


Fig. 4 XRD patterns of NiZn-AcO adsorbed (a) Se(IV) and (b) Se(VI), and NiZn-Cl adsorbed (c) Se(IV) and (d) Se(VI)..

NiZn-AcO and NiZn-Cl have the  $d_{003}$  values of 13.0 and 8.09 Å, respectively (Fig. 1), and these peaks shifted after the adsorption of Se(IV) or Se(VI) (Fig. 4). and NiZn-Cl host layer thickness is 4.6 Å, the NiZn-AcO interlayer distance decreased significantly from 8.4 Å to 4.63 Å (Se(IV)), 4.52 Å (Se(VI)), and the NiZn-Cl interlayer distance increased from 4.49 to 4.53 Å (Se(IV), Se(VI)). Se(IV), Se(VI). The interlayer distances after selenium adsorption were almost equal, suggesting that the interlayer acetate anions and Cl<sup>-</sup> were replaced by Se(IV) or Se(VI).

#### 4. Conclusions

NiZn adsorbents NiZn-Cl, NiZn-NO<sub>3</sub>, and NiZn-SO<sub>4</sub> were prepared by ion exchange method using NiZn-AcO obtained by hydrothermal synthesis. Experimental investigating the adsorption of arsenic and selenium oxyanions from aqueous solutions using the NiZn adsorbents indicated that the arsenic and selenium oxyanions could be adsorbed on NiZn-AcO, NiZn-Cl, NiZn-NO<sub>3</sub>, and NiZn-SO<sub>4</sub>. Se(IV), Se(VI) and As(V) were found to be adsorbed on NiZn adsorbent by Langmuir isotherm model. The adsorption isotherm for As(V) shows that NiZn-Cl has twice higher adsorption capacity than NiZn-AcO. The adsorption of Se(IV) by NiZn-NO<sub>3</sub> was slightly increased compared to NiZn-AcO. The exchange of acetate anion in the NiZn interlayer with chloride ions improved the adsorption performance of As(V) and Se(VI).

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