Adsorption Equilibrium of Selenium Oxyanions Using FeY Mixed Oxides

Kaoru Ohe*, Amu Wakamatsu, Tatsuya Oshima
University of Miyazaki, 1-1 Gakuenkibanadai-Nishi,, Miyazaki, 889-2192, Japan
Email: okaoru@cc.miyazaki-u. ac.jp, amu.wakamatsu@gmail.com, oshimat@cc.miyazaki-u.ac.jp

** Corresponding author*

Abstract

Selenium oxyanions (Se(IV) and Se(VI)) in wastewater are of concern as serious pollutants due to their easy bioaccumulation and toxicity to living organisms. In this study, mixed oxides with various Y/Fe molar composition ratios (x=0.5, 1, 2) were investigated in the adsorption properties of selenium oxyanions, and were studied their adsorption mechanism. The experimental data best fits the Langmuir adsorption model, which is characteristic of monolayer adsorption (r^2 >0.991). The maximum adsorption capacity (q_{max}) of Se(IV) and Se(VI) increased in the order of FeY2 > FeY1 > FeY0.5 and of Fe2 > FeY1, respectively. It was suggested that FeY2 adsorbed Se(IV) by formation of inner-sphere complexes and outer-sphere complexes, and adsorbed Se(VI) by outer-sphere complexes.

Keywords: selenium oxyanions, mixed oxides, adsorption, iron, yttrium

1. Introduction

Selenium is a toxic element that is released into the environment due to human-induced pollution, such as mining activities and irrigated agriculture, and natural pollution, such as the dissolution of minerals [1], [2]. Because ingesting these elements can cause serious health problems in the human body, their removal from environmental water is an issue that needs to be urgently addressed. The World Health Organization (WHO) strictly regulates the guideline drinking water standard value at 0.01 mg dm^3. Selenium in environmental water exists as selenite Se(IV) and selenate Se(VI) . The pK_a values indicate that Se(IV) exists predominantly as H_2SeO_3, $HSeO_3^-$ and SeO_3^{2-} (pK_{a1}= 2.61 and pK_{a2}=8.46) [11] and Se(VI) as $HSeO_4^-$ and SeO_4^{2-} (pK_a= 1.70) [11]. Both oxyanions could result in health problems and are known to bioaccumulate in tissues.

Generally, the methods used to remove harmful metal ions from water include coagulation and coprecipitation with iron or aluminum, but these methods require a long time for treatment and produce a large amount of sludge. Adsorption using metal oxides is a useful technique for removing these pollutants from environmental water due to its effectiveness and simplicity. Magnetic adsorbents have attracted attention because they can be separated from water more easily and quickly under an external magnetic field [3]. Previous studies have reported that adsorbents with a high point of zero charge (PZC) and a large specific surface area exhibit high adsorption performance for arsenic and selenium [4], [5]. Since iron has a high affinity for selenium and it is known that the compounds of yttrium have a high isoelectric point (PZC Y_2O_3 : 9.3 [6], $Y(OH)_3$: 10.3 [7]). We prepared an adsorbent by mixing iron and yttrium, and obtained a higher PZC and higher specific surface area than conventional iron-based adsorbents [8].

In this study, we investigated the adsorption behavior of selenium oxyanions using FeY mixed oxides prepared using the method of Ohe *et al* [8]. We studied the adsorption mechanism of selenium oxyanions by measuring the effect of ionic strength on selenium adsorption and the zeta potential before and after selenium adsorption.

2. Experimental

2.1. *Adsorbents*

The specific surface area and PZC of FeYx (x is molar ration of Y(III)/Fe(II) = 0.5, 1, 2) prepared by the method of Ohe *et al* [8] increased with increasing x value. The adsorbents used for comparison, Fe_3O_4 and amorphous yttrium compound (AYA), were prepared using $FeCl_2$ and YCl_3, respectively, by the same method as FeYx. The specific surface area and PZC of FeYx, Fe_3O_4 and AYA were 140 m^2/g and 8.8 (FeY0.5), 166 m^2/g and 9.8 (FeY1), 183 m^2/g and 10.3 (FeY2), 29.4 m^2/g and 5.7 (Fe_3O_4), 59.1 m^2/g and 7.8 (AYA), respectively.

2.2. *Selenium adsorption experiments*

All adsorption experiments were carried out using batch method. For the pH dependence experiments, 1.0 $\times10^{-4}$ mol dm^{-3} metal solution was adjusted to the specified pH by adding 1.0 $\times10^{-2}$ mol dm^{-3} HCl solution or 1.0 $\times10^{-2}$ mol dm^{-3} NaOH aqueous solution. In the adsorption isotherm experiments, Se(IV) and Se(VI) concentrations were used to 5.0×10^{-5}- 3.0×10^{-3} mol dm^{-3} and 1.0×10^{-5}-4.0×10^{-3} mol dm^{-3}, respectively, and the pH was adjusted to the specified value using 1.0×10^{-2} mol dm^{-3} N, N-Bis(2-hydroxyethyl)-2-aminoethane sulfonic acid (BES) buffer and 1.0×10^{-2} mol dm^{-3} NaOH aqueous solution. In the experiment for the effect of ionic strength on selenium adsorption, metal solution of 1.0×10^{-4} mol dm^{-3} was prepared, containing 1.0×10^{-3} - 1.0×10^{-1} mol dm^{-3} NaCl.

The pH was adjusted using 1.0×10^{-2} mol dm^{-3} HCl solution or 1.0×10^{-2} mol dm^{-3} NaOH aqueous solution. FeYx 10 mg and 15 cm^3 of the metal solution were added to a sample tube, and the mixture was shaken at 303 K, 120 rpm, for 24 h in water bath. After shaking, the mixture was filtered through 0.45 μm hydrophilic PTFE membrane filter, and the equilibrium pH of the filtrate was measured. The metal concentrations of the filtrate were measured using atomic absorption spectrophotometer (AAS, HITACHI Z-2310, SHIMADZU AA-7000) or ICP emission spectrometer (ICP-AES, SHIMADZU ICPS-8100). The percentage of adsorption (A%, Eq.(1)) and the amount of selenium adsorbed (q, Eq.(2)) were calculated as follows:

$$A\% = 100\cdot(C_i - C_{eq})/ C_i \quad (1)$$

$$q = (C_i - C_{eq})\cdot v/w \quad (2)$$

where C_i is initial concentration of selenium, C_{eq} is equilibrium concentration of selenium, q is the amount of selenium adsorbed [mmol/g], w is the weight of adsorbents [mg], v is the volume of the solution [cm^3]

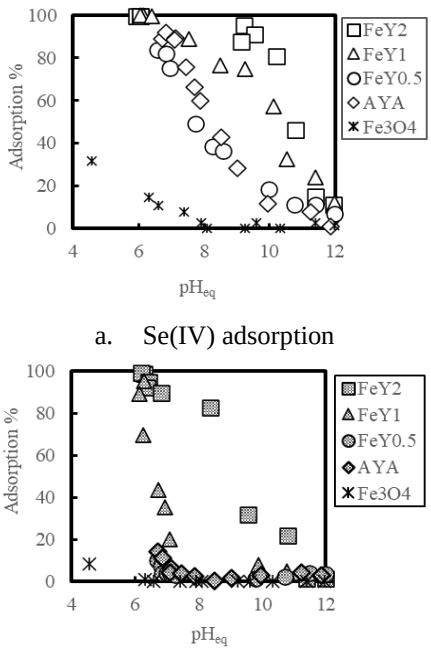
3. Results and Discussion

3.1. *Effect of pH on selenium oxyanions adsorption*

Fig.1a and Fig.1b show the effect of pH on selenite (Se(IV) and selenate(VI) adsorption. The maximum adsorption percentage for Se(VI) on FeY2 (pH 5.9) and FeY1 (pH 6.1) showed 100% (Fig.1a). At pH 4.0 -12, FeYx showed an adsorption rate equal to or higher than that of the comparative samples Fe_3O_4 and amorphous yttrium adsorbent (AYA). In addition, FeY2 showed an adsorption rate of over 90% in a wide range of pH 5.9-9.5. From Fig. 1b, it can be seen that FeY1 and FeY2 adsorbed Se(VI) in the pH range of 6.0-12, while the other adsorbents hardly adsorbed any. FeY2 showed an adsorption rate of over 90% at pH 6.0 exhibited an adsorption rate of over 90%, but it was found that the adsorption rate decreased as the pH increased. FeY1 showed a significant decrease in adsorption rate at pH 6.0-7.0, and at pH 7.0, the adsorption rate was 10%. FeY2 adsorbed Se(VI) over a wider pH range than FeY1. Se(IV) exists as $HSeO_3^-$ or SeO_3^{2-} in the pH range 4<pH<12 (Fig.2a), and Se(VI) exists as SeO_4^{2-} in aqueous solution(Fig.2b). Thus, at pH >PZC, the adsorption rate is thought to have decreased due to the electrostatic repulsion between the negatively charged adsorbent surface and Se(IV) and Se(VI).

3.2. *Adsorption isotherms of selenium oxyanions*

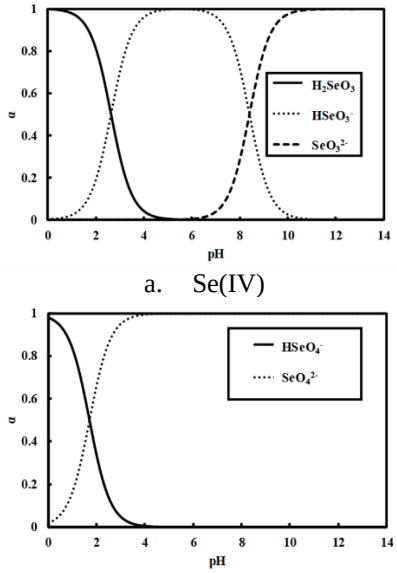
Adsorption isotherms for Se(IV) and Se(VI) at pH_{eq} 6.3-6.7 (303 K) were investigated. All adsorption isotherms (Fig.3) fit well Langmuir adsorption isotherms as shown by Eq. (3)



a. Se(IV) adsorption

b. Se(VI) adsorption

Fig. 1. The pH dependence for Se(IV) and Se(VI) adsorptions



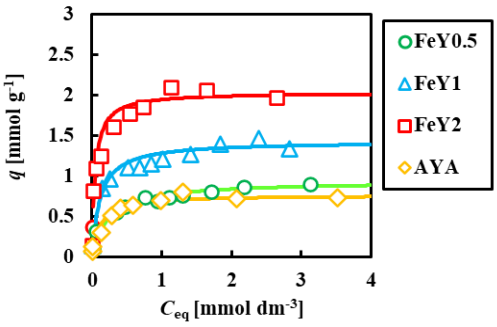
a. Se(IV)

b. Se(VI)

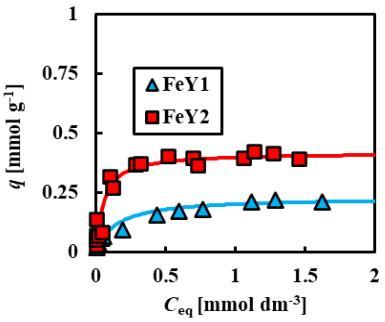
Fig. 2. Distribution ratio (α) of chemical species of Se(IV) and Se(VI).

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

where q_{max} is amount adsorbed at saturation (mmol/g), and K_L is adsorption equilibrium constant (dm^3/mmol). The parameters for the adsorption isotherms of Se(IV) and Se(VI) are summarized in Table 1. Se(IV) and Se(VI) weren't almost adsorbed on Fe_3O_4 at pH_{eq} 6.1. For the adsorption of Se(IV), it was found that q_{max} increased in the order of FeY0.5 < FeY1 < FeY2. Furthermore, the q_{max} of FeYx was higher than that of



a. Se(IV) adsorption



b. Se(VI) adsorption

Fig. 3. Adsorption isotherms of Se(IV) and Se(VI) at 303K with FeYx and AYA. Solid lines are calculation curves of Langmuir adsorption

Table. 1. The maximum adsorption capacity (q_{max}) for Se(IV) and Se(VI) at 303K.

Adsorbents	q_{max}		References
	Se(IV) [mmol g^{-1}]	Se(VI) [mmol g^{-1}]	
FeY2	2.04 (pH 6.3-6.5)	0.418 (pH6.5-6.7)	this study
FeY1	1.43 (pH 6.2-6.4)	0.230 (pH6.5-6.7)	this study
FeY0.5	0.936 (pH 6.3-6.5)	Almost no adsorption	this study
AYA	0.761 (pH6.6-6.7)	Almost no adsorption	this study
Fe-Mn	0.0832 (pH 4.0)	0.00974 (pH 7.0)	12
Fe-Cu	0.179 (pH 7.4)	0.0756 (pH 7.4)	2

AYA. These results show that FeYx adsorbs more Se(IV) than Fe-Mn [12] , Fe-Cu [2] adsorbents and AYA, and that FeY2 is the most suitable for Se(IV) adsorption. The q_{max} of Se(VI) by FeY1 and FeY2 was 0.230×10^{-3} mol g^{-1} and 0.418×10^{-3} mol g^{-1}, respectively. On the other hand, FeY0.5, Fe_3O_4 and AYA did not adsorb Se(VI) at all. These results show that adsorbents with high PZC can effectively adsorb Se(VI). In other words, it was found that FeY2 is most suitable for the adsorption of Se(IV) and Se(VI). The q_{max} of Se(VI) with FeY2 were 2.4 times higher than that of Se(VI), respectively. FeY2 has very high adsorption performance for Se(IV).

3.3. *Adsorption Mechanism*

The following experiments were conducted using FeY2, which showed a high saturation adsorption capacity for selenium. PZC shift refers to shift of PZC to lower pH, which is used as evidence of strong adsorption with specific ions and the formation of inner-sphere complexes. Adsorption by inner-sphere complexes is a direct coordination bond formed between the adsorbed ion and the metal ion on the surface of the adsorbent without the inclusion of water molecules. On the other hand, adsorption by outer-sphere complexes is adsorption by electrostatic attraction involving one or more water molecules between the metal ion on the adsorbent surface and the adsorbed ion. Assuming that the outer-sphere complex is located outside the slip plane, it is possible to distinguish between outer-sphere complexes and inner-sphere complexes by measuring the zeta potential [9].

Fig. 4 shows zeta potential of FeY2 before and after adsorption of selenium oxyanions. As there is no PZC shift before and after selenium adsorption, it is thought that Se(VI) forms an outer-sphere complex and is adsorbed onto FeY2. Whereas the PZC of FeY2 after Se(IV) adsorption shifted to lower pH than before the adsorption. Se(IV) was adsorbed inner-sphere complex on the surface of FeY2.

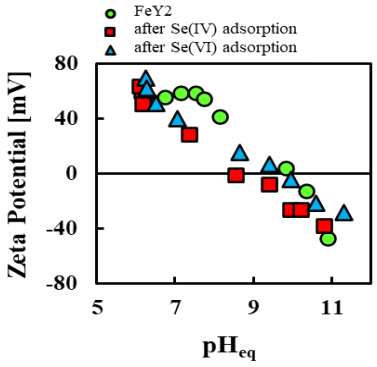


Fig. 4. Zeta potential of FeY2 after Se(IV) and Se(VI) adsorption.

By investigating the effect of ionic strength using a neutral electrolyte, it is possible to indirectly determine whether surface complex of adsorbed selenium oxyanion and adsorbent is an inner-sphere complex or an outer-sphere complex [10]. If selenium adsorption is due to formation of outer-sphere complex, adsorption decreases as the ionic strength of the solution increases due to competition with the anion of neutral electrolyte. On the other hand, Selenium adsorption is due to the formation of inner-sphere complexes, selenium is adsorbed by coordination bonding with the adsorption site on adsorbent, so it is thought that it is not affected by ionic strength. Fig.5 shows the effect of ionic strength on Se(IV) adsorption with FeY2. It was found that the adsorption percentage decreased significantly with the addition of NaCl. The adsorption of Se(VI) was also significantly affected on ionic strength and its adsorption behavior indicated the same as Se(IV) adsorption. Thus,

Se(IV) wa inner-sphere complexes and outer-sphere complexes and Se(VI) was adsorbed on FeY2 by forming outer-sphere complexes.

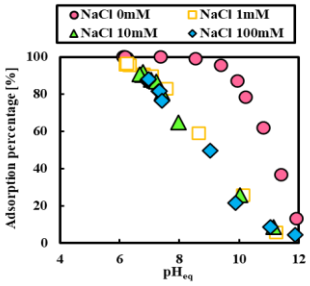


Fig. 5. Effect of ionic strength on Se(IV) adsorption with FeY2.

4. Conclusions

In this study, mixed iron and yttrium oxides (FeYx, where x is the molar ratio of Y(III)/Fe(II)) were prepared as adsorbents for selenium anions in water. FeY2 was found to have the largest specific surface area and the highest PZC among the FeYx, these values improved on magnetite and AYA. FeY2 adsorbed selenium over a wider pH range than conventional adsorbents, and increased the maximum adsorption capacities of Se(IV) and Se(VI) were increased. The influence of zeta potential and ionic strength showed that Se(IV) was adsorbed on FeY2 by the formation of inner-sphere complexes and harmful-sphere complexes, and that Se(VI) was adsorbed on FeY2 by the formation of outer-sphere complexes. FeY2 is expected to be applied to the treatment of high-contamination water.

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Authors Introduction

Dr. Kaoru Ohe

She received her Ph.D. degrees from University of Miyazaki, Japan, in 2014. Currently she is an Associate Professor of Center for Science and Engineering Education, Faculty of Engineering. Her researches are separation engineering especially adsorption hazardous heavy metals and oxyanions.

Ms Amu Wakamatsu

She received Master's degree in Engineering in 2018 from Faculty of Engineering, University of Miyazaki in Japan.

Prof. Dr. Tatsuya Oshima

He received his Ph.D. degrees from Kyushu University, Japan, in 2001. Currently he is an Professor of the Department of Applied Chemistry, Faculty of Engineering. His researches are separation engineering (especially solvent extraction for precious metal ions) and formulation techniques for poorly water-soluble drugs and nutrients.