

Selective Removal of Selenium in Wastewater by Hydrotalcite with High Layer Charge

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Selenium (Se) has been widely used in industries, e.g., metal refineries, glass works, electronics industries, and others. These works and power stations generate liquid waste containing Se from the chemical process and burning fossil fuels. It is volatile along with Hg and has received environmental concerns. The standard for discharge of Se to aqueous environment is 0.1mg/dm^3 ($1.3 \times 10^{-6}\text{M}$). Its selective removal from wastewater stream is required to meet the standard for discharge to the aqueous environment. The objective of the present study was to describe ion exchange materials with selective properties for Se(IV) ion in aqueous solution. They are exemplified by highly Al^{3+} -substituted hydrotalcites which were synthesized by adding Na_2CO_3 solution to mixed solution of $\text{Al}(\text{NO}_3)_3$ and $\text{M}(\text{NO}_3)_2$ (M = divalent metals). The synthetic hydrotalcites showed excellent selectivity for Se(IV) and several toxic oxyanions in NaCl solution. These selective properties can be ascribed to high layer charge and suitable filling space for accommodation of the anion.

1. INTRODUCTION

Wastewater containing inorganic and organic toxics for the aqueous environment is generated in various industries. These toxics include inorganic Se, As, and Sb. These elements form an oxoanion in aqueous solution. The discharge of waste solution to aqueous environment is regulated with regard to concentration of these elements. Their discharge standard for municipal wastewater has been set to 0.1mg/dm^3 [1]. Normally industrial wastewaters contain a variety of anionic impurities. Hence the highly selective separation method is preferable for removal of toxic chemicals from waste stream to meet the standard of discharge.

The inorganic ion exchange materials often indicate specific selectivity toward some selected ions. The high selectivity occurs due to limited space of the ion-exchange sites in the crystal structure of ion exchange materials. It can be typically exemplified by the high selectivity for Cs^+ on Al^{3+} -substituted tobermorite[2,3], K^+ on a cryptomelane-type manganic acid[4], and Li^+ on Sn(IV)- and Ti(IV)-antimonates [5], λ -type manganese dioxide [6] and rancieite-type manganic acid[7].

Hitherto a lot of cation exchange materials have been studied as briefly mentioned above. Another type of adsorbents is an inorganic solid with the amphoteric nature. A titanate acid has the amphoteric nature and been known to show high selectivity toward As(III) and Sb(V) [8]. The adsorption onto the solid adsorbent occurs through the acid-base reaction with the oxoanion. On the other hand, anion exchange materials

have not been extensively studied in comparison with the cation exchange materials. Hydrotalcite is one of the typical anion exchange materials [9]. The charge responsible for the anion exchange comes from the substitution of the trivalent cation, Al^{3+} , in the brucite layer. The extent of Al^{3+} -substitution in a family of hydrotalcite was believed to be limited in 0.20~0.33 [10]. Later, a high Al^{3+} -substitution of 0.45 for Cu-Al combination has been reported by one of the present authors, et al. [11] and F. Thevenot, et al. [12].

The present paper describes selective properties of hydrotalcites toward some oxyanions with hazardous nature. The highly Al^{3+} -substituted hydrotalcites for various combinations of M^{2+} and Al^{3+} were studied as possible adsorbents for Se(IV).

2. Experimental

2.1 Preparation of hydrotalcites in the CO_3^{2-} form

Hydrotalcites were synthesized in a similar manner reported previously [13]. It is described briefly as follows. A solution of $0.1\text{M Al}(\text{NO}_3)_3$ and a solution of $0.1\text{M M}(\text{NO}_3)_2$ (M=Mg, Ni, Zn, Co, or Cu) were mixed in a vessel with a given mole ratio of $\text{Al}^{3+}/(\text{M}^{2+} + \text{Al}^{3+}) = 0.5$. Precipitate was allowed to form by slowly adding $2\text{M Na}_2\text{CO}_3$ with vigorous stirring to the mixed solution with a twenty-fold of $(\text{M}^{2+} + \text{Al}^{3+})$ on a mole basis. The precipitate was aged overnight at room temperature, and then centrifuged to separate the solid and solution phases. The solid

products were repeatedly washed with deionized water until pH of the solution became 10 to remove any soluble components and air-dried at room temperature for about a week. Hereafter, they are referred to as M-Al where M denotes divalent metal.

The dried material was ground and sieved to obtain 100~200 mesh size (74-37 μ m). The sieved material was washed to remove very fine particles and repeatedly immersed in 4M Na₂CO₃ solution at 80°C to exchange CO₃²⁻ for NO₃⁻ which was incorporated in the material. The washed and air-dried products were identified by powder X-ray diffraction (XRD), infrared absorption spectra (IR), thermogravimetry (TG) / differential thermal analysis (DTA). XRD was carried out using Ni-filtered CuK α or Mn-filtered FeK α radiation with a Rigaku X-ray diffractometer RINT 1000 at a scanning speed of 2°/min. TG & DTA were undertaken with a Rigaku Thermoflex-type thermal analyzer at a heating rate of 10 °C/min by using α -Al₂O₃ as a reference material. Elemental analysis was performed by inductively coupled plasma atomic emission spectrometry (ICP-AES) with a Seiko Instruments spectrometer model SPS 15000 or by atomic absorption spectrometry with a Varian atomic absorption spectrometer model AA-1100.

2.2 Ion exchange

A 20ml aliquot of Na₂SeO₃ solution was equilibrated with 0.200g of the hydrotalcite M-Al in the CO₃²⁻ form at room temperature. The ionic strength was adjusted to 0.1M with NaCl. Then, supernatant solution was analyzed for Se and pH. Amount of Se adsorbed was calculated using the decrease in the concentration of Se after equilibration.

3. Results and Discussion

3.1 Hydrotalcites (HTs) synthesized

XRD study of products treated with 4M Na₂CO₃ solution showed that all M-Al samples except Cu-Al are hydrotalcites belonging to the hexagonal system, and that the Cu-Al belongs to the monoclinic system. Any other phase was not observed on the XRD patterns of these samples. The crystallite size in nm was calculated using Scherrer's equation for the layered compounds. It was 19nm for Mg-Al, 4.6nm for Ni-Al, 36nm for Zn-Al, 9.6nm for Co-Al and 31nm for Cu-Al.

IR spectra showed that the absorption band by NO₃⁻ ion was diminished by treating M-Al with 4M Na₂CO₃ solution. Thus, the hydrotalcite in the pure CO₃²⁻ form was prepared.

Al³⁺-substitution of the tetrahedral Si⁴⁺ in tobermorite enlarges the interlayer distance, because the crystal ionic radius of Al³⁺(0.0535nm) is much larger than Si⁴⁺(0.0400nm)[14]. An increase in 'd' spacing in tobermorite corroborates the Al³⁺-substitution as well as the MASNMR studies [3,15]. On the other hand, the lattice

parameter a₀ of the hydrotalcite decreases with an increase in the extent of Al³⁺-substitution in the brucite layer because the ionic radius of Al³⁺ is smaller than those of the divalent metal ions: Mg²⁺(0.0720nm), Ni²⁺(0.0690nm), Co²⁺(0.0745nm), Zn²⁺(0.0740nm) and Cu²⁺(0.073nm). Hence, the Al³⁺-substitution in the brucite layer can be evidenced by decrease in the a₀ value. It corresponds to the b₀ value in the monoclinic system. The Al³⁺-substituted hydrotalcites obtained in the present study showed smaller a₀ values than those of the hydrotalcites with the lower Al³⁺-substitutions reported previously by other authors [10,16-18]. A linear decrease in the a₀ value with an increase in the mole ratio of Al/(Mg+Al) in the Mg-Al samples was found in the range of 0.2 to 0.45 with almost the same slope as reported by Miyata [9]. Approximately the same trends for the a₀ value were found on the other hydrotalcites studied in the present work. These findings corroborate high Al³⁺-substitution of about 0.45 in hydrotalcites. These parameters were in good agreement with those reported previously [13]. Thus, M-Al materials could be synthesized with reproducibility.

The chemical analyses indicated that metal compositions of hydrotalcites were in good agreement with those of the mixed solution used for synthesis. This shows that all metal ions were incorporated into the hydrotalcite crystals. The CO₃²⁻ and H₂O of these compounds were determined based on the weight loss from the TG curves coupled with the mass spectrometry. The chemical compositions and the lattice parameters of the synthetic hydrotalcites are given in Table I.

Table I Chemical composition and lattice parameters of synthesized hydrotalcites.

M-Al	Chemical composition	a ₀ and c ₀ (nm)
Mg-Al	[Mg _{0.56} Al _{0.44} (OH) ₂] · [(CO ₃) _{0.22} · 0.53H ₂ O]	a ₀ 0.3025
		c ₀ 2.315
Ni-Al	[Ni _{0.54} Al _{0.46} (OH) ₂] · [(CO ₃) _{0.23} · 0.51H ₂ O]	a ₀ 0.2986
		c ₀ 2.323
Zn-Al	[Zn _{0.54} Al _{0.46} (OH) ₂] · [(CO ₃) _{0.23} · 0.35H ₂ O]	a ₀ 0.3052
		c ₀ 2.275
Co-Al	[Co _{0.56} Al _{0.44} (OH) ₂] · [(CO ₃) _{0.22} · 0.35H ₂ O]	a ₀ 0.3002
		c ₀ 2.127
Cu-Al	[Cu _{0.50} Al _{0.50} (OH) ₂] · [(CO ₃) _{0.24} · 0.88H ₂ O]	a ₀ 1.53
		b ₀ 0.291
		c ₀ 0.586
		β 100.30°

3.2 Adsorption of selected oxyanions by Cu-Al and Ni-Al.

Selected oxyanions were tested for adsorption by synthesized Cu-Al using the mixed solution (Table II). Oxyanions include Se(IV), Te(IV), Sb(V), As(V), Sn(IV), Cr(VI), Mo(VI) and W(VI).

They were adsorbed quantitatively in mixed solution at pH 8.29. The adsorption of oxyanions was decreased with an increase in pH. Stronger acids, Cr(VI), Mo(VI) and W(VI), were weakly adsorbed, while other weaker acids were strongly adsorbed at pH 9.30. Similar adsorption profiles were observed on Ni-Al.

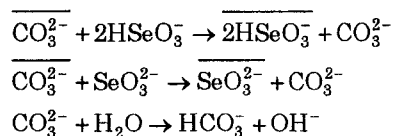
Table II Adsorption of selected oxyanions by Cu-Al.

Oxyanions	Adsorption(%)	
	pH 8.29	pH 9.30
Se(IV)	>99	73
Te(IV)	>99	95
Sb(V)	98	75
As(V)	>99	97
Sn(IV)	>99	61
Cr(VI)	>99	50
Mo(VI)	>99	17
W(VI)	>99	24

Conditions: Cu-Al 0.250g, initial concn. of each anion 10^{-4} M, solution 50cm^3 , temperature 30°C , equilibration time 4d.

3.3 Adsorption of Se(IV) by synthesized HTs.

Selenium(IV) ion was quantitatively adsorbed by synthesized HTs at pH 7.5 (Table III). The pH was increased upon adsorption of Se(IV). This can be understood as follows. The dissociation constant of H_2SeO_3 , pK_{a2} , is 8.32 [19]. Hence, at about pH 7.5, the existing chemical species are HSeO_3^- and SeO_3^{2-} , the former being more abundant. They are exchanged with CO_3^{2-} in the HT, and CO_3^{2-} is subjected to hydrolysis which results in a rise of pH value.



where the bar on the symbol denotes the chemical species fixed in the interlayer of the hydrotalcites. This selective property can be used in order to eliminate Se(IV) from wastewater by the hydrotalcites. The selectivity of HT for Se(IV) is enough to meet the standard for treatment of waste solution.

The maximum ion exchange capacity is important for thermodynamic treatment using the selectivity plot [20-22]. However, generally it is not necessarily easy to determine the maximum ion exchange capacity, because ingoing ions cannot always occupy all the ion exchange sites due to the steric hindrance by the limitation in crystal structure. In the present case, the maximum anion exchange capacity of hydrotalcites can be calculated using the Al^{3+} -

Table III Adsorption of Se(IV) by HTs.

HT	Adsorption(%)	Equilibrium pH
Cu-Al	>99	7.53
Co-Al	95	7.49
Ni-Al	>99	7.44
Zn-Al	>99	7.49
Mg-Al	>99	7.46
KW*	95	7.52

Conditions: HT 0.200g, initial concn. of Se(IV) 10^{-4} M(7.92ppmSe), solution 20cm^3 , temperature 30°C , equilibration time 4d, initial pH of solution 7.18, coexisting electrolyte 0.1M NaCl.

KW*: Mg/Al hydrotalcite supplied by Kyowa Chemicals, Ltd.

substitution. It was 5.3meq/g for Mg-Al, 4.5meq/g for Ni-Al, 4.4meq/g for Zn-Al, 4.3meq/g for Co-Al, and 4.4meq/g for Cu-Al. In the present preliminary study, the uptake of Se(IV) was determined in specified conditions (Table IV), where two ionic species are involved in the ion exchange reaction with the hydrotalcite. Therefore, the uptake is represented in mmol/g. The uptake of Se(IV) was the largest in the Ni-Al, amounting to 0.90mmol/g. On the contrary, KW showed the smallest uptake (only 0.17mmol/g). A definite relation between the rise in pH for the synthesized HT was observed upon the uptake of Se(IV). But it was not true for KW hydrotalcite. A partial dissolution may have set in due to its chemical instability.

Table IV Uptake of Se(IV) in mmol/g by HTs.

HT	Adsorption (%)	Uptake (mmol/g)	Equil. pH
Cu-Al	22	0.43	7.32
Co-Al	22	0.43	7.36
Ni-Al	45	0.90	7.54
Zn-Al	25	0.50	7.36
Mg-Al	22	0.43	7.66
KW*	17	0.17	8.09

Conditions: HT 0.200g, initial concn. of Se(IV) 0.02M(1584ppmSe), solution 20ml, equilibrium temperature 30°C , equilibration 4d, initial pH of solution 6.66, coexisting electrolyte 0.1M NaCl.

KW*: supplied by Kyowa Chemicals, Ltd.

4. Conclusion

A highly Al^{3+} -substituted hydrotalcite has been studied for removal of Se(IV) in two concentrations at moderate pH region. Such conditions for removal often occur in industrial effluents and environmental samples. The discharge for toxic elements is getting more stringent. The discharge standard for Se (0.1ppm) has been the hard challenge for

companies. In the present study, Se(IV) was used. At the pH region studied, mono- and divalent anionic species are present. These anions were effectively adsorbed by using the highly Al³⁺-substituted hydrotalcites. Especially Al³⁺-substituted Ni-hydrotalcite showed the excellent selectivity and large uptake for Se(IV). It will be a candidate material for removal of Se(IV) in industrial wastewater. The standard will be met by removing Se(IV) with the materials described above.

Wastewater may be admixed with Se(VI) besides Se(IV). The former has the dissociation constants, pK_{a1} -3.0 and pK_{a2} 1.70. Therefore, the most abundant chemical species is SeO₄²⁻ in industrial effluents at moderate pH. The adsorption behavior can be elucidated by investigating the corrected selectivity plot for Se(IV) and Se(VI). These are to be studied.

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