Evaluation of Adsorption Mechanism of Chromium(VI) Ion Using Ni-Al Type and Ni-Al-Zr Type Hydroxides

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Abstract: To evaluate the feasibility of nickel–aluminum (the Ni^{2+}:Al^{3+} molar ratios of 1.0:1.0 and 1.0:2.0 are denoted as NA11 and NA12, respectively) and nickel–aluminum–zirconium type (the Ni^{2+}:Al^{3+}:Zr^{4+} molar ratios of 0.9:1.0:0.09 and 0.9:2.0:0.09 are denoted as NAZ1 and NAZ2, respectively) hydroxides for Cr(VI) removal from aqueous media, the adsorption capability and adsorption mechanism of Cr(VI) using the above-mentioned adsorbents were investigated in this study. The quantity of Cr(VI) adsorbed onto NA11, NA12, NAZ1, and NAZ2 was 25.5, 25.6, 24.1, and 24.6 mg g^{-1}, respectively. However, the quantity of aluminum (base metal) released from NA11 (approximately 0.14 mg g^{-1}) was higher than that from NAZ1 (approximately 1.0 μg g^{-1}), indicating that NAZ1 was more suitable for Cr(VI) removal than NA11. In addition, the effects of pH, contact time, and temperature on the adsorption of Cr(VI) were evaluated. Moreover, to elucidate the adsorption mechanism of Cr(VI) using NA11 and NAZ1, the elemental distribution, X-ray photoelectron spectrometry spectra, and ion exchange capability were also determined. Cr(VI) adsorbed onto the NAZ1 surface was easily desorbed using a sodium hydroxide solution under our experimental conditions. The information regarding this study can be useful for removing Cr(VI) from aqueous media.

Keywords: nickel–aluminum complex hydroxide; nickel–aluminum–zirconium complex hydroxide; chromium(VI); adsorption

1. Introduction

In 2015, the United Nations announced the 2030 agenda for sustainable development. Among the 17 Sustainable Development Goals (SGDs), Goal No. 6 (clean water and sanitation) and Goal No. 14 (life below water), which are directly and strongly related to the water environment, focused on resolving global aquatic environmental problems. Exposure to high level of water contamination by heavy metals is considered as a serious variety of adverse health outcomes [1]. As one of the most important contaminants, two main oxidation states including Cr(VI) and Cr(III) is present in the environment. Importantly, Cr(VI) compounds are widely used in various industrial processes. On the other hand, Cr(III) is used as a nutritional supplement [2]. Cr(VI) is usually considered more toxic and carcinogenic than Cr(III) [3,4]. Therefore, Cr(VI) compounds were classified as a group 1 carcinogenic to humans by the International Agency for Research on Cancer (IARC). In addition, the World Health Organization (WHO) and U.S. Environmental Protection Agency (USEPA) has established the maximum permissible Cr(VI) content for industrial

wastewater, surface water, and drinking water in the values of 0.25, 0.10, and 0.05 mg L^{-1}, respectively [5,6]. Conversely, chromium is stockpiled in Japan because it is a relatively rare metal with several applications. Japan is one of the main consumers of rare metals worldwide. However, the recycling technology of rare metals, including chromium, has not yet been developed. Therefore, the development of removal and/or recycling techniques for Cr(VI) from aqueous media is very important for establishing a sustainable society [7,8].

Numerous techniques have been studied and applied to evaluate the Cr(VI) removal including membrane filtration, chemical precipitation, solvent extraction, adsorption, electrochemical reduction and oxidation, and photoreduction [9–12]. Adsorption is one of the best choice and most cost-effective technique of heavy metals removal such as Cr(VI), and the adsorption process indicates that adsorbents bind heavy metals by chemical binding, ion exchange, and physical attractive forces [1].

Currently, the physicochemical properties and feasibility of metal complex hydroxides have received more attention, and their application has been evaluated for the capability on heavy metals removal from aqueous media [13]. Various studies have reported previously for the capability of Mg-Al-CO_3-hydrotalcite [14,15], hydrotalcite-hydroxyapatite material doped with carbon nanotubes [16], Mg-Al hydrotalcite kaolin clay [17], hydrotalcite/carbon [18], sulfide assembled hydrotalcite compounds [19], calcined nano-Mg/Al hydrotalcite [20], and metal oxide as dual-functional adsorbents [1] on Cr(VI) removal from aqueous media. In addition, our previous studies reported that Fe-Mg-type hydrotalcite and nickel–aluminum complex hydroxide showed excellent adsorption capability for Cr(VI) from aqueous media [8,21]. However, there are few reports on the adsorption/removal of heavy metals using ternary metal complex hydroxides from aqueous media. In addition, multi-complex metal hydroxides are useful adsorbents for removing heavy metals from aqueous media [8,21]. Multi-complex metal hydroxides exhibit quite different physicochemical properties compared to their single or double metal hydroxides.

Additionally, our previous studies reported that nickel–aluminum complex hydroxide and/or nickel–aluminum–zirconium complex hydroxide are useful for the removal of oxyanions, such as arsenic and phosphate ions, from aqueous media [22,23]. The incorporation of zirconium (Zr^{4+}) into a metal complex hydroxide induces an increase in the charge in the metal layer and strongly affects its physicochemical properties. These changes affect to the capability on adsorption and removal of heavy metals from aqueous media. We have already evaluated the Cr(VI) adsorption capability using nickel–aluminum complex hydroxide [21]. Additionally, Cr(VI) (oxyanion form) is ubiquitously present in the water environment. Therefore, the incorporation of zirconium in the nickel–aluminum complex hydroxide might be useful adsorbent for removal of Cr(VI) from aqueous media or might show the superior adsorption capability of Cr(VI). However, no information is available regarding Cr(VI) adsorption using the incorporation of zirconium in the nickel–aluminum complex hydroxide.

Therefore, this study mainly focused on Cr(VI) adsorption using the incorporation of zirconium in the nickel–aluminum complex hydroxide. Additionally, various parameters including the effects of initial concentration, temperature, pH, and contact time on adsorption were also evaluated here.

2. Materials and Methods

2.1. Materials and Chemicals

Standard solutions of Cr(VI) ($K_2Cr_2O_7$ in 0.1 mol L^{-1} HNO_3) was purchased from FU-JIFILM Wako Pure Chemical Co., Osaka, Japan. Different molar ratios of nickel–aluminum complex hydroxides and nickel–aluminum–zirconium complex hydroxide were prepared in the molar ratios of Ni^{2+} to Al^{3+} of 1.0, and 0.5, referred as NA11 and NA12, respectively. Additionally, the molar ratios of 0.9:1.0:0.09 and 0.9:2.0:0.09 of $Ni^{2+}:Al^{3+}:Zr^{4+}$ were denoted as NAZ1 and NAZ2, respectively. The synthesis method and physicochemical characteristics were reported in our previous studies [22]. Briefly, the materials were synthesized by the following method. $NiSO_4 \cdot 6H_2O$, $Al_2(SO_4)_3 \cdot 18H_2O$, and $Zr(SO_4)_2 \cdot 4H_2O$ were mixed

and then the reaction solution was heated. After that, the reaction solution was added to the distilled water at pH 9.0 for 800 rpm at 25 °C. After mixing for 2 h, the suspension was filtered, washed, and dried at 110 °C for 12 h. The adsorbent morphology and crystal structure were measured using SU1510 (Hitachi Ltd., Tokyo, Japan) and Mini Flex II (Rigaku, Tokyo, Japan), respectively. NOVA4200*e* instrument (Yuasa Ionics, Osaka, Japan) was used to measure the specific surface area. Amount of surface hydroxyl groups and pH_{pzc} of the adsorbents were measured by the fluoride ion adsorption method [24] and the method reported by Faria et al. [25], respectively.

To elucidate the adsorption mechanism of Cr(VI), elemental analysis and electron spectroscopy were analyzed using JXA-8530F (JEOL, Tokyo, Japan) and AXIS-NOVA instruments (Shimadzu Co., Ltd., Kyoto, Japan), respectively. Finally, the amount of sulfate ions released from the adsorbent in the adsorption experiment was also measured using a DIONEX ICS-900 (Thermo Fisher Scientific Inc., Tokyo, Japan). The measurement conditions were already reported in our previous study [23]. Finally, the amount of base metal released from NA11 and NAZ1 was measured. NA11 or NAZ1 (0.05 g) was added to the distilled water (50 mL, pH 7.0). The suspension was shaken at 100 rpm and 25 °C for 24 h. The suspension was filtered through a 0.45 μm membrane filter. The concentration of aluminum released from NA11 and NAZ1 were measured using an iCAP-7600 Duo instrument (Thermo Fisher Scientific Inc., Tokyo, Japan).

2.2. Quantity of Cr(VI) Adsorbed

Each adsorbent (0.05 g) and the Cr(VI) solution at 50 mg L^{-1} (50 mL, pH 7.0) were mixed and then shaken at 100 rpm and 25 °C for 24 h. Cr(VI) concentrations of the obtained solutions after filtrated through a 0.45 μm membrane filter were measured using an iCAP-7600 Duo instrument (Thermo Fisher Scientific Inc., Tokyo, Japan). The adsorption capability on Cr(VI) of each tested adsorbent was calculated by the difference between Cr(VI) concentration before and after adsorption. All data are presented as mean ± standard error from triplicate experiments.

2.3. Effect of pH, Contact Time, and Temperature on the Removal of Cr(VI)

Initially, to investigate the effect of pH, 0.05 g of each tested adsorbent (NA11 and NAZ1), and different pH conditions of 50 mL Cr(VI) solution in the concentration of 50 mg L^{-1} were mixed. The solution pH was adjusted between 3, 5, 7, 9, and 11, using either nitric acid or sodium hydroxide solutions (FUJIFILM Wako Pure Chemical Co., Osaka, Japan). The suspension was shaken at 100 rpm and 25 °C for 24 h. The suspension was filtered through a 0.45 μm membrane filter. Second, to elucidate the contact time effect, 0.05 g of same adsorbents and the 50 mL Cr(VI) solution at 50 mg L^{-1} were mixed, and then shaken at 100 rpm and 25 °C for 30 s, 1, 5, 10, and 30 min, and 1, 3, 6, 9, 15, 18, 21, 24, 30, 42, and 48 h. Third, to elucidate the effect of temperature, 0.05 g of same adsorbents and the Cr(VI) solution at different concentrations (10, 20, 30, 40, and 50 mg L^{-1}) were mixed, and then shaken at 100 rpm and 5, 25, and 45 °C for 24 h. The quantity of Cr(VI) adsorbed was also calculated using the above-mentioned method. The student's *t*-test was used for a comparative analysis of two groups. A minimum *p*-value of 0.05 ($p < 0.05$) was chosen as the significant level. All data are presented as mean ± standard error from triplicate experiments.

2.4. Recovery of Cr(VI) From NAZ1 using Desorption Solutions

To investigate the recovery of Cr(VI) adsorbed onto the NAZ1 surface, the adsorption/desorption performance of NAZ1 was evaluated in this section. First, NAZ1 (0.1 g) and the Cr(VI) solution at 100 mg g^{-1} (50 mL) were mixed, and then the suspension was shaken at 100 rpm and 25 °C for 24 h. Quantity of Cr(VI) adsorbed was also calculated as described the above. Second, NAZ1 was collected after adsorption, and then dried at 25 °C for 24 h. Collected NAZ1 was added to the sodium hydroxide solution at 1, 10, and 100 mmol/L (50 mL). The suspension was shaken at 100 rpm and 25 °C for 24 h. Cr(VI)

concentrations of the obtained solutions after filtrated through a 0.45 μm membrane filter were measured using an iCAP-7600 Duo instrument. The quantity of Cr(VI) desorbed was calculated from the difference between the concentration of Cr(VI) before and after adsorption. All data are presented as mean ± standard error from triplicate experiments.

3. Results and Discussion

3.1. Physicochemical Properties

First, NA11 and NA12 were selected for Cr(VI) removal from aqueous media. Because our previous study elucidated the optimal molar ratios condition of nickel and aluminum in the metal complex hydroxide for removal of Cr(VI) [21]. Additionally, previous studies showed that the incorporation of Zr^{4+} into a Ni-Al type hydroxide significantly improved the adsorption capability of oxyanions such as arsenic ions [22] and phosphate ions [23]. Therefore, the compositions of NA11, NA12, NAZ1, and NAZ2 were selected in this study. The physicochemical characteristics of NA11, NA12, NAZ1, and NAZ2 used in this study have already been reported in our previous studies [22]. Therefore, we briefly describe these properties. The prepared adsorbents were not perfectly spherical in shape under our experimental conditions. Additionally, no significant differences between each adsorbent were observed in this study. NA11 and NA12 have an amorphous nature [23]. The XRD patterns of NAZ1 and NAZ2 showed similar trends to those of NA11 and NA12. In addition, the XRD patterns of NAZ1 and NAZ2 showed that the incorporation of zirconium in the NA series could be successful, and then the distances between metals and between the octahedral layers changed in this study [22,26,27]. The specific surface areas of NA11, NA12, NAZ1, and NAZ2 were 22.8, 26.4, 51.9, and 27.8 $m^2\,g^{-1}$, respectively. Additionally, the amount of surface hydroxyl groups was 1.92, 1.62, 1.08, and 1.51 $mmol\,g^{-1}$, respectively. Therefore, the incorporation of Zr^{4+} into a Ni-Al type hydroxide affects the increasing specifics surface area and the decreasing amount of surface hydroxyl groups under our experiment conditions. The pH_{pzc} value of each adsorbent was between 6.2 and 6.4 under our experimental conditions.

3.2. Quantity of Cr(VI) Adsorbed

The quantity of Cr(VI) adsorbed onto NA11, NA12, NAZ1, and NAZ2 was $25.5 \pm 0.25\ mg\,g^{-1}$ ($1.1 \pm 0.011\ mg\,m^{-2}$), $25.6 \pm 0.12\ mg\,g^{-1}$ ($0.97 \pm 0.005\ mg\,m^{-2}$), $24.1 \pm 0.45\ mg\,g^{-1}$ ($0.46 \pm 0.001\ mg\,m^{-2}$), and $24.6 \pm 0.13\ mg\,g^{-1}$ ($0.88 \pm 0.005\ mg\,m^{-2}$), respectively. No significant difference was observed in Cr(VI) removal using the NA and NAZ series under our experimental conditions. The adsorption capability of Cr(VI) from aqueous media was not improved by incorporating zirconium in the nickel–aluminum complex hydroxide. In addition, the relationship between the quantity of Cr(VI) adsorbed and the physicochemical characteristics was evaluated. The correlation coefficient between the quantity of Cr(VI) adsorbed, and the surface hydroxyl groups was 0.890, which indicates that this parameter was related to the adsorption of Cr(VI) using the NA and NAZ series.

The base metal released from the adsorbent is one of the most important issues in adsorption treatment. This phenomenon directly and strongly affects the adsorption capability of Cr(VI) using an adsorbent. Therefore, we evaluated the quantity of base metal released from NA11 and NAZ1 in a preliminary experiment. As a result, the quantity of aluminum released from NA11 (approximately $0.14\ mg\,g^{-1}$) was greater than that from NAZ1 (approximately $1.0\ \mu g\,g^{-1}$), which suggests that NAZ1 was more suitable for Cr(VI) removal than NA11. The incorporation of Zr^{4+} into NA11 increases the positive charge, and then more occupies the octahedral holes in a close-packed configuration of hydroxide ions. This phenomenon indicates that NAZ1 is more suitable compared to NA11 in this study. This result is very important for the application of NAZ1 in the field. Therefore, NAZ1 was used in the following adsorption experiment, and NA11 was also selected for comparison in this study.

Table 1 shows the comparison of the Cr(VI) adsorption capacities of NA11 and NAZ1 with those of other reported adsorbents. The adsorption capability of Cr(VI) using NA11

and NAZ1 exhibited a similar trend to that of other reported adsorbents (except for calcined nano-Mg/Al hydrotalcite, and NiAl-LDH). Therefore, NAZ1 can be applied for the removal of Cr(VI) from aqueous media.

Table 1. Comparison of Cr(VI) adsorption capacity of NA11 and NAZ1 with other reported adsorbents.

Adsorbents	Adsorption Capability (mg/g)	pH	Temp. (°C)	Initial Concentration (mg/L)	Contact Time (h)	Adsorbent (g/L)	Ref.
Calcined Mg-Al-CO$_3$ hydrotalcite	Approximately 24	6.0	30	10	4	0.2	[15]
Calcined nano-Mg/Al hydrotalcite	52.4	3.0	22	110	2	1	[20]
MgAl-LDH	30.28	6–7	25	30–55	24	0.2	[28]
NiAl-LDH	57.50	6–7	25	30–55	24	0.2	[28]
Ni-Fe-LDH	26.78	-	-	4–20	4–5	0.2	[29]
Mg-Al-Cl LDH	20.10	4.0	15	40	2	2	[30]
Mg-Al-CO$_3$ hydrotalcite	17.00	6	30	10	24	1	[31]
NA11	25.5	7	25	100	24	1	This study
NAZ1	24.1	7	25	100	24	1	This study

3.3. Effect of pH, Contact Time, and Temperature on the Removal of Cr(VI)

Solution pH is one of the most important parameters that directly and strongly affects the adsorption capability of Cr(VI) from aqueous media. Figure 1 exhibited the effect of pH on Cr(VI) adsorption using NA11 and NAZ1. In this experiment, the optimal pH condition for Cr(VI) removal using NA11 and NAZ1 was approximately between 7.0 and 9.0. Similar trends were reported by previous studies using Mg-Al-Cl LDH and Mg-Al LDH [30,32]. Cr(VI) oxyanion species in an aqueous solution depend on the solution pH and chromium concentration. The Cr(VI) oxyanion species in solution are chromate (CrO_4^{2-}), dichromate ($Cr_2O_7^{2-}$), and hydrogen chromate ($HCrO_4^{-}$) [33]. The surfaces of NA11 and NAZ1 are protonated in acidic condition and therefore acquire positive charges. However, under strongly acidic condition (pH 3.0), low Cr(VI) adsorption was observed. These phenomena can be explained by the dissolution of the adsorbent at low pH solution. Similar trends were reported by previous studies [17,32]. On the other hand, only chromate is stable in solution, and there are many hydroxide ions above a pH of 6.8. Therefore, competitive adsorption between hydroxide ions and chromate ions onto NA11 and NAZ1 occurred easily [20,33,34]. The removal efficiency of Cr(VI) using NA11 and NAZ1 decreased pH from 9.0 to 11. Considering the adsorption capability of Cr(VI) using NA11 and NAZ1, an initial pH of 7.0 was selected in the following experiments in this study.

Figure 2 demonstrated the contact time effect on Cr(VI) adsorption using NA11 and NAZ1 with adsorption kinetics. The data showed that the rapidly adsorption occurred during the initial 10 min, and then it gradually became slower over time, reaching equilibrium in approximately 20 h. Previous studies reported the adsorption capability of metal complex hydroxide on heavy metals was a very rapid process [29,32]. It takes within 2 h for Cr(VI) solution with an initial concentration of from 5 to 200 mg g^{-1} to reach equilibrium. However, the quantity of Cr(VI) adsorbed using NA11 and NAZ1 was slightly higher compared to the reported adsorbent. Additionally, amount adsorbent (adsorbents reported in previous studies) was more needed for Cr(VI) removal from aqueous media. Therefore, NA11 and NAZ1 were useful for removal of Cr(VI) from aqueous media. The process of Cr(VI) adsorption from aqueous media using an adsorbent can be elucidated by kinetic models, such as the pseudo-first-order and pseudo-second-order models. These kinetic models can explain the rate-controlling mechanism of the Cr(VI) adsorption process, such as chemical reaction, diffusion control, and mass transfer [32]. Therefore, the adsorption

kinetic data were analyzed in terms of the pseudo-first-order and pseudo-second-order models (Table 2).
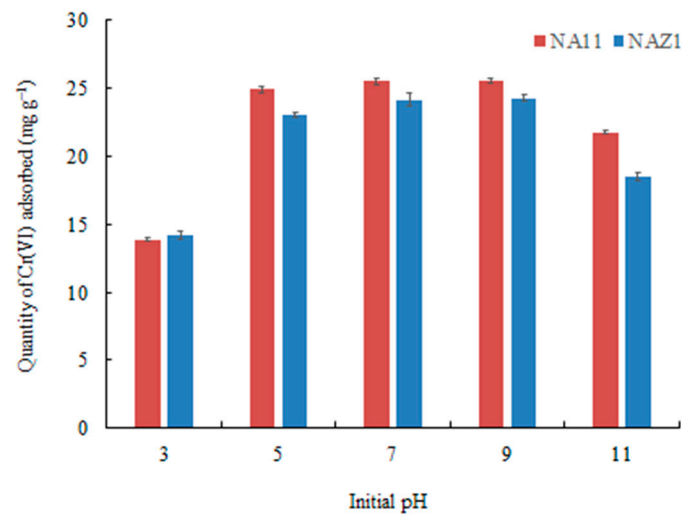

Figure 1. Effect of pH on the adsorption of Cr(VI) using NA11 and NAZ.
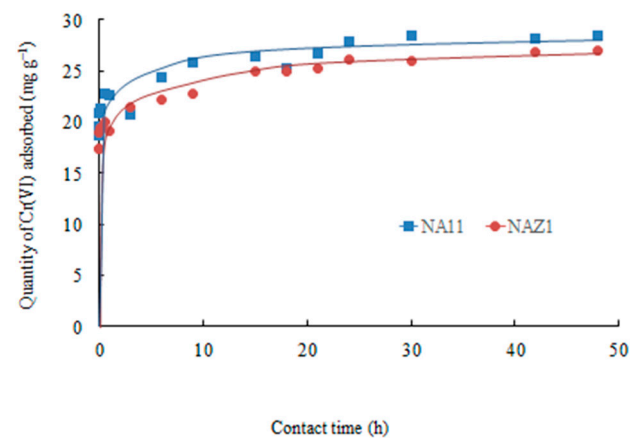

Figure 2. Effect of contact time on the adsorption of Cr(VI) using NA11 and NAZ1.

Table 2. Kinetic parameters for the adsorption of Cr(VI).

Adsorbents	q_e (mg g^{-1})	Pseudo-First-Order Model			Pseudo-Second-Order Model		
		k_1 (h^{-1})	q_e (mg g^{-1})	r	k_2 (g mg^{-1} h^{-1})	q_e (mg g^{-1})	r
NA11	28.5	0.22	8.0	0.870	0.04	28.4	0.999
NAZ1	27.0	0.09	8.8	0.972	0.04	26.8	0.999

The pseudo-first-order and pseudo-second-order models were based on physical sorption and chemical sorption, respectively [35,36]. These equations are expressed as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t, \tag{1}$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 \times q_e^2}, \tag{2}$$

where q_e and q_t are the quantity of Cr(VI) adsorbed (mg g^{-1}) at equilibrium and given time t, and k_1 and k_2 are the pseudo-first-order (h^{-1}) and pseudo-second-order (g mg^{-1} h^{-1}) rate constants, respectively. The correlation coefficient (r) in the pseudo-second-order model

(0.999) was higher than that in the pseudo-first-order model (0.870–0.972). In addition, closer values of q_e in the calculation (26.8 ± 0.01–28.4 ± 0.02 mg g^{-1}) and experiment (27.0 ± 0.01–28.5 ± 0.02 mg g^{-1}) indicate that the Cr(VI) adsorption data fit well with the pseudo-second-order model compared to the pseudo-first-order model. These results suggest that Cr(VI) oxyanions diffuse through the solution to the adsorbent's external surface and boundary layer [29].

Previous studies reported that metal hydroxide complexes can remove heavy metals from aqueous media by various mechanisms [32]. First, the adsorption onto the adsorbent external surface. Second, intercalation by ion exchange mechanism with anions in the interlayer adsorbent. Usually, a combination of the above-mentioned mechanisms easily occurs to remove heavy metals from aqueous media. We have already described the relationship between the amount of Cr(VI) adsorbed and the surface functional group in the above section, which indicates that the adsorption mechanism of Cr(VI) using NA11 and NAZ1 was related to the adsorbent surface. Additionally, the conditions of NA11 and NAZ1 surfaces before and after adsorption were observed (Figure 3). Warm color and cold color shows high concentration and low concentration, respectively. The value of chromium (Cr) intensity was from 2 to over 15 and from 2 to 15 for NA11 and NAZ1 before and after adsorption. Therefore, the chromium quantity clearly increased on the NA11 and NAZ1 surfaces after Cr(VI) adsorption.
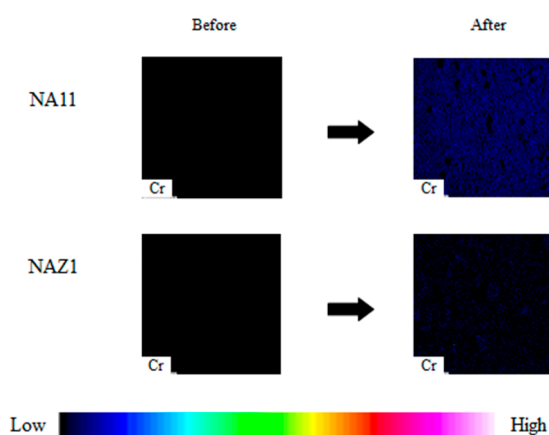

Figure 3. Elemental distribution of Cr(VI) onto NA11 and NAZ1 surface before and after adsorption.

The adsorption mechanism of Cr(VI) from aqueous media using NA11 and NAZ1 was also investigated in detail, anion exchange in the adsorption treatment (from Figure 2) was evaluated in this study. We measured the X-ray photoelectron spectra of the NA11 and NAZ1 surfaces before and after adsorption (Figure 4). Cr(2p) peaks at 575–577 eV were detected after adsorption, which was not detected before adsorption. On the other hand, the intensity of sulfur (165 eV for S(2p)) peak slightly or significantly decreased after adsorption of Cr(VI) using NA11 or NAZ1 in this study. In addition, Figure 5 shows the relationship between the quantity of Cr(VI) adsorbed and the quantity of sulfate ions released from the interlayer of NA11 and NAZ1. As shown in Figure 5, a positive linear relationship (correlation coefficient was 0.918 and 0.945 for NA11 and NAZ1, respectively) was observed under our experimental conditions. This result was proposed here that the sulfate ions in the interlayer of NA1 and NAZ1 were exchanged with Cr(VI).

Figure 6 exhibited the effect of temperature and the adsorption isotherms on Cr(VI) adsorption using NA11 and NAZ1. The quantity of Cr(VI) adsorbed using NA11 and NAZ1 was not different and slightly increased, respectively, at adsorption temperatures between 5 and 45 °C. Therefore, the adsorption temperature did not strongly affect the adsorption capability of Cr(VI) using NA11 and NAZ1 under our experimental conditions.
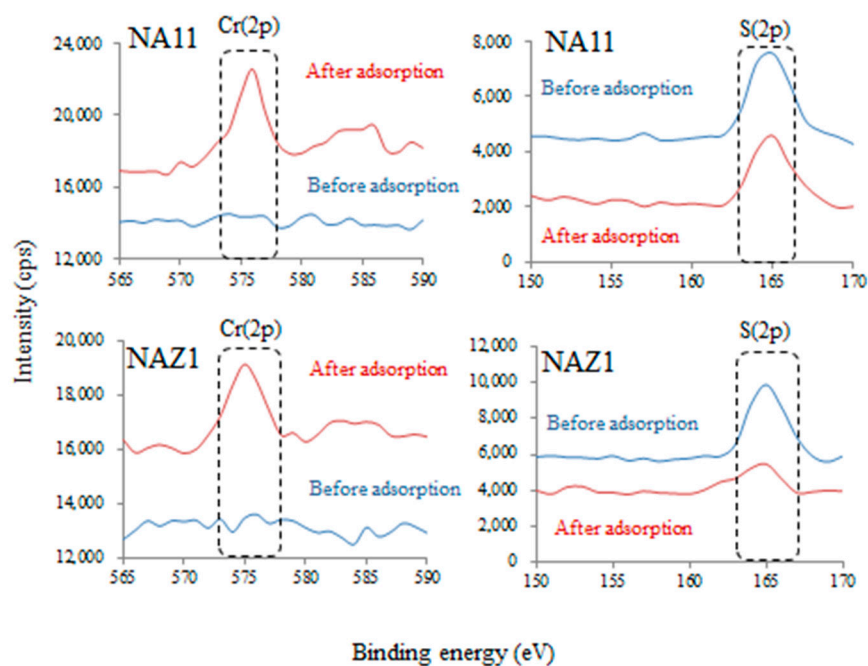
Figure 4. X-ray photoelectron spectrometry spectra of NA11 and NAZ1 before and after adsorption.
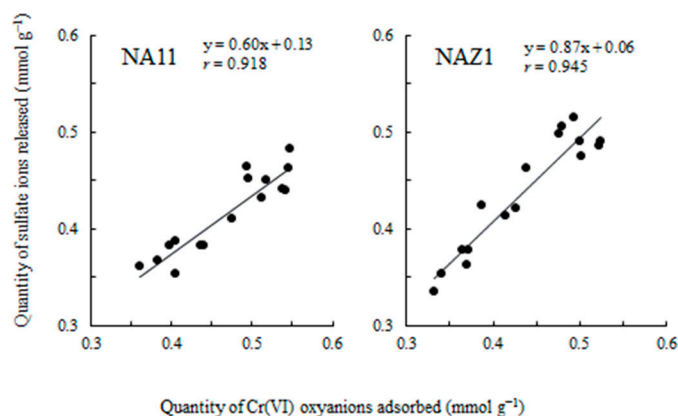

Figure 5. Relationship between quantity of Cr(VI) adsorbed and quantity of sulfate ions released.

Adsorption isotherm models are usually used to describe the interactions between adsorbates and adsorbents. Freundlich and Langmuir isotherms are empirical expressions of the adsorption process attributed to the special micro and macro structures of the adsorbents [37]. Freundlich's isotherm model allows for multilayered adsorption of adsorbates onto adsorbent surfaces [28]. Additionally, the Langmuir isotherm assumes an energetically homogeneous support surface with pervasively identical adsorption sites [38]. The Freundlich model is described by Equation (3) [39]:

$$\log q = \frac{1}{n} \log C_e + \log k, \tag{3}$$

The Langmuir model is described by Equation (4) [40]:

$$1/q = 1/(W_s a C_e) + 1/W_s, \tag{4}$$

where q is the quantity of Cr(VI) adsorbed (mg g^{-1}), W_s is the maximum quantity of adsorbed Cr(VI) (mg g^{-1}), and C_e is the equilibrium concentration (mg L^{-1}). The adsorption

capacity and strength of adsorption are k and $1/n$, respectively. Additionally, a is the Langmuir isotherm constant (binding energy) (L mg^{-1}).
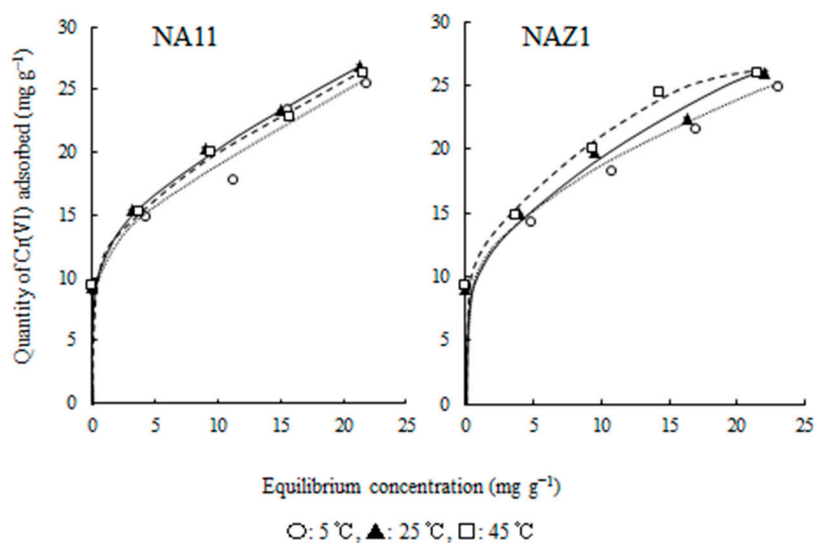

Figure 6. Adsorption isotherms of Cr(VI) using NA11 and NAZ1.

Table 3 showed the Freundlich and Langmuir constants for Cr(VI) adsorption using NA11 and NAZ1. As a result, the regression correlation coefficients (over 0.987) were presented for the Freundlich model, which were higher than those of the Langmuir model (over 0.917). These results indicate that the Freundlich isotherm model was more suitable for describing the adsorption equilibrium of Cr(VI) onto NA11 and NAZ1. The maximum adsorption capability (W_s) of Cr(VI) increased with increasing adsorption temperature from 5 to 45 °C. These phenomena agree with the adsorption behaviors of Cr(VI) using NAZ1. Finally, when the value of $1/n$ is 0.1–0.5, Cr(VI) adsorption using NA11 and NAZ1 easily occurs. On the other hand, when the value of $1/n$ is over 2, adsorption is difficult [41]. In this study, the value of $1/n$ is 0.31–0.34, and then Cr(VI) adsorption from aqueous media using NA11 and NAZ1 were more favorable under our experimental condition.

Table 3. Freundlich and Langmuir constants for the adsorption of Cr(V).

Adsorbents	Temperature (°C)	Freundlich Constants			Langmuir Constants		
		log$k$	$1/n$	r	W_s (mg g^{-1})	a (L mg^{-1})	r
NA11	5	0.96	0.33	0.987	27.4	0.28	0.917
	25	0.99	0.34	0.993	27.9	0.38	0.979
	45	0.98	0.33	0.998	28.5	0.30	0.984
NAZ1	5	0.96	0.31	0.997	28.0	0.22	0.979
	25	0.96	0.33	0.998	28.4	0.27	0.986
	45	0.97	0.34	0.998	30.0	0.26	0.989

3.4. Adsorption/Desorption Capability of Cr(VI) using NAZ1

To evaluate the recovery of Cr(VI) adsorbed onto the NAZ1 surface, the adsorption/desorption capability of Cr(VI) using NAZ1 was investigated in this study (Figure 7). As a result, the quantity of Cr(VI) desorbed from NAZ1 using a sodium hydroxide solution increased with increasing concentration of the desorption solution. The recovery percentages of Cr(VI) using 1, 10, and 100 mmol L^{-1} was 29.8%, 72.9%, and 80.1%, respectively, under our experimental conditions. The in-use studies in real samples are needed to elucidate the application of NAZ1 in further experiments.
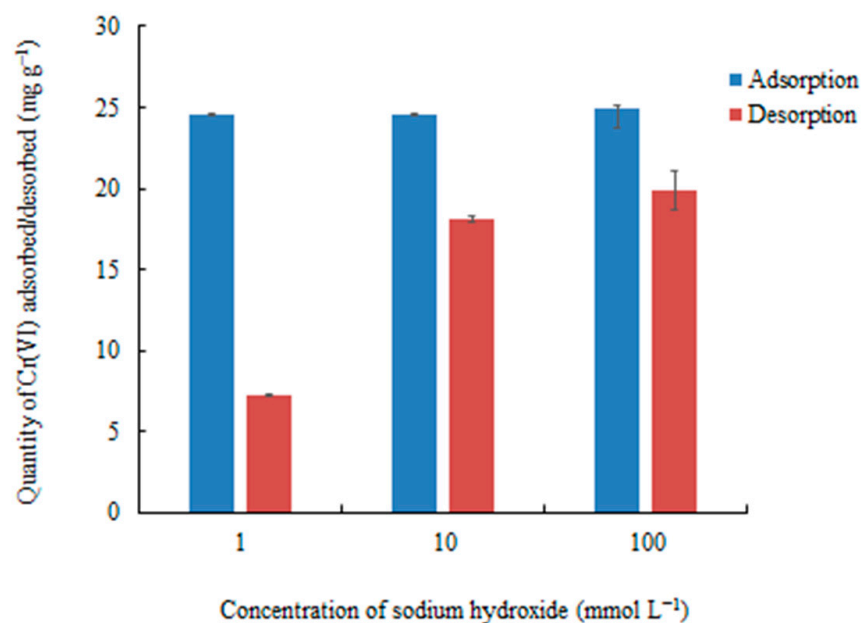
Figure 7. Adsorption/Desorption capability of Cr(VI) using NAZ1.

4. Conclusions

We prepared the NA and NAZ series adsorbents for Cr(VI) removal from aqueous media. Our results showed that NAZ1 was more suitable for Cr(VI) removal than NA11 under our experimental conditions. The optimal pH condition was approximately from 7.0 to 9.0 for removal of Cr(VI) from aqueous media. The kinetic experiments indicated that the adsorption process could reach equilibrium in approximately 20 h, and the kinetic data were accurately described by pseudo-second-order model (Correlation coefficient was 0.999 for NA11 and NAZ1). From the results of elemental distribution, binding energy analysis, and relationship between quantity of Cr(VI) adsorbed and quantity of sulfate ion released from adsorbents, adsorption mechanism related to the adsorbent surface properties (surface hydroxyl groups), and ion exchanges in this study. The adsorption isotherm data agreed with well with the Freundlich model (Correlation coefficient was over 0.987) compared to Langmuir model (Correlation coefficient was over 0.917). Additionally, the recovery percentage of Cr(VI) from NAZ1 using 100 mmol L^{-1} was approximately 80%. These findings are useful for the removal of Cr(VI) from aqueous media.

Abbreviations

$1/n$	adsorption strength
a	the Langmuir isotherm constant (binding energy) (L mg^{-1})
C_e	the equilibrium concentration (mg L^{-1})
IARC	the International Agency for Research on Cancer
k	adsorption capacity
k_1	the pseudo-first-order (h^{-1}) rate constant
k_2	the pseudo-second-order (g mg^{-1} h^{-1}) rate constants
NA11	nickel-aluminum type hydroxide (the Ni^{2+}:Al^{3+} molar ratios of 1.0:1.0)
NA12	nickel-aluminum type hydroxide (the Ni^{2+}:Al^{3+} molar ratios of 1.0:2.0)
NAZ1	nickel-aluminum-zirconium type hydroxide (the Ni^{2+}:Al^{3+}:Zr^{4+} molar ratios of 0.9:1.0:0.09)
NAZ2	nickel-aluminum-zirconium type hydroxide (the Ni^{2+}:Al^{3+}:Zr^{4+} molar ratios of 0.9:2.0:0.09)
q_e	the quantity of Cr(VI) adsorbed (mg g^{-1}) at equilibrium
q_t	the quantity of Cr(VI) adsorbed (mg g^{-1}) at given time t
SGDs	Sustainable Development Goals
USEPA	U.S. Environmental Protection Agency
WHO	World Health Organization
W_s	the maximum quantity of adsorbed Cr(VI) (mg g^{-1})

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