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Adsorption of metal ions from aqueous solution by recycled aggregate: estimation of pretreatment effect

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ABSTRACT

Heavy metal ions (Pb^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, and Zn^{2+}) were adsorbed by recycled aggregate (RA), which was pretreated with acidic or basic solution. Brunauer–Emmett–Teller analysis, Fourier transform infrared spectroscopy, and scanning electron microscopy/energy dispersive spectroscopy were used to investigate the differences in the physicochemical and adsorption characteristics between RA and pretreated RA. The results suggest that RA treated with NaOH (NRA) had improved physical and chemical characteristics. The adsorption kinetics of NRA for heavy metals was pseudo-second-order, and most of the heavy metal ions were bound to the NRA within 360 min. The maximum adsorption capacities assumed by Langmuir isotherms were in the order $Pb^{2+} > Cu^{2+} > Cd^{2+} > Ni^{2+} > Zn^{2+}$. Equilibrium adsorption data for the heavy metal ions fit well with the Langmuir model with regression coefficients $R^2 > 0.95$. At solution pH lower than 5, the adsorption specificity of the NRA for heavy metals was $Pb^{2+} \geq Cu^{2+} > Cd^{2+} > Zn^{2+} \geq Ni^{2+}$. Moreover, in harmful substance tests, all the heavy metals were detected in small amounts, but were found to be below the corresponding acceptance standards (as defined by the waste official test and toxicity characteristic leaching procedure).

Keywords: Adsorption; Construction waste; Heavy metals; Pretreatment; Recycled aggregate

1. Introduction

The contamination of water and sediment with toxic heavy metals through the discharge of industrial wastewater is a global environmental problem. In particular, lead, cadmium, zinc, nickel, and copper are widely used metal ions employed in various industries, such as the refining industry, textile and paint industry, foundries, and metal-finishing industry [1,2]. Moreover, unlike organic waste, heavy metals are non-biodegradable and can be accumulated in organisms, causing various diseases and disorders; therefore, they must be removed before discharge [3].

At present, a number of technologies are employed to remove heavy metals from contaminated water, such as filtration, adsorption, chemical precipitation, and ion exchange [4]. Among these techniques, adsorption is a promising method that does not have the disadvantages of low efficiency and high cost that are associated with other techniques. In particular, adsorbents composed of carbonaceous (i.e. activated

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carbon) waste material such as rice husk [5], wood [6], coconut shell [7], and coal [8] are of great interest for the purpose of pollution removal from wastewater. However, the manufacture of activated carbon is very expensive [9]; therefore, there is a need for low-cost, effective, and regenerable adsorbent materials that are capable of removing metal ions from wastewater.

Over the last few years, a large number of investigations have focused on low-cost adsorbents for the removal of heavy metals [9]. Waste biomass, industrial waste, and mineral waste have been investigated by many, and have shown good adsorption properties [10]. In particular, recycled aggregate (RA) is a renewable mineral resource that is available in large quantities and can be used as a good base for the development of adsorbent materials [11,12]. Coleman et al. [11] reported that the adsorption of heavy metal ions by crushed concrete fines was strongly dependent on pH, and described the uptake capacities of concrete fines in heavy metal solution. However, this study focused only on the adsorption performance of crushed concrete fines (i.e. contact time and adsorption amount) in single heavy metal solutions (Pb^{2+}, Zn^{2+}, and Cu^{2+}). Meanwhile, Shin and Kim [12] examined the removal rate of mixed heavy metals from aqueous solution by RA. However, it was found that heavy metal removal by RA was lower than that of other types of biomass and other sorbents [9,13]. In addition, contaminated wastewaters commonly contain multi-heavy metal ions, but there have not been sufficient investigations on the importance of multi-heavy metal adsorption mechanisms for the development of adsorbent materials for contaminated wastewaters. Hence, it is necessary to research the adsorption characteristics in multi-heavy metal ions contaminated wastewater.

The adsorption of metal ions on RA is affected by several factors, such as the specific surface area and presence of surface functional groups. RA is composed mainly of metal oxides, such as CaO, SiO_2, Al_2O_3, and Fe_2O_3 [12]. Moreover, the surface functional groups of RA include some groups capable of metal binding, for example, C=O, Si–O, and Si–O–Al groups [12,14]. The physicochemical properties of RA may be changed by pretreatment, and thus, its adsorption of heavy metals may be improved.

The goal of the current research is to investigate RA as an adsorbent, elaborating on its adsorption performance and adsorption mechanism for applications in both the removal of heavy metal pollutants from aquatic environments and the recycling of RA as construction waste. The adsorption capacities of two kinds of adsorbents pretreated under different conditions are compared with that of untreated RA. The sorption mechanism of RA is discussed on the basis of its physical and chemical characteristics.

2. Materials and methods

2.1. RA preparation

The RA samples used in this study were obtained from Dawan Environment Co., Ltd., Korea. The samples were washed thoroughly with distilled water to remove dirt and other impurities, and oven-dried at 60˚C for 24 h. The dried RA was passed through sieves with pore sizes of 0.5 and 1.0 mm (testing sieve, Chung Gye Sang Sa, Korea). Two different types of treatment were applied to the RA: (1) treatment with 1 M NaOH (NRA) and (2) treatment with 1 M HCl (HRA). In the case of HRA, the dried RA was soaked in 1 M HCl for 3 h, and rinsed with distilled water until the pH reached a value of 6. In the case of NRA, the dried RA was soaked in 1 M NaOH (NRA) for 3 h, and rinsed with distilled water until the pH reached a value of 6. The pretreated RAs were then dried again at 60˚C for 24 h. The dried RAs were stored in a desiccator until further use.

2.2. Adsorbates

Stock solutions of nickel, zinc, cadmium, copper, and lead (1,000 mg/L) were all prepared from standard stock metal solutions obtained from Kanto Chemical Co., Inc., Japan. The metal ion solutions, containing 5, 10, 20, 30, 50, 100, or 200 mg/L of Zn^{2+}, Ni^{2+}, Pb^{2+}, Cu^{2+}, or Cd^{2+} ions, were prepared by diluting with deionized distilled water. Before mixing the adsorbates with the adsorbent, the initial pH of solution was adjusted to 4 by adding 1 M HNO_3 and 1 M NaOH solution.

2.3. Batch sorption experiment

The experiments were performed in a batch reactor (50 mL) at 25 ± 0.5˚C with continuous stirring at 100 rpm. The adsorbents (0.03 g) were left in contact with 30 mL of metal ion solution (10 mg/L) at the initial pH value of 4. For the investigation of the effect of contact time, a set of solutions was prepared as described above, and samples were collected at time intervals of 10, 30, 60, 120, 180, 360, and 1,440 min. For the investigation of the sorption isotherms, the adsorbents (0.03 g) were left for 1,440 min in contact with 30 mL of metal ion solution (concentrations of 5, 10, 20, 30, 50, 100, and 200 mg/L) with an initial pH value of 4. For the study of the effect of pH, the solutions were adjusted to various initial pH values between 2 and 10. The contact time in the pH experiments was fixed at 1,440 min, the shaking rate was 100 rpm, and the metal concentrations were maintained at 10 mg/L. After adding adsorbent into solution, pH was not controlled during sorption experiments. The experiments were performed in duplicate and mean values were considered. A group of experiments was repeated a number of times to ascertain the reproducibility of the results. The supernatants of all samples were filtered with a 0.45 μm filter (Advantes No. 6784 2504, Japan). The filtrates were acidified with 2% HNO_3 to decrease the pH value to below 3 to avoid any precipitation before the inductively coupled plasma–optical emission spectrometry (ICP-OES) measurements (Optima 8300, PerkinElmer, USA). The pH of the solution was measured with a Mettler Toledo pH meter (Mettler Toledo Corp., USA) with an integrated thermal probe for temperature adjustment. The amount of metal absorbed was calculated from its initial and final concentrations.

2.4. Test methods for harmful substances in RA

In this study, the harmful substance tests of RA and NRA were executed according to the waste official test (WOT) [15] and toxicity characteristic leaching procedure (TCLP) [16]. These tests provide useful information on the potential leachability of harmful substances from RA (or NRA) under moderately (pH 5.8) or strongly (pH 2.9) acid conditions. The conditions of the WOT and TCLP test are shown in Table 1. In case of WOT (or TCLP) test, a 10 g RA sample was taken and then extraction fluid equal to 10 times (or 20 times) the amount of sample taken was added to it. The system was tightly closed and then placed on the shaker for 6 h (or 18 h), shaking at 200 rpm (or 30 rpm) at a room temperature (or 23 ± 2˚C). Heavy metal analysis was carried out on ICP-OES.

2.5. Data analysis

To evaluate the kinetic mechanism that controls the adsorption process, pseudo-first-order and pseudo-second-order equations were used [17,18]:

$$q_t = q_e[1 - \exp(-k_1 t)] \tag{1}$$

$$\frac{1}{q_e - q_e} = \frac{1}{q_e} + k_2 t \tag{2}$$

where q_t is the amount of heavy metal removed at time t (mg/g), q_e is the amount of heavy metal removed at equilibrium (mg/g), k_1 is the pseudo-first-order rate constant (1/min), and k_2 is the pseudo-second-order velocity constant (g/mg min). The equilibrium data can be analyzed using the following Langmuir and Freundlich isotherm models:

$$q_e = \frac{Q_m K_L C}{1 + K_L C} \tag{3}$$

$$q_e = K_F\, C^n \tag{4}$$

where C is the equilibrium concentration of the adsorbate in solution (mg/L), K_L is the Langmuir constant related to the binding energy (L/mg), Q_m is the maximum adsorption amount of metal ions (mg/g), K_F is the distribution coefficient (L/g), and n is the Freundlich constant. The values of K_L, Q_m, K_F, and n can be determined by fitting the Langmuir and Freundlich models to the observed data.

2.6. Physical and chemical characterization of RA

The microstructures of untreated and pretreated RA were analyzed by scanning electron microscopy (SEM) (JSM-6701F; JEOL Ltd., Japan) and energy dispersive spectrometry (EDS) (X-Max^N; Oxford, UK). The surface areas were measured through the N_2 adsorption method at liquid nitrogen temperature (i.e. −196˚C) with a surface area analyzer (Autosorb IQ-Kr/MP, Quantachrome, USA). The surface area and average pore diameter were determined for RA, NRA, and HRA using the BET surface area analyzer and a Micromeritics instrument, respectively. The functional groups of RA and NRA were analyzed by Fourier transform infrared spectroscopy (FT-IR) (Vertex 70; Bruker, Germany). RA sample powders

Table 1
Elution methods of WOT and TCLP for harmful substances

	WOT	TCLP
Agitating time	6 h	18 h
Agitating condition	200 rpm	30 rpm
Liquid:Solid ratio	10:1	20:1
Type of leachant	Deionized water + HCl (pH 5.8–6.3)	Deionized water + CH_3COOH (pH 2.97 ± 0.03)
Operating condition	Room temperature	23 ± 2˚C

were pressed in air into KBr pellets and then characterized by FT-IR.

3. Results and discussion

3.1. Effects of pretreatment on physicochemical characteristics of RA

The adsorption capacities of three different types of RA samples, abbreviated as RA, HRA, and NRA, were compared by adsorption experiments using 10.0 mg/L mixed heavy metal solution (Fig. 1). The adsorbed amounts of Ni^{2+}, Zn^{2+}, Cu^{2+}, Pb^{2+}, and Cd^{2+} were 0.38, 0.35, 1.04, 1.20, and 0.27 mg/g, respectively, for RA. The adsorption capacities of HRA and NRA for Ni^{2+}, Zn^{2+}, Cu^{2+}, Pb^{2+}, and Cd^{2+} were 0.16 and 0.68, 0.23 and 0.77, 0.04 and 1.86, 0.21 and 1.92, and 0.15 and 0.61 mg/g, respectively. The surface areas of RA, HRA, and NRA measured through the BET method were 5.17, 3.81, and 10.74 m^2/g, respectively (Table 2), so the surface area of NRA was about 5.57 m^2/g greater than that of RA. Interestingly, RA showed a larger pore size (11.16 nm) than NRA (8.01 nm) and HRA (4.90 nm). Meanwhile, HRA, RA, and NRA had

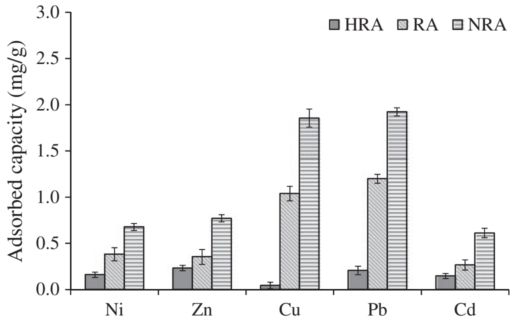
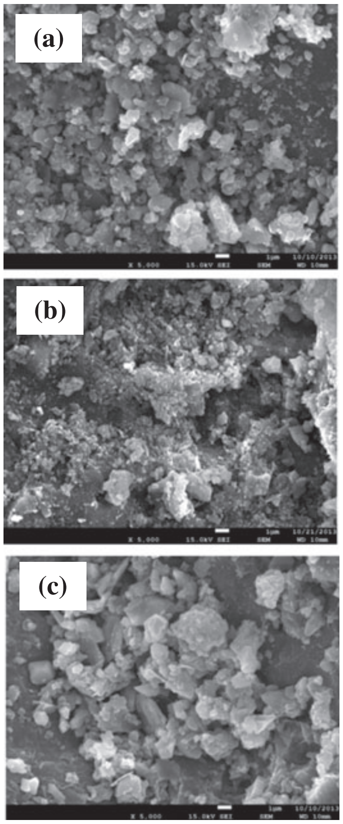


Fig. 1. Adsorption capacities of heavy metals by RA, HRA, and NRA from aqueous solution.

Table 2
Comparison of average pore radius, total pore volume, and BET surface areas for RA, HRA, and NRA

Pretreatments	Pore size (nm)	Total pore volume (cm^3/g)	BET surface area (m^2/g)
RA	11.16	0.014	5.17
HRA	4.90	0.005	3.81
NRA	8.01	0.022	10.74



Element(%)	RA	NRA	HRA
C	18.85	12.99	10.12
O	51.58	44.06	50.01
Na	0.12	1.61	0.00
Mg	0.23	0.45	0.35
Al	0.99	3.95	0.94
Si	2.70	10.66	33.05
S	0.51	0.35	1.17
Cl	0.00	0.00	0.27
K	0.36	1.27	0.50
Ca	24.01	19.66	1.38
Ti	0.00	0.18	0.37
Fe	0.64	4.43	1.83
Total	100	100	100

Fig. 2. SEM/EDS images of RA after different pretreatments: (a) untreated, (b) 1 M HCl, and (c) 1 M NaOH. All magnifications are 5,000×.

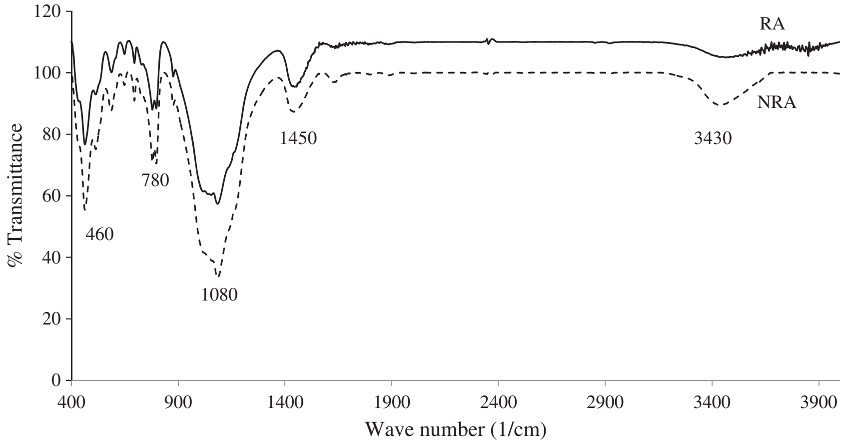


Fig. 3. FT-IR spectra of RA and NRA. RA: recycled aggregate; NRA: treated with 1 M NaOH.

total pore volumes of 0.005, 0.014, and 0.022 cm^3/g, respectively (Table 2). Upon treatment with NaOH, the adsorption capacity improved, which could be explained by the increase in the BET surface area and pore volume. On the other hand, the maximum decrease in the BET surface area and total pore volume for HRA is caused by the destruction of the pore walls and micropores through treatment with HCl.

The SEM/EDS pictures of RA, NRA, and HRA are shown in Fig. 2. It is evident from Fig. 2(a) and (c) that the surfaces of the original RA and NRA look very similar. However, after treatment with HCl (HRA), the surface of the precursor RA changes significantly (Fig. 2(b)). The narrowing of the pores in HRA, as exemplified by the BET surface area (see Table 2) and total pore volume, is also observed in these figures. Moreover, Fig. 2(b) shows that HRA has a very uneven surface, which is probably caused by the destruction of the pore walls, as already shown by the studies on the BET surface area and total pore volume of HRA. EDS data for the chemical analysis of RA, HRA, and NRA are presented in Fig. 2. These elements are typical constituents of RA; however, HRA and NRA differ on a surface scale. In comparison with RA, the carbon and calcium contents of NRA decreased to 5.86 and 4.35%, respectively. However, the aluminum, silica, and iron contents of NRA increased to 2.96, 7.96, and 3.79%, respectively. Meanwhile, the silica content of HRA increased to 30.35%, whereas the calcium content decreased to 22.63%. Hence, the constituent ratios vary according to the surface pretreatment applied.

The FT-IR results for RA and NRA are shown in Fig. 3, and they demonstrate the presence of the same types of functional groups in the adsorbents. The region between 400 and 3,900 cm^{-1} shows two major absorption bands centered at about 1,080.0 and 460.0 cm^{-1}. The most intense absorption bands lie in the 400–1,100 cm^{-1} region, with the next most intense at 1,450.0 cm^{-1} and the least intense at 3,440.0 cm^{-1}. All the samples show a band at 3,440.0 cm^{-1}, which is related to O–H stretching and bending modes of molecular water [19,20]. All the tested samples contain carbonate bands (C=O) at 1,400–1,500 cm^{-1}, which are attributed to the asymmetric stretching and out-of-plane bending modes of CO_3^{2-} ions [21,22]. The absorption band at 1,080.0 cm^{-1} is attributed to the stretching vibrations of the Si–O–Al group, and the band observed at 460.0 cm^{-1} may correspond to the Si–O bending vibration in RA and NRA [19,20]. The bands

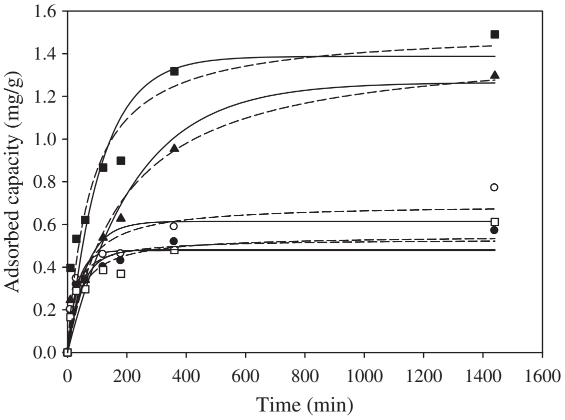


Fig. 4. Comparison of the adsorption time profiles for heavy metal ions on NRA. Symbols: (●) Ni^{2+}, (○) Zn^{2+}, (▲) Cu^{2+}, (■) Pb^{2+}, and (□) Cd^{2+}. Lines: pseudo-first-order model (solid line) and pseudo-second-order model (dashed line).

Table 3
Pseudo-first and second-order rate constants on NRA

	Pseudo-first-order model			Pseudo-second-order model		
Metal	q_e (mg/g)	K_1 (1/min)	R^2	q_e (mg/g)	K_2 (g/mg min)	R^2
Ni^{2+}	0.478	0.031	0.884	0.531	0.077	0.957
Zn^{2+}	0.615	0.016	0.823	0.695	0.087	0.915
Cu^{2+}	1.266	0.004	0.943	1.445	0.004	0.960
Pb^{2+}	1.388	0.009	0.892	1.514	0.009	0.940
Cd^{2+}	0.482	0.020	0.827	0.549	0.045	0.917

found for NRA are not very significant, being very similar to those of the precursor RA (Fig. 3); this implies that the NaOH pretreatment did not introduce any functional groups on the RA surface.

3.2. Adsorption kinetics for heavy metal ions by NRA

The effect of contact time on the adsorption of heavy metals by RA and NRA was investigated, and the results are shown in Fig. 4. The heavy metal concentrations decrease rapidly during the first 360 min, and then decrease gradually. It is clear that RA and NRA were saturated by the sorption of heavy metals after 360 min for all initial concentrations. According to the literature, the adsorption of Cd^{2+}, Cu^{2+}, and Zn^{2+} by zeolite-Portland cement and limestone occurs rapidly and reaches equilibrium in 30 and 60 min, respectively [23,24].

The parameters for the pseudo-first-order and pseudo-second-order models obtained from the kinetic experiments are provided in Table 3. The calculated and measured amounts of sorbed solute at equilibrium suggest that the removal of heavy metal ions by RA and NRA fits the pseudo-second-order kinetic model better than the pseudo-first-order model. Moreover, the pseudo-first and second-order models for RA and NRA fitted the data well for Ni^{2+} and Cu^{2+}, respectively. The calculated amounts of metal ions adsorbed on RA and NRA at equilibrium decrease in the order: $Pb^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+} \approx Ni^{2+}$.

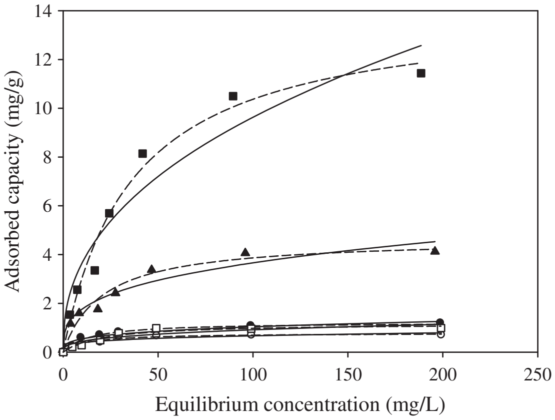


Fig. 5. Comparison of Langmuir and Freundlich models with experimental results for heavy metal adsorption by NRA. Symbols: (●) Ni^{2+}, (○) Zn^{2+}, (▲) Cu^{2+}, (■) Pb^{2+}, and (□) Cd^{2+}. Lines: Langmuir model (dashed line) and Freundlich model (solid line).

3.3. Adsorption isotherms

The Langmuir and Freundlich adsorption isotherms of five metals, Zn^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, and Cd^{2+} on NRA are presented in Fig. 5. The Langmuir isotherm parameters obtained from the fitting curves and the correlation coefficients (R^2) are summarized in Table 4. The order of the metal sorption capacities (Q_{max}) is $Pb^{2+} > Cu^{2+} > Cd^{2+} > Ni^{2+} > Zn^{2+}$. These results are in agreement with those obtained by Ok et al. [23], who reported that the order of metal

Table 4
Langmuir and Freundlich parameters for the adsorption of heavy metals on NRA

	Langmuir model			Freundlich model		
Metal	Q_m (mg/g)	K_F (L/mg)	R^2	K_L (L/g)	$1/n$	R^2
Ni^{2+}	14.082	1.224	0.980	0.289	0.278	0.950
Zn^{2+}	12.090	0.782	0.961	0.222	0.240	0.887
Cu^{2+}	20.777	4.667	0.962	0.856	0.316	0.948
Pb^{2+}	36.459	14.150	0.984	1.392	0.420	0.939
Cd^{2+}	20.520	1.177	0.951	0.216	0.314	0.855

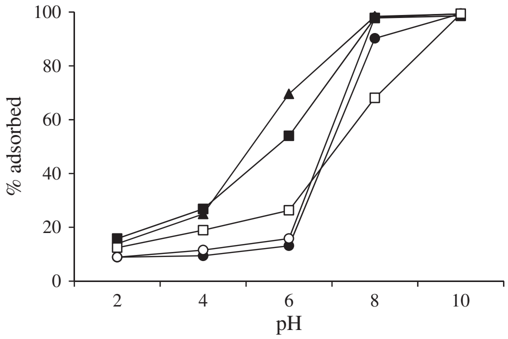


Fig. 6. Effects of initial pH on adsorption of heavy metals by the NRA in the aqueous solution. Symbols: (●) Ni^{2+}, (○) Zn^{2+}, (▲) Cu^{2+}, (■) Pb^{2+}, and (□) Cd^{2+}.

removal was $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$ for metal ion adsorption on zeolite-Portland cement. The order of heavy metal adsorption is known to correlate with the ionic radius [25] and electronegativity [26]. The electronegativities (ionic radii) of Cd^{2+}, Pb^{2+}, and Cu^{2+} are 1.69 (4.26 Å), 2.33 (4.01 Å), and 1.90 (4.19 Å), respectively [27]. Some studies have explained that the smaller the ionic radius and the greater the valence, the more closely and strongly the ion is adsorbed [28,29]. The ionic radii follow the order Pb > Cu > Cd, which coincides with the adsorption capacities of NRA. Moreover, this selectivity may vary according to the sources of adsorbents, kinds of metals, and experimental conditions. The adsorption by NRA also fitted the Langmuir isotherms well, with $R^2 > 0.95$ for all heavy metals, suggesting a monomolecular adsorption process.

3.4. Effect of pH on heavy metal adsorption by the NRA

The pH of the aqueous solution is an important controlling parameter in the heavy metal adsorption processes [30]. Adsorption of Ni^{2+}, Zn^{2+}, Cu^{2+}, Pb^{2+}, and Cd^{2+} onto the NRA generally increased as the pH increased (Fig. 6). For pH values higher than 6.0, the percentage of adsorbed heavy metals significantly increased, possibly due to precipitation of metal complexes, which is indicative of typical adsorption edges [31]. Adsorption edge is the narrow range of pH, where adsorption of the heavy metals onto the adsorbents is jumped completely to 100%. The values of pH_{50}, where 50% of the Cu^{2+} and Pb^{2+} were sorbed onto the NRA, were 5.5 and 6.0, respectively. The values for Ni^{2+}, Zn^{2+}, and Cd^{2+} were 7.0. Meanwhile, pH_{100} values for all heavy metals were over 10.0. For pH values lower than 5, the adsorption specificity of the NRA followed the order of $\text{Pb}^{2+} \geq \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} \geq \text{Ni}^{2+}$. Similarly, Ok et al. [23] reported that the order of affinity of the formulated zeolite-portland cement mixture (ZeoAds) was Pb > Cu > Cd > Zn in an aqueous solution. They showed that ZeoAds was more efficient for heavy metal sorption capacity than commercial activated carbon.

Table 5
Comparison of the adsorption capacities and adsorption affinities of NRA and other materials

Metal	Adsorbent	Q_m (mg/g)	K_F (L/mg)	R^2	References
Ni^{2}	NRA	14.08	1.224	0.980	This study
	Red mud	10.95	0.072	0.986	[33]
	Hizikia fusiformis	13.90	4.214	0.978	[13]
	Lime stone	0.038	0.805	0.977	[34]
Zn^{2+}	NRA	12.09	0.782	0.961	This study
	ZeoAds	12.85	101.50	0.912	[23]
	Red mud	12.59	0.120	0.943	[33]
	Hizikia fusiformis	10.56	6.10	0.982	[13]
Cu^{2+}	NRA	20.78	4.667	0.962	This study
	ZeoAds	23.25	51.50	0.979	[23]
	Red mud	19.72	0.020	0.905	[33]
Pb^{2+}	NRA	36.46	14.150	0.984	This study
	ZeoAds	27.03	50.60	0.984	[23]
	Hizikia fusiformis	26.75	10.39	0.971	[13]
	Lime stone	0.017	2.005	0.961	[34]
Cd^{2+}	NRA	20.52	1.177	0.951	This study
	ZeoAds	10.87	163.00	0.931	[23]
	Red mud	10.57	0.263	0.969	[33]
	Hizikia fusiformis	14.42	5.134	0.986	[13]

Table 6
Harmful substance acceptance standards and results (WOT and TCLP)

	WOT			TCLP		
Heavy metal	RA	NRA	WOT standards (mg/L)	RA	NRA	USEPA standards (mg/L)
Ni^{2+}	ND	ND	–	0.002	ND	7.0
Zn^{2+}	ND	ND	–	0.045	0.017	–
Cu^{2+}	0.001	0.002	3.0	0.010	0.007	–
Pb^{2+}	ND	ND	3.0	ND	ND	5.0
Cd^{2+}	ND	ND	0.3	0.005	ND	1.0

Note: ND: not detected.

3.5. Comparison with other studies

The adsorption capacities of heavy metals on NRA were compared with those on different types of materials derived from minerals, waste, and marine algae (Table 5). The maximum adsorption (Q_m) and K_F values of heavy metals for some of the materials were higher than those for NRA. The K_F value is related to the adsorption performance (e.g. the binding strength between an adsorbent and heavy metal ion) of heavy metals [30,32], so our results show that NRA is a promising choice of adsorbent from a practical and economic point of view for wastewater treatment through heavy metal adsorption.

3.6. Harmful substance test

Five types of heavy metal were analyzed on RA and NRA by applying the two test methods (WOT and TCLP according to Korea Ministry of Environment and EPA method, respectively), and the results are presented in Table 6. All heavy metals were detected below the corresponding acceptance standards. These results are in agreement with those obtained by Lee et al. [35], who reported that the adsorbed amounts of Pb and Cu for RA were 0.07 and 0.04 mg/L, respectively. The harmfulness of RA and NRA was verified by applying the two test methods (WOT and TCLP) as described above.

4. Conclusions

The adsorption of heavy metals by RA is strongly dependent on the pretreatment applied. The adsorbed amounts of heavy metal ions were for NRA > RA > HRA and the same ordering in the case of surface areas: NRA > RA > HRA. In particular, the adsorption of heavy metals from aqueous solution increases for RA treated with basic solution in comparison with untreated RA. The adsorption of NRA follows pseudo-second-order kinetics, reaching a pseudo-equilibrium state within 360 min. The long exposure time of NRA to saturation compared to those of zeolite-Portland cement and limestone (30 and 60 min, respectively) is a beneficial property as adsorbents. High adsorption capacities might be related to the large binding area on the RA. The adsorption of metal ions onto NRA follows a Langmuir-type isotherm. The order for the maximum adsorption capacities on NRA is $Pb^{2+} > Cu^{2+} > Cd^{2+} > Ni^{2+} > Zn^{2+}$. Moreover, the adsorption of heavy metals increased most noticeably between pH 4 and 8, after which it reached a plateau at pH 10.0. These results strongly suggest that NRA has a high adsorption capacity, and may be applicable to the treatment of heavy metal-contaminated environments.

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