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Removal of cationic and oxyanionic heavy metals from water using hexadecyltrimethylammonium-bromide-modified zeolite

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ABSTRACT

The objective of this study was to develop a dual-electronic adsorbent using hexadecyltrimethylammonium (HDTMA)-modified NaY zeolite. HDTMA-modified zeolite (HMZ) possesses a positive charge on the external surface and a negative charge on the micropore surface, and therefore it simultaneously adsorbs cationic (Cu^{2+}, Zn^{2+}, Ni^{2+}, Pb^{2+}, and Cd^{2+}) and oxyanionic (MnO_4^-, $Cr_2O_7^{2-}$) metal ions. The surface properties of NaY zeolite and HMZ were characterized according to scanning electron microscopy and Fourier transform infrared spectroscopy. The specific surface area, the elemental composition, and cation-exchange capacities were also examined. The obtained data were fitted with three types of kinetic adsorption models, pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. The amount of test metal ions adsorbed and the absorption mechanisms were illustrated. Moreover, competitive adsorption between cations and oxyanions was discussed. The results demonstrated that the HMZ behaved as a dual-electronic adsorbent. The pseudo-second-order kinetic equation exhibited the optimal fitting result. Ion exchange and complexation were regarded as primary mechanisms, and the adsorption capacities of cations and oxyanions followed the order $Pb^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+}$ and $Cr_2O_7^{2-} > MnO_4^-$, respectively. In addition, Pb^{2+} and $Cr_2O_7^{2-}$ were dominant species during competitive adsorption.

Keywords: Dual-electronic adsorbent; Hexadecyltrimethylammonium; Ion exchange; Heavy metal; Zeolite

1. Introduction

In general, industrial wastewater contains various heavy metal ions. Wastewater discharged into water bodies affects human health and the environment. Because heavy metal ions have low biodegradability, physicochemical processes constitute the main approach used to remove heavy metal ions from wastewater. Several treatment processes have been developed for removing heavy metal ions from

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wastewater [1–3]. Among these processes, ion exchange is the most common method. Ion-exchange resins or natural minerals are frequently used to remove heavy metal ions in low concentrations [4–9]. Although ion-exchange resins can effectively remove heavy metal ions from water or wastewater, the high operation cost limits the application of these resins to only water purification. In addition, ion-exchange resins adsorb only one type—cationic or anionic—of heavy metal ions. If wastewater contains both cations and anions, two types of ion-exchange resins must be used to remove all ions. Natural minerals, such as zeolite, can adsorb only cations. However, surfactant-modified zeolites have been used to remove oxyanions [10–14]. Therefore, developing an adsorbent that can simultaneously adsorb both cations and anions is essential and can simplify the treatment of different ions in wastewater.

Zeolites are porous materials with a high surface area and cation-exchange capacity (CEC). They have been widely applied to remove contaminants from various types of wastewaters [15–20]. Zeolite is used as an adsorbent to remove cationic metal ions because of its high CEC induced by the isomorphic substitution of cations in the crystal lattice. Although zeolites can adsorb cationic contaminants, they cannot effectively adsorb anionic contaminants because of the mutual repulsive force. Accordingly, several previous studies have modified zeolite or other minerals using cationic surfactants to alter their surface charge [10,13,14,21–28]. When a cationic surfactant is adsorbed onto the zeolite surface, admicelles form, and when the surfactant concentration exceeds its critical micelle concentration (CMC), the admicelles aggregate to form structural bilayers. The hydrophobic tails of the surfactant molecules on the zeolite surface then associate with the tails of other surfactant units in the solution to form a bilayer, with positive charges oriented toward the solution. Scientists have used this characteristic to remove chromate and arsenate ions [29–31].

Among tested cationic surfactants, hexadecyltrimethylammonium (HDTMA) ions are particularly useful for changing the surface charge from negative to positive. The surface characteristics of HDTMA-modified zeolite (HMZ) have been widely discussed [13,21,23,29]. However, the adsorption of cationic heavy metal ions on HMZ has been rarely studied. In general, it is difficult for organic substances with a high molecular size, such as HDTMA, to enter the micropores in zeolite [32–34], and the internal surface of micropores maintains a negative surface charge. Thus, HMZ possesses a positive charge on the external surface and a negative charge on the internal surface. In such a case, HMZ can be regarded as a dual-electronic adsorbent that can simultaneously adsorb cationic and oxyanionic heavy metal ions.

Previous studies on HMZ have focused on the adsorption of oxyanionic metal ions. According to the aforementioned surface chemical characteristics, HMZ has the potential to become a dual-electronic material, enabling simultaneous adsorption of cationic and anionic contaminants. In this study, the CECs on the external zeolite surface (ECEC) and the entire zeolite surface (ACEC) were examined. Adsorption kinetic data on cationic and oxyanionic heavy metal ions on HMZ were collected. The ability of HMZ to adsorb various heavy metal ions was evaluated. In addition, the competitive adsorption of multiple metal ions was analyzed. The results can be applied to develop an adsorbent that can simultaneously adsorb cationic and anionic heavy metal ions.

2. Material and methods

HY zeolite (sigma) was used as a raw material, and 0.1 g of this zeolite was added to 100 mL of 3 M aqueous NaOH. This solution was stirred for 24 h and filtered using a 0.2-μm filter. The collected solid samples were washed with distilled water until the pH was nearly neutral and were then dried at 150℃ in an oven for 6 h. The obtained product was NaY zeolite. HDTMA bromide [$(CH_3)_3N(CH_2)_{15}CH_3Br$; Merck] was used as a cationic surfactant to modify NaY zeolite. Four cationic heavy metal ions (Pb^{2+}, Zn^{2+}, Ni^{2+}, and Cu^{2+}; Merck) and two oxyanionic heavy metal ions ($Cr_2O_7^{2-}$ and MnO_4^-; Merck) were used as adsorbates. These heavy metal ions were prepared using 1,000 mg/L stock solutions.

Before the HDTMA was modified on zeolite, the adsorption experiment was run. The ideal weight ratio of HDTMA to zeolite that resulted in the maximum adsorption of HDTMA on NaY zeolite was 1:2. HDTMA (1.2 g) and NaY zeolite (1.0 g) were placed in a 200-mL beaker, and the volume was increased to 100 mL by adding deionized water. The solution was stirred for 24 h at 25℃ and was then filtered using a 0.2-μm filter. The solid was washed with distilled water until bromide ions were not detected ($AgNO_3$ test). The solid was dried in an oven at 70℃ for 6 h to obtain powdered HMZ [34]. The CMC of HDTMA is approximately 0.9 mmol/L; therefore, the added concentration was greater than the CMC.

The differences in the surface properties of NaY zeolite and HMZ were examined. The surface morphologies of the adsorbents were analyzed using scanning electronic microscopy (SEM, Hitachi S-3000 N) coupled with energy dispersive X-ray spectroscopy, which was conducted to analyze the elemental composition of adsorbents. The functional groups of the adsorbents were determined using Fourier transform infrared spectroscopy (FTIR, PerkinElmer Model 1600). The results of zeta potential meter (ZEN3600, Malvern Nano-ZS) analysis indicated the surface charge of adsorbents. A Brunauer–Emmett–Teller analyzer (Micromeritics TriStar 3000) was used to measure the changes in the pore and surface structures. In addition, the ACEC and ECEC were determined [35].

The adsorption experiment was divided into two parts, the use of a single adsorbate to estimate the adsorption amount and the competitive adsorption of multiple adsorbates. For a single-adsorbate experiment involving cationic heavy metal ions and oxyanions, 2.0 g of the adsorbent was added to a 500 mL-solution containing the adsorbates at 1,000 mg/L. To avoid the precipitation of heavy metal ions and maintain dichromate and permanganate in the state of $Cr_2O_7^{2-}$ or $HCr_2O_7^-$ and MnO_4^- ions, respectively, the pH of the solution was controlled at 5.0 ± 0.1. An electromagnetic stirrer (300 rpm) was used to mix the solution completely at 25℃. To analyze the adsorbate concentration in the solution, 1-mL aliquots of the solution were pipetted at regular intervals. In addition, the adsorption amounts of the adsorbates that reached an equilibrium state were measured after stirring for 24 h. The sample was filtered, diluted, and analyzed using atomic absorption spectrometry (Avanta, GBC).

The competitive adsorption experiment was conducted using identical molar concentrations of adsorbates. The molar concentration of each cationic adsorbate was set at 8.0 mmol/L and that of each anionic adsorbate was set at 3.0 mmol/L. The experimental conditions for competitive adsorption were the same as those for single-adsorbate adsorption.

In this study, three types of kinetic adsorption models, a pseudo-first-order model, a pseudo-second-order model, and an intraparticle diffusion model, were used to examine the kinetic data. The adsorption amount varying with time in the pseudo-first-order model is expressed as follows:

$$\frac{\mathrm{dq_t}}{\mathrm{d}t} = k_1(q_e - q_t) \tag{1}$$

where q_e and q_t (mg/g) are the amounts of adsorbed metal ions at equilibrium and at any time t, respectively, and k_1 is the rate constant (min^{-1}). After definite integration by applying the initial conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Eq. (1) can be written as follows:

$$\ln(q_\mathrm{e} - q_\mathrm{e}) = \ln q_\mathrm{e} - K_1 t \tag{2}$$

The pseudo-second-order model can be expressed as:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_2(q_\mathrm{e} - q_t)^2 \tag{3}$$

where k_2 is the rate constant (g/mg-min). After definite integration by applying the initial conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Eq. (3) can be written as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_\mathrm{e}^2} + \frac{1}{q_\mathrm{e}} t \tag{4}$$

The intraparticle diffusion model is expressed as follows:

$$q_t = k_\mathrm{p} t^{1/2} + C, \tag{5}$$

where k_p is the rate constant (mg/g $\mathrm{min}^{1/2}$) and C is the constant (mg/g). The k_p values can be divided into two stages; k_p1 (k_p2) is the rate constant evaluated using the kinetic data in the first (second) stage regarding the adsorption of adsorbates on the external (internal) zeolite surface.

In this study, HMZ was regarded as a dual-electronic material, and surface chemical characteristics, such as the ACEC and ECEC, were critical factors that determined its adsorption behaviors. Moreover, because the nitrogen atoms in HDTMA undergo complexation with heavy metal ions, the properties of cationic heavy metal ions may affect the adsorption amount [36]. The adsorption mechanisms were analyzed on the basis of the obtained adsorption amounts.

3. Results and discussion

To observe the changes in the morphologies of zeolites before and after the modification process, Fig. 1 indicates the SEM images for the NaY zeolite and HMY.

The size of the zeolite was lower than 1 μm. As shown in Fig. 1, because HDTMA bonded only on the zeolite surface, ion exchange induced by HDTMA had an insignificant effect on the shape of NaY zeolite. The FTIR spectra of NaY zeolite and HMZ are shown in Fig. 2 and confirm that HDTMA was adsorbed on the NaY zeolite surface. The absorbance peaks near 3,400 cm^{-1} represent the surfaces of the NaY zeolite and HMZ possessing OH groups. OH groups existed on the HMZ possibly because it is difficult for HDTMA to enter the micropores (less than 2.0 nm in size) in zeolites. However, the chain length of HDTMA exceeds 2.5 nm. This result implies that HDTMA was adsorbed only onto some surface sites on the NaY zeolite, and the HMZ still possessed cation-exchangeable sites. The absorbance of the HMZ in a region below 3,000 cm^{-1} might have resulted from the alkyl groups of HDTMA on the zeolite surface. The absorbance near 1,000 cm^{-1} indicates the presence of Si–O groups on the NaY zeolite and HMZ surfaces.

Although HDTMA may be adsorbed only onto some surface sites on NaY zeolite, it may still generate changes in the pore structures and surface chemical characteristics of NaY zeolite. Table 1 shows the specific surface area, average pore size, surface charge, ACEC, and ECEC of the NaY zeolite and HMZ.

As listed in Table 1, the modification led to a reduction in the specific surface area and pore volume. However, it increased the average pore size of the zeolite, because HDTMA covered some micropores. A positive zeta potential indicates a positive surface charge, and vice versa. The surface charges of the NaY zeolite and HMZ were negative and positive, respectively. The ACEC values represent the ability of an adsorbent to adsorb cations. Zeolites with high ACEC values can effectively adsorb cationic contaminants. The ECEC values indicate the CEC on the external zeolite surface. The internal pore surface provided the most cation-exchangeable sites. Thus, the HMZ could still effectively adsorb a large amount of cations.

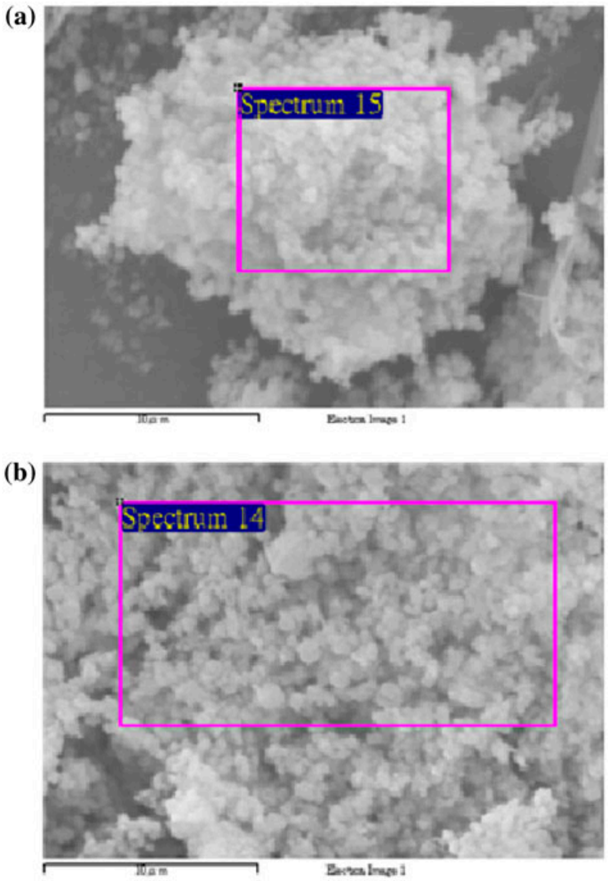

Fig. 1. SEM images of (a) NaY zeolite and (b) HMZ.

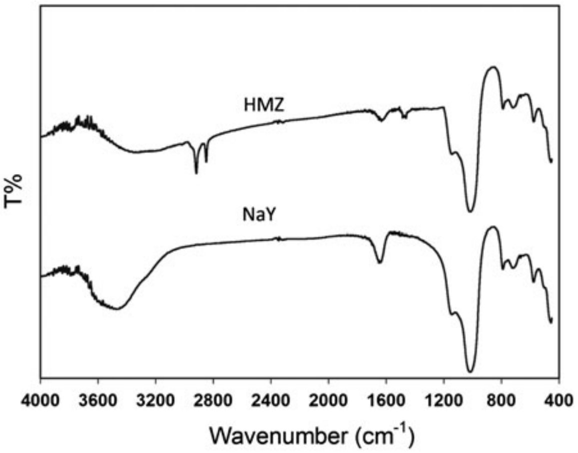

Fig. 2. FTIR spectra of NaY zeolite and HMZ.

Table 2 lists the major element compositions of the NaY zeolite and HMZ. The HMZ had 1.56% carbon atoms and 0.08% N atoms, confirming that HDTMA was adsorbed onto the zeolite surface. In addition, the HMZ had a high Na ion content, evidencing that some of the surface sites were not exchanged by HDTMA. The results demonstrated that the HMZ possessed a positive charge on the external surface and a negative charge on the internal pore surface.

HDTMA is adsorbed onto the zeolite surface and forms a bilayer, which then adsorbs oxyanions [37]. In this study, HMZ was regarded as a dual-electronic adsorbent. According to the aforementioned results, HMZ was expected to simultaneously uptake cationic and anionic heavy metal ions. Fig. 3 illustrates the kinetics of the adsorption of the four cationic heavy metal ions onto NaY zeolite and HMZ.

The adsorption increased in the beginning and reached a near-equilibrium state within 60 min. The external mass transfer, intraparticle diffusion, and interaction forces are regarded as potential factors that determine the adsorption amount. The adsorption amounts for the four heavy metal ions onto the NaY zeolite and HMZ followed the order $\mathrm{Pb}^{2+} > \mathrm{Zn}^{2+} \approx \mathrm{Cu}^{2+} > \mathrm{Ni}^{2+}$ and $\mathrm{Pb}^{2+} > \mathrm{Cu}^{2+} > \mathrm{Zn}^{2+} > \mathrm{Ni}^{2+}$, respectively.

Table 1
Pore structures and surface chemical characteristics of NaY zeolite and HMZ

	Specific surface area (m^2/g)	Pore size (nm)	Pore volume (cm^3/g)	Zeta potential at pH 5.0 (mv)	ACEC (meq/100 g)	ECEC (meq/100 g)
NaY	336	1.86	0.324	−66.2	269	42.3
HMZ	278	2.17	0.306	33.5	224	–

Table 2
Major element compositions (%) of NaY zeolite and HMZ

	C	O	Al	Si	Na	N
NaY	–	53.6	9.93	25.7	6.13	–
HMZ	1.56	52.2	9.24	23.9	5.26	0.08

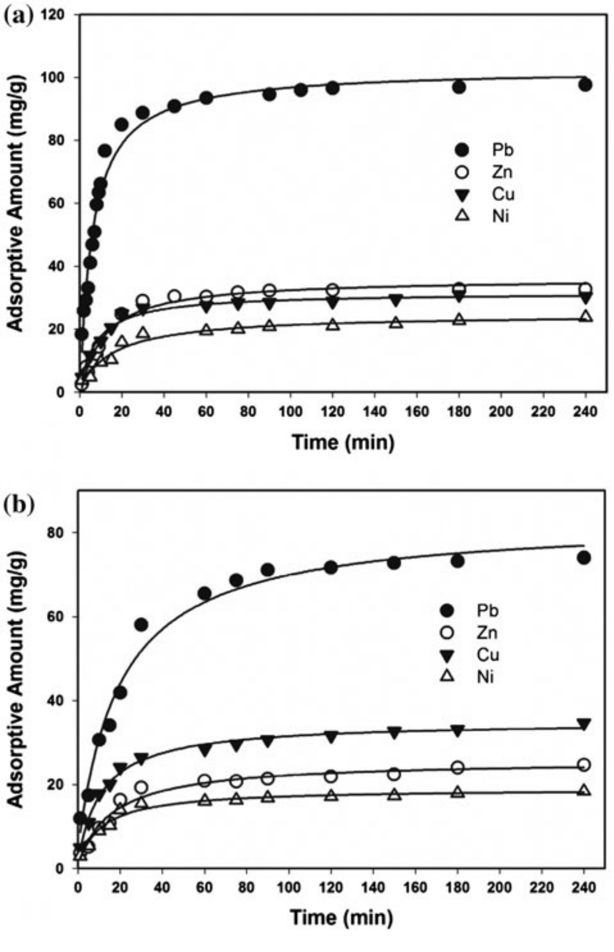

Fig. 3. Effect of time on the adsorption of heavy metal ions on the (a) NaY zeolite and (b) HMZ.

In general, functional groups containing oxygen or nitrogen atoms provide nonbonding electrons to coordinate with divalent metals. For the HMZ, because Cu^{2+} ions can quickly undergo complexation with nitrogen atoms in HDTMA, the adsorption capacity of Cu^{2+} ions was higher than that of both Zn^{2+} and Ni^{2+} ions. Moreover, because the cation-exchangeable sites on zeolite were partially occupied by HDTMA, the adsorption amounts of heavy metal ions on the HMZ were lower than those on the NaY zeolite. By contrast, if HDTMA occupies all cation-exchangeable sites, HMZ cannot adsorb cationic metal ions. However, HMZ can still effectively uptake cationic contaminants. The results demonstrated that the HMZ was adsorbed only onto the external surface. NaY zeolite is not an excellent adsorbent for oxyanions. Fig. 4 shows the adsorption kinetics of oxyanions onto the HMZ. The adsorption amount of $Cr_2O_7^{2-}$ was higher than that of MnO_4^-. Thus, the oxyanion with a large ionic radius has a relatively high adsorption, and this corresponds with the principle of ion exchange.

Previous studies have extensively discussed HDTMA-modified adsorbents that adsorb anionic contaminants. However, these studies have rarely presented the adsorption of cationic contaminants onto HDTMA-modified adsorbents. When HDTMA forms admicelles on the zeolite surface, the positively

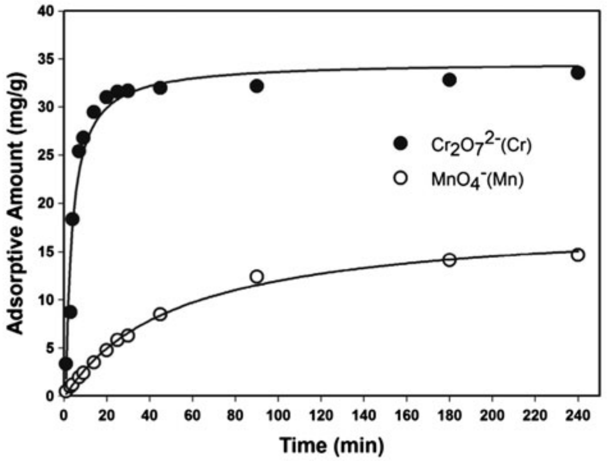

Fig. 4. Effect of time on the adsorption of oxyanions on the HMZ.

charged HDTMA moiety orients the solution. Cations, such as Pb^{2+}, Zn^{2+}, Cu^{2+}, and Ni^{2+}, experience difficulty in replacing the adsorbed HDTMA units from the external surface [38]. Furthermore, HDTMA is adsorbed only onto the external zeolite surface. Thus, HMZ possesses a negative charge on the internal pore surface and a positive charge on the external surface. Therefore, HMZ can be considered a dual-electronic material that enables the adsorption of both cationic and anionic contaminants. In water or wastewater treatment, HMZ can simultaneously adsorb cationic and anionic contaminants.

Fig. 5 shows the fitting of the adsorption kinetics of the four metal ions on the HMZ with three models at given intervals. The three kinetic models represent different adsorption characteristics. The pseudo-first-order model had a remarkable bias in data fitting. The good linear fitting of the pseudo-second-order model represents that concentrations of metal ions generate relatively stronger effects. The HMZ had relatively high adsorption for the test metal ions. The intraparticle diffusion model can be divided into two steps. In the first step, the metal ions are quickly adsorbed onto the external surface at relatively high adsorption rates. In the second step, the metal ions enter the internal surface through intraparticle diffusion, which is the rate control step. The intraparticle diffusion model was used to elucidate the adsorption characteristics of contaminants adsorbed onto adsorbents with micropores. Although a few data bias for the fitting, the intraparticle diffusion model can be regarded as having a good fit, because HMZ has numerous micropores.

Fig. 6 shows the fitting of kinetic data on the two oxyanions being adsorbed onto HMZ with three models. As in the cation adsorption model fitting, the bias in the fit of the pseudo-first-order model was high and the fit of the pseudo-second-order model was good. The good fitting for the pseudo-second-order model indicates that HMZ can effectively adsorb $Cr_2O_7^{2-}$ and MnO_4^-. The concentration of oxyanion is a key factor for the adsorption process. Because most exchangeable sites for anions are located on the HMZ surface, intraparticle diffusion for oxyanion adsorption on HMZ is less crucial. Consequently, oxyanions are quickly adsorbed onto HMZ and reach an equilibrium state. The curve in the second step is nearly horizontal. Moreover, the results demonstrated that oxyanions are primarily adsorbed onto the external HMZ surface.

Fig. 7 illustrates the fitting of kinetic data on cationic heavy metals being adsorbed onto the NaY zeolite with three models. The results for NaY zeolite were expected to be similar to those for HMZ. The fitting of the pseudo-first- order model exhibited a high bias. The pseudo-second-order and intraparticle diffusion models exhibited a more satisfactory fitting. Except for the external surface charge, the surface properties of HMZ are similar to those of NaY zeolite. Thus, the main difference between NaY zeolite and HMZ lies in oxyanion adsorption.

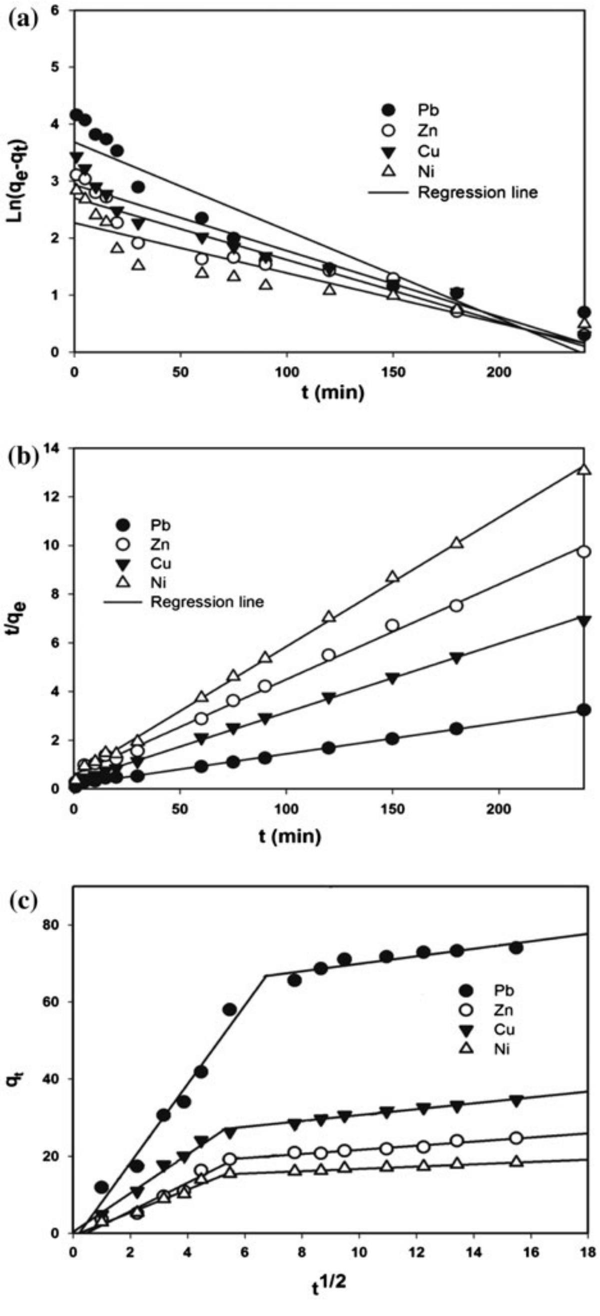

Fig. 5. Three kinetic model plots for the adsorption of Pb, Cu, Zn, and Ni onto HMZ: (a) first-order, (b) second-order, and (c) intraparticle diffusion.

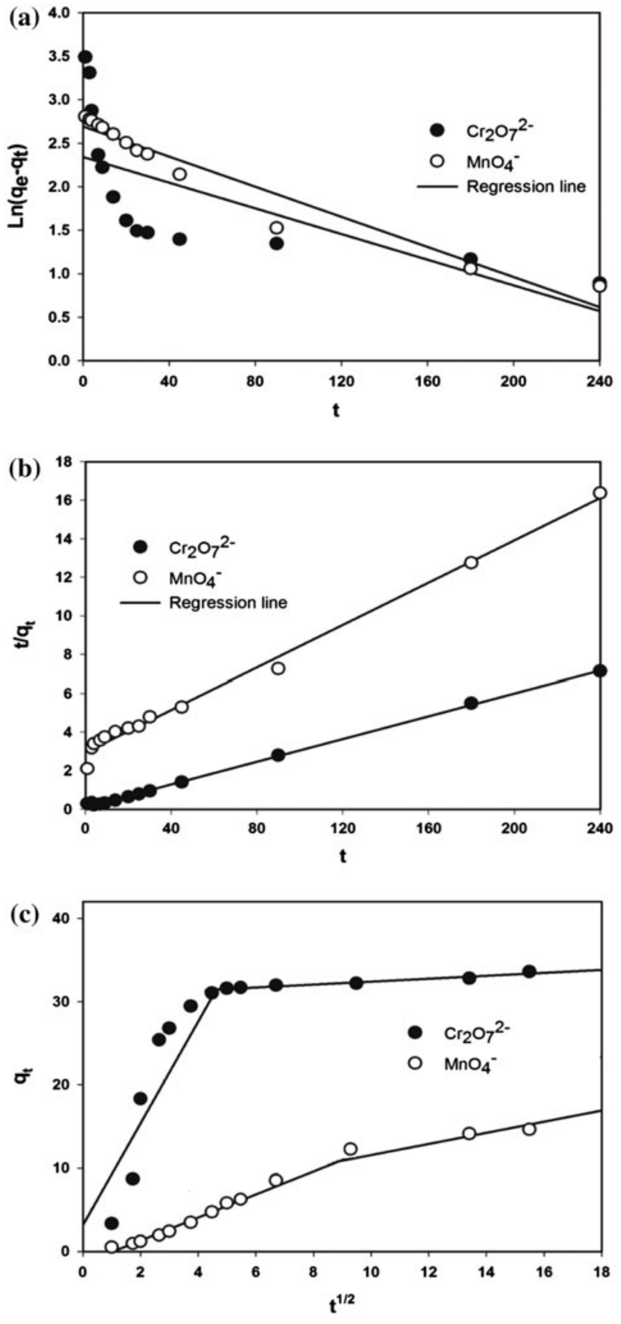

Fig. 6. Three kinetic model plots for the adsorption of $Cr_2O_7^{2-}$ and MnO_4^- onto HMZ: (a) first-order, (b) second-order, and (c) intraparticle diffusion.

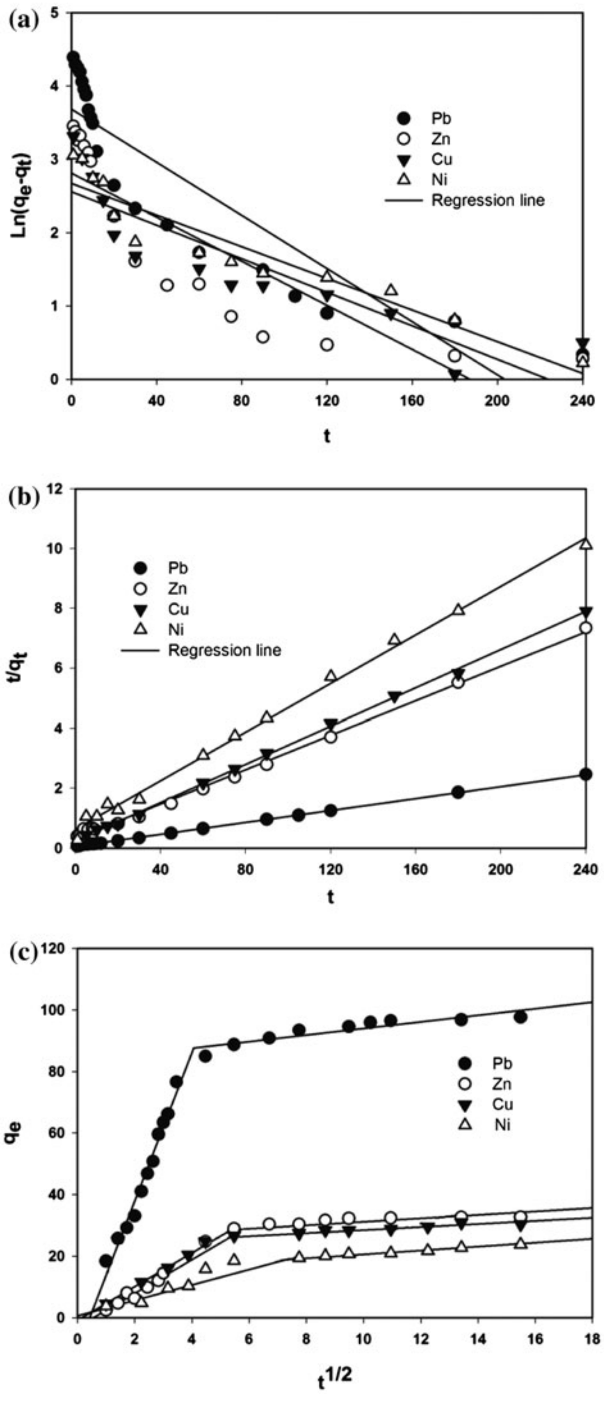

Fig. 7. Three kinetic model plots for the adsorption of Pb, Cu, Zn, and Ni onto NaY zeolite: (a) first-order, (b) second-order, and (c) intraparticle diffusion.

Table 3 presents parameters for the kinetic adsorption of cationic and anionic metal ions onto the NaY zeolite and HMZ. The amounts of adsorbed metal ions at equilibrium (q_e) were obtained through 24 h experiments on kinetic adsorption. The results demonstrated that the presence of HDTMA on the zeolite surface led to a reduction in the adsorption amounts of cationic metals. Nevertheless, the HMZ simultaneously adsorbed cationic and anionic contaminants. Moreover, the results demonstrated that the q_e values of the NaY zeolite were proportional to the ionic radius. Cu^{2+} ions on the HMZ generated a relatively higher q_e than did those on the NaY zeolite. As mentioned, complexation might be a critical mechanism.

According to the results of fitting the kinetic adsorption models, the pseudo-second-order reaction exhibited the highest R-square values. The rate constants for cationic metals followed the order $Ni^{2+} > Cu^{2+} > Zn^{2+} > Pb^{2+}$, which is inversely proportional to the atomic weight of the metals. This is because heavier atoms move relatively more slowly in micropores. In addition, the rate constant for $Cr_2O_7^{2-}$ was higher than that for MnO_4^-. Because oxyanions are adsorbed only on the external HMZ surface, diffusion in the micropores is less crucial. Electronic valence is the primary factor that determines the reaction rate for oxyanion adsorption.

For the intraparticle diffusion model, the slope coefficients can be divided into two stages. The slope coefficients in the first stage for all adsorbates are considerably higher than those in the second stage. Although some adsorbates showed a relatively poor fitting, most adsorbates had high *R*-squared values. NaY zeolite and HMZ have numerous micropores. The results correspond to the assumption of the intraparticle diffusion model.

The adsorption amounts of the test metal ions were compared with their theoretical amounts, that is, ACEC and ECEC. The real adsorption amounts of the cations and anions were 30–40% of the CEC. The reason for this difference was discussed in a previous study (34). Oxyanions are adsorbed in high amounts at a low pH solution, and a high pH solution is favorable for cation adsorption. If the solution pH can be controlled at an optimal value, the adsorption amount can increase significantly.

Fig. 8 illustrates competitive adsorption among the test metal ions. The selected adsorbates with the same molar concentration (8.0 and 3.0 mmol/L for cations and anions, respectively) were mixed in a solution containing HMZ for 240 min to examine the adsorption amounts. The adsorption amount followed the order $Pb^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+}$. The adsorption amounts of multiple adsorbates followed the same order as that for a single adsorbate. Moreover, the adsorption amount of Pb^{2+} ions was considerably higher than those of the other ions. Pb^{2+} ion possesses the highest ion radius, leading to the relatively higher adsorptive amount on the HMZ. It can be expected that Pb^{2+} ion is a dominant species in the competitive adsorption experiment. The results evidenced that dominant ions replaced other ions on the HMZ. Among the other ions, Cu^{2+} ions exhibited a relatively high adsorption amount. This is because Cu^{2+} ions underwent a complexation reaction with HDTMA on the zeolite. Pb^{2+} ions replaced Cu^{2+} ions adsorbed only on HMZ through ion exchange. For oxyanions, the adsorption amount of $Cr_2O_7^{2-}$ was considerably higher than that of MnO_4^-. $Cr_2O_7^{2-}$ had a high negative charge, causing it to have a high adsorption amount. Because the main mechanism of oxyanions adsorption on the HMZ is ion exchange, the oxyanion with the high ion radius can generate the high adsorptive amount. The results indicated that a high exchange level and large ionic radius are the dominant factors that determine competitive ion adsorption.

In this study, the produced HMZ was regarded as a dual-electronic adsorbent. The results demonstrated that the HMZ simultaneously adsorbed cationic and anionic contaminants. Therefore, it can be used to simplify water or wastewater treatment, because only one

Table 3
Parameters of the selected kinetic models of the adsorption of heavy metal ions onto NaY zeolite and HMZ

			First-order		Second-order		Intraparticle diffusion	
Adsorbent	Adsorbate	q_e (mg/g)	k_1 (×10^{-3})	R^2	k_2 (×10^{-3})	R^2	k_{p1} (R^2)	k_{p2} (R^2)
NaY	Pb^{2+}	99	18.1	0.800	1.81	1.00	22.8 (0.965)	1.07 (0.826)
	Zn^{2+}	34	15.0	0.723	2.56	0.997	5.48 (0.937)	0.577 (0.675)
	Cu^{2+}	32	11.4	0.792	2.42	0.999	5.48 (0.999)	0.483 (0.873)
	Ni^{2+}	25	10.8	0.898	2.63	0.996	2.50 (0.893)	0.623 (0.910)
HMZ	Pb^{2+}	76	15.5	0.875	1.48	0.997	10.2 (0.959)	0.970 (0.856)
	Zn^{2+}	26	11.1	0.889	2.51	0.996	3.69 (0.943)	0.532 (0.942)
	Cu^{2+}	36	11.2	0.926	2.46	0.998	5.02 (0.980)	0.766 (0.980)
	Ni^{2+}	20	8.8	0.794	2.61	0.999	2.98 (0.976)	0.298 (0.981)
	$Cr_2O_7^{2-}$	36	7.4	0.447	7.52	0.999	6.10 (0.802)	0.176 (0.922)
	MnO_4^-	17	8.7	0.945	1.02	0.992	1.38 (0.982)	0.667 (0.890)

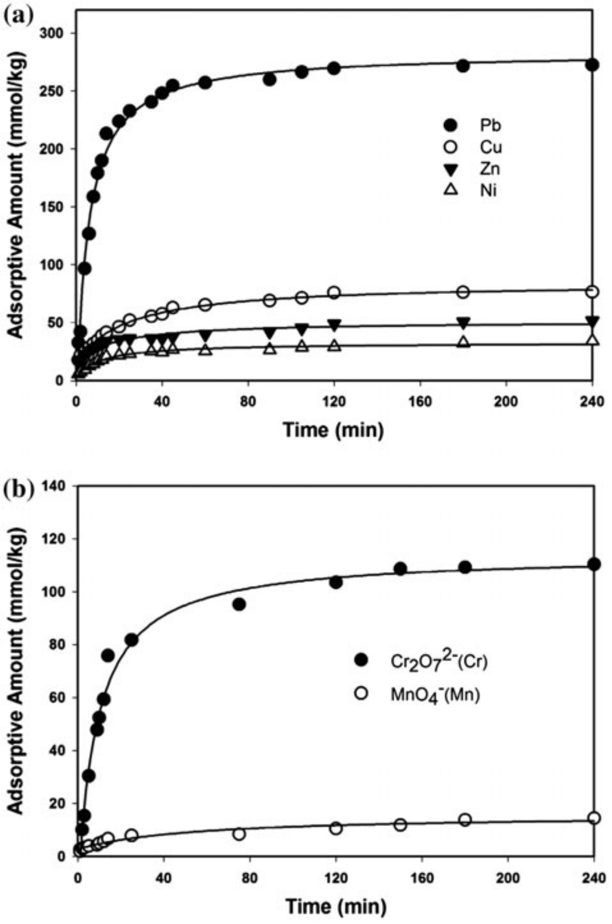

Fig. 8. Adsorption of multiple heavy metal ions onto HMZ over time: (a) cationic metal and (b) oxyanionic metal.

adsorbent is required to remove both cationic and anionic contaminants.

4. Conclusions

The produced HMZ was used to simultaneously adsorb metal ions (Cu^{2+}, Zn^{2+}, Ni^{2+}, and Pb^{2+}) and oxyanions ($Cr_2O_7^{2-}$ and MnO_4^-). The HDTMA modified on the zeolite surface formed bilayers or admicelles, resulting in the formation of a dual-electronic adsorbent with a positive charge on the external surface and a negative charge on the micropore surface. The surface properties of NaY zeolite and the HMZ were examined according to FTIR patterns, the ACEC, and the ECEC, and the elemental composition, which confirmed the preceding description. The adsorption capacities of the cationic metal ions were dependent on their ionic radii. Cu^{2+} ions underwent a complexation reaction with HDTMA and, thus, were adsorbed in relatively high amounts. Electronic valence is the primary factor that determines the adsorption amounts of oxyanions. Under conditions involving multiple adsorbates, dominant ions occupy the most adsorption sites, reducing the adsorption of other ions. The results illustrate that HMZ effectively removes cationic and anionic contaminants in wastewater.

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