

Article

Potassium Recovery from Potassium Solution and Seawater Using Different Adsorbents

Sora Shin ¹, Eun Hea Jho ^{2,*} , HyunJu Park ³, Sungjong Lee ⁴ and Joon Ha Kim ¹

¹ School of Earth Sciences and Environmental Engineering, Gwangju Institute of Science and Technology, 123 Cheomdan-gwagi-ro, Gwangju 61005, Korea; sorashin@gist.ac.kr (S.S.); joonkim@gist.ac.kr (J.H.K.)

² Department of Agricultural and Biological Chemistry, Chonnam National University, 77 Yongbong-ro, Gwangju 61186, Korea

³ Institute of Engineering Research, Seoul National University, Seoul 08826, Korea; narjji@snu.ac.kr

⁴ Department of Environmental Science, Hankuk University of Foreign Studies, Yongin 17035, Korea; sjlee80@hufs.ac.kr

* Correspondence: ejho001@jnu.ac.kr; Tel.: +82-62-530-2134; Fax: +82-62-530-2139

Abstract: The potassium (K) sorption characteristics with three adsorbents, natural zeolite, ammonium acetate-treated zeolite, and manganese nodule, were studied and compared to see the potential use of manganese nodule as an alternative K adsorbent. In general, the Langmuir isotherm could fit the K sorption in the KCl solutions at different pH conditions better than the Freundlich isotherm. Based on the Langmuir parameters, the maximum K sorption was greater for the zeolite-based adsorbents (i.e., 40–42 mg g⁻¹) than the manganese nodule (i.e., 2.0 mg g⁻¹) at acidic conditions, while the manganese nodule (i.e., 9.7 mg g⁻¹) showed better K sorption at neutral conditions. With the seawater samples, the zeolite-based adsorbents showed higher K recovery (4–14%) than the manganese nodule (0–8.8%). The K sorption on the zeolite-based adsorbents followed the pseudo-second-order kinetics and the K sorption rates were higher for the treated zeolite than the natural zeolite. The repeated sorption tests showed that the natural zeolite could potentially be reused up to three times without any significant loss of K sorption capacity, while the ammonium acetate-treated zeolite lost its K sorption capacity after the single sorption test. Overall, the results show that the manganese nodule may potentially be the alternative to zeolite for K recovery under certain conditions, yet the zeolite-based adsorbents are generally better than the manganese nodule. Thus, more studies to enhance the K recovery using zeolite, including surface modified zeolite, are recommended.



Citation: Shin, S.; Jho, E.H.; Park, H.; Lee, S.; Kim, J.H. Potassium Recovery from Potassium Solution and Seawater Using Different Adsorbents. *Appl. Sci.* **2021**, *11*, 8660. <https://doi.org/10.3390/app11188660>

Academic Editor: Francisco José Alguacil

Received: 14 August 2021

Accepted: 14 September 2021

Published: 17 September 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Keywords: potassium; sorption; seawater; manganese nodule; zeolite

1. Introduction

The adsorption process has been widely applied to recover valuable elements, such as lithium (Li), potassium (K), uranium (U), and strontium (Sr) from seawater, wastewaters, or concentrated brines produced in the desalination process [1–3]. Among many methods for mining elements from seawater, the adsorption process is a relatively economic and simple process. Due to the vast amount of seawater, the presence of elements at very low concentrations in seawater can provide useful amount of elements [2]. Seawater contains cations such as sodium (Na), magnesium (Mg), calcium (Ca), K, and Sr in decreasing order of amount in seawater [2].

Potassium can be used for the production of fertilizers, but the terrestrial K resources are limited compared to K in seawater. Thus, previous studies tried to recover K from seawater, both synthetic seawater and real seawater, at a laboratory scale [4,5]. Different methods, such as precipitation and extraction [6,7], membrane separation [5], and adsorption on sorbents [1,4] have been used to recover K. With adsorption, K-selective adsorbents have been synthesized to enhance the K recovery from seawater [4,8].

In previous studies, zeolite has been used to recover K from seawater by sorption process, and these studies synthesized or modified zeolite for better K uptake [1,4,9]. With surface modification of zeolite, the K adsorption capacity was increased [9]. Similarly, the sodium ion sorption capacity of zeolite increased after treatment with ammonium acetate [10,11]. Moreover, the synthesized adsorbent (i.e., zeolite W) showed a higher selectivity to K [4].

Manganese nodule residue that is generated during the processing of manganese nodules has been used for adsorption of heavy metals, such as chromium and lead (Pb) [12,13]. Moreover, one previous study used ocean manganese nodules to make a K ionic sieve for K recovery from seawater [14]. However, ocean manganese nodule has not been studied for its sorption capacity of K.

The sorption-based K recovery studies are largely limited to using zeolite as an adsorbent, and other types of adsorbents have not been explored much. Thus, there is a need for more studies on other possible adsorbents for K recovery from seawater. Therefore, this study was set to study and compare the adsorption characteristics of different adsorbents for K recovery from seawater. The zeolite-based adsorbents, both natural zeolite (i.e., clinoptilolite) and modified natural zeolite, and manganese nodule, a potential adsorbent, were used in this study to explore and compare the K recovery potential. The natural zeolite was treated with ammonium acetate to prepare the modified natural zeolite in this study.

2. Materials and Methods

2.1. Preparation of Adsorbents

In this study, three types of adsorbents were used—natural zeolite (i.e., clinoptilolite), ammonium acetate-treated natural zeolite, and manganese nodule. Clinoptilolite (1–3 mm diameter), a natural zeolite, was purchased from the Handu Trade (Duksan, South Korea), and the major components of the natural zeolite include SiO₂ (69.8%), Al₂O₃ (13.2%), CaO (2.31%), Na₂O (2.18%), and K₂O (3.10%). Prior to sorption experiments, the natural zeolite was ground (<0.5 mm diameter), washed with deionized water, and dried at 105 °C for 24 h. To prepare the ammonium acetate-treated zeolite, the natural zeolite (40 g) was placed and stirred in 1 M ammonium acetate (NH₄C₂H₃O₂; Reagents grade, Duksan, South Korea) solution for 24 h [10]. The treated natural zeolite was rinsed three times with deionized water. The liquid phase and solid phase were separated by filtration and the solid phase was dried at 105 °C for 24 h before use. Ocean manganese nodules, sampled from the Clarion-Clipperton Zone (i.e., CC zone) of the Pacific Ocean, were provided by the Korea Institute of Geoscience and Mineral Resources. The manganese nodules consisted of 8.85% Fe, 0.73% Cu, 0.97% Ni, 0.18% Co, and 22.35% Mn [15]. Prior to sorption experiments, the manganese nodule was ground to <2 mm. The specific surface areas and porosities of the natural zeolite, ammonium acetate-treated zeolite, and manganese nodule were analyzed using the Brunauer–Emmett–Teller (BET) surface area and porosimetry analyzer (ASAP2420, Micromeritics Instrument Corporation, Norcross, GA, USA). The SEM images of the three adsorbents used can be found in the supplementary material.

2.2. Sorption Experiments with KCl Solutions

2.2.1. Batch Sorption Experiments with KCl Solution

Batch sorption tests were conducted at room temperature (21–23 °C) to investigate the K sorption characteristics of the prepared adsorbents. The K stock solution (1000 mg L⁻¹) was prepared from KCl (Yakuri Pure Chemicals Co. Ltd., Kyoto, Japan, Guaranteed Reagent), and the solution pH was adjusted to pH 4.57 ± 0.03 and pH 6.99 ± 0.04 with a pH 4 buffer solution (CH₃COOH-CH₃COONa) and a pH 7 buffer solution (NaH₂PO₄-Na₂HPO₄), respectively. The K stock solution was diluted to prepare solutions with different initial K concentrations (0–200 mg L⁻¹ for tests at pH 4 and 0–150 mg L⁻¹ for tests at pH 7). The prepared adsorbents (0.1 g) were placed in a 100 mL polypropylene bottle and the K solutions of different initial concentrations (100 mL) were added. The

bottles were then shaken at 100 rpm on a shaker (SH30L, FinePCR, Seoul, Korea). Duplicate samples were used for each condition. After 48 h, the samples were filtered using 0.45 µm syringe filters. The K concentrations of the filtrates were analyzed by using ICP-OES (iCAP 7400 Duo, Thermo Fisher Scientific, Waltham, MA, USA).

With the zeolite-based adsorbents, the K sorption kinetics were studied at the average pH of 4.4. The natural zeolite or ammonium acetate-treated zeolite (0.1 g) was placed in a 100 mL polypropylene bottle and the K solution (100 mL, initial concentration = $170 \pm 0.084 \text{ mg L}^{-1}$) was added. The bottles were then shaken at 100 rpm in a shaking incubator (SH30L, FinePCR, Seoul, Korea). During the 48 h sorption tests, samples were taken at 0, 2, 4, 6, 8, 10, 24, and 48 h. Duplicate samples were used for each condition.

2.2.2. Sorption Isotherm and Kinetic Models

The K sorption test results were fitted to the Langmuir (Equation (1)) and Freundlich (Equation (2)) isotherm models to characterize the sorption potential of the different adsorbents. The Langmuir constant related to the maximum K sorption capacity, q_m (mg g^{-1}), and the affinity of the binding sites, K_d (mg L^{-1}), derived from the Langmuir isotherm model and the constants related to the sorption capacity, K_F , and magnitude of the sorption driving force, n , derived from the Freundlich isotherm model were compared for the different adsorbents.

$$q_e = \frac{q_m C_e}{(K_d + C_e)} \quad (1)$$

$$q_e = K_F C_e^{\frac{1}{n}} \quad (2)$$

where q_e (mg g^{-1}) and C_e (mg L^{-1}) are the K sorbed per unit mass of adsorbents and K concentration at equilibrium, respectively.

The sorption kinetics data were fitted to the pseudo-first-order kinetics (Equation (3)) and the pseudo-second-order kinetics (Equation (4)) equations.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{t}{q_e} \quad (4)$$

where q_e and q_t are the amounts of K sorbed (mg g^{-1}) at equilibrium and time t , respectively, and k_1 and k_2 are the pseudo-first-order (h^{-1}) and pseudo-second-order ($\text{g mg}^{-1} \text{ h}^{-1}$) rate constants, respectively.

2.3. K Sorption Experiments with Seawater

The seawater sample was provided by the Doosan Heavy Industries & Construction (Changwon, Korea). The seawater samples with different K concentrations were prepared by concentrating or diluting the original seawater sample. The concentrated sample was prepared by reducing the sample volume by about 50% via evaporation, while the diluted sample was prepared by adding deionized water to double the sample volume. The initial pH values of the seawater samples were 8.33 ± 0.15 . Moreover, the seawater pH was adjusted to $\text{pH } 5.08 \pm 0.04$ to study the effect of pH conditions on K recovery from seawaters. The average initial K concentrations of the diluted, original, and concentrated seawater samples were 23, 50, and 120 mg L^{-1} , respectively. For comparison of K recovery at different pH conditions, the initial K concentrations of 23 mg L^{-1} were used. The batch sorption tests were conducted by placing each of the three adsorbents used in this study (0.1 g) and the prepared seawater samples (100 mL) in a 100 mL polypropylene bottle. Duplicate samples were used for each condition. The sorption tests were carried out for 72 h, and the residual K concentrations in the supernatants were measured after filtration.

2.4. Regeneration Study Using Natural Zeolite

The potential for reusing the adsorbents was assessed by running repeated sorption-regeneration tests using the KCl solution and the natural zeolite as an adsorbent. After the 72 h sorption tests, the natural zeolites were separated from the supernatants. The recovered K sorbed adsorbents were placed in 20 mL of 0.5 N HCl solution and shaken for 3 h at 100 rpm in a shaking incubator. Then the adsorbents were rinsed with deionized water until the pH reaches >4.5, and dried at 60 °C in an oven. The regenerated adsorbents were used for the sorption tests and the sorption tests were repeated four times. For each sorption test, more than triplicate samples were used to measure the K sorption potential.

3. Results and Discussion

3.1. K Sorption by Different Adsorbents

3.1.1. K Sorption Isotherms Using KCl Solutions

Figure 1 shows the sorption isotherms of K on three different adsorbents under acidic conditions (i.e., pH = 4.57). The K sorption capacities, indicated by q_e , increased with increasing initial K concentrations (Figure 1a). The sorption data were fitted to the linearized forms of the Langmuir and Freundlich isotherm models (Figure 1b,c). Table 1 shows the parameters for the Langmuir and Freundlich isotherms derived from the experimental data using Equations (1) and (2) and the regression coefficients (R^2).

Table 1. Langmuir and Freundlich isotherm parameters for potassium sorption at pH 4.57 and 6.99.

pH	Adsorbent	Langmuir Isotherm			Freundlich Isotherm		
		q_m (mg g ⁻¹)	K_d	R^2	K_F	n	R^2
4.57	Natural zeolite	40	0.011	0.77	0.80	1.4	0.92
	Ammonium acetate-treated zeolite	42	0.057	0.93	2.9	1.8	0.90
	Manganese nodule	2.0	0.17	0.80	0.84	5.2	0.14
6.99	Natural zeolite	5.8	0.045	0.54	0.55	2.0	0.77
	Ammonium acetate-treated zeolite	8.1	0.037	0.66	2.2	4.9	0.30
	Manganese nodule	9.7	0.018	0.11	2.1	3.8	0.14

The K sorption on the adsorbents tested can be described by the L-type sorption isotherm, which suggests no strong competition between solvent and sorbate for the sorption sites [3]. Considering the R^2 values, the Freundlich isotherm model (i.e., $R^2 = 0.92$) could fit the K adsorption on the natural zeolite better than the Langmuir isotherm model (i.e., $R^2 = 0.77$), while the Langmuir isotherm model could fit the K adsorption on the ammonium acetate-treated zeolite and, in particular, the manganese nodule, better than the Freundlich isotherm model (Table 1).

The q_m values, related to the maximum K sorption capacity, derived from the Langmuir isotherm model show that the ammonium acetate-treated zeolite has the greatest K adsorption capacity among the adsorbents studied, followed by the natural zeolite and manganese nodule (Table 1). However, the K_d value indicating the affinity of the binding sites of the manganese nodule was higher than that of the ammonium acetate-treated zeolite (Table 1). These results suggest that the manganese nodule has the higher affinity for K sorption than the ammonium acetate-treated zeolite, but there may be less binding sites available for K sorption on the manganese nodule than the ammonium acetate-treated zeolite. The Freundlich isotherm model parameters showed similar results. For example, the K_F value related to the sorption capacity of the ammonium acetate-treated zeolite was higher than the other K_F values (Table 1). The n value related to the sorption driving force of the manganese nodule was also higher than the n values of the other adsorbents (Table 1).

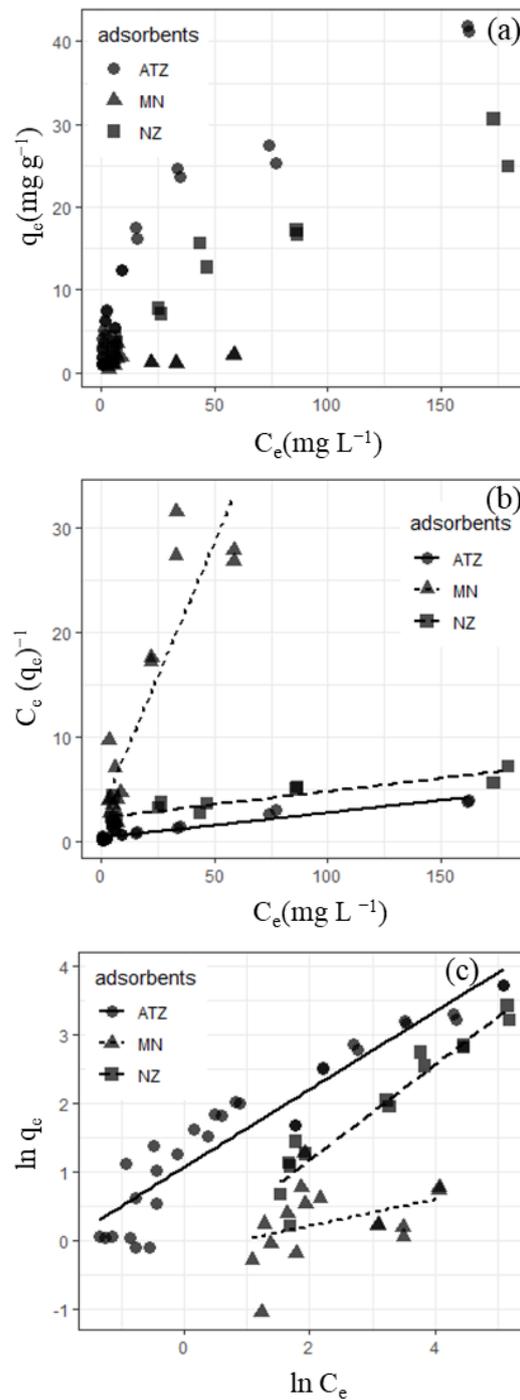


Figure 1. (a) Adsorption isotherm; (b) Langmuir isotherm; and (c) Freundlich isotherm of potassium (K) in potassium chloride (KCl) solutions on natural zeolite (zeolite), ammonium acetate-treated natural zeolite (Treated zeolite), and manganese nodule (manganese nodule) at pH 4.57.

When the natural zeolite and the ammonium acetate-treated zeolite are compared, the K sorption capacities indicated by the q_m values and K_F values were greater for the ammonium acetate-treated zeolite (Table 1). This agrees with previous studies where the ammonium acetate-treated zeolite showed an improved Na sorption capacity over the untreated natural zeolite [10]. The greater K sorption capacity of the ammonium acetate-treated zeolite than the natural zeolite is also supported by the higher specific surface area and pore volume. The specific surface areas of the natural zeolite and the ammonium acetate-treated zeolite were 29.2 and 33.0 m² g⁻¹, respectively, and the pore volumes of

the natural zeolite and the ammonium acetate-treated zeolite were 0.088 and $0.10 \text{ cm}^3 \text{ g}^{-1}$, respectively.

Figure 2 shows the sorption isotherms of K on three different adsorbents under neutral conditions (i.e., $\text{pH} = 6.99$). The sorption data were fitted to the Langmuir and Freundlich isotherm models (Figure 2b,c), and the parameters calculated are shown in Table 1.

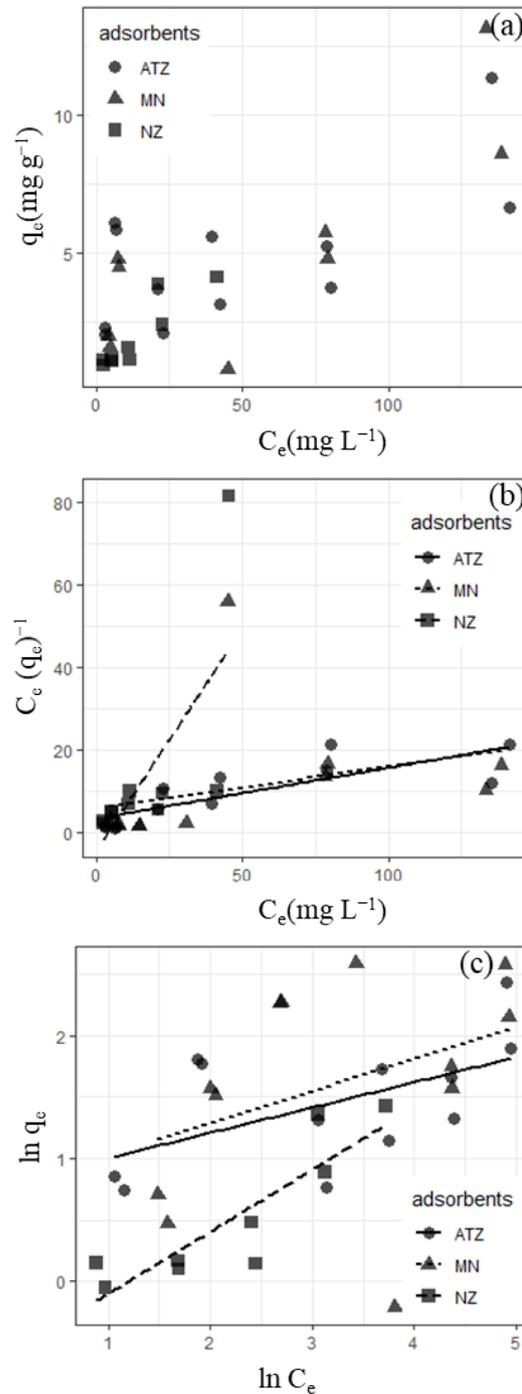


Figure 2. (a) Adsorption isotherm; (b) Langmuir isotherm; and (c) Freundlich isotherm of potassium (K) in potassium chloride (KCl) solutions on natural zeolite (zeolite), ammonium acetate-treated natural zeolite (treated zeolite), and manganese nodule (manganese nodule) at pH 6.99.

The K sorption capacities (i.e., q_e) increased with increasing K concentrations at equilibrium (i.e., C_e) (Figure 2a). Considering the R^2 values, the Freundlich isotherm

model fitted the K adsorption on the natural zeolite and manganese nodule better than the Langmuir isotherm model, while the Langmuir isotherm model fitted the K adsorption on the ammonium acetate-treated zeolite better than the Freundlich isotherm model (Table 1). The maximum sorption capacity (i.e., q_m) derived from the Langmuir isotherm was greater for the manganese nodule (i.e., 9.7 mg g^{-1}) than the zeolite-based adsorbents than the (i.e., 5.8 and 8.1 mg g^{-1}). However, the affinity of the binding sites (i.e., K_d) was greater for the zeolite than the other adsorbents (Table 1).

3.1.2. Effect of pH on K Sorption

In this study, pH conditions were changed to find out the effect of pH on K sorption with three adsorbents. Figure 3 compares the maximum K sorption capacity of the three adsorbents used in this study derived from the Langmuir isotherm model.

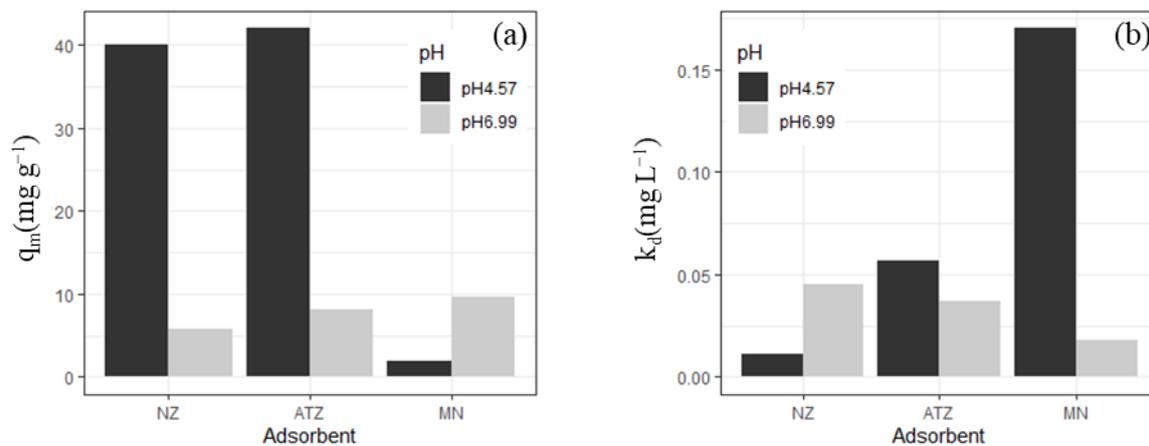


Figure 3. (a) Maximum potassium (K) sorption capacity (q_m) and (b) the affinity of the binding sites (K_d) of the natural zeolite (NZ), ammonium acetate-treated zeolite (ATZ), and manganese nodule (MN) at pH 4.57 and 6.99 derived from the Langmuir isotherm model.

The maximum K sorption capacity was greater under acidic condition for the zeolite-based adsorbents, while it was greater under neutral condition for the manganese nodule (Figure 3a). On the other hand, the affinity of the binding sites increased with increasing pH for the natural zeolite, while the opposite was observed with the treated zeolite and the manganese nodule (Figure 3b).

Adsorption process can be affected by several factors including temperature, pH, and contact time [3]. As pH increases, the sorbent surface becomes more negatively charged resulting in more metal uptake [16]. Previous study reported a positive linear relationship between the ammonium ion (NH_4^+) sorption on natural zeolite and the pH condition [17]. The NH_4^+ sorption capacity increased by about 30% as pH increased from 4 to 7. Moreover, the sorption of lead (Pb) and copper (Cu) on zeolite increased with increasing pH from 3 to 5 [16,18]. However, the opposite was observed with K in our study (Figure 3a). The K sorption capacity decreased with increasing pH from 4.57 to 6.99 (Figure 3a). The presence of other ions such as sodium (Na^+) ion and lithium ion (Li^+) can compete with K^+ ions for sorption sites. A recent study reported that, under the coexistence of Li^+ , K^+ , and Na^+ ions, EAB zeolite showed higher selectivity towards sorption of Na^+ and K^+ ions over Li^+ ions, and the sorption of K^+ ions was preferred over Na^+ ions [19]. In this study, when pH was adjusted to neutral pH conditions, phosphate buffers (NaH_2PO_4 - Na_2HPO_4) were used, and the Na^+ ion added with the buffers may compete with K^+ ion in K sorption.

3.2. K Sorption Kinetics

The K sorption kinetics were studied in order to find out information about the rate of K adsorption on the natural zeolite and the ammonium acetate-treated zeolite, since they were better adsorbent than the manganese nodule. With the natural zeolite, the equilibrium

reached approximately after 24 h (indicated with the dashed line in Figure 4a). With the ammonium acetate-treated zeolite, the equilibrium almost reached within 2 h (indicated with the dashed line in Figure 4a).

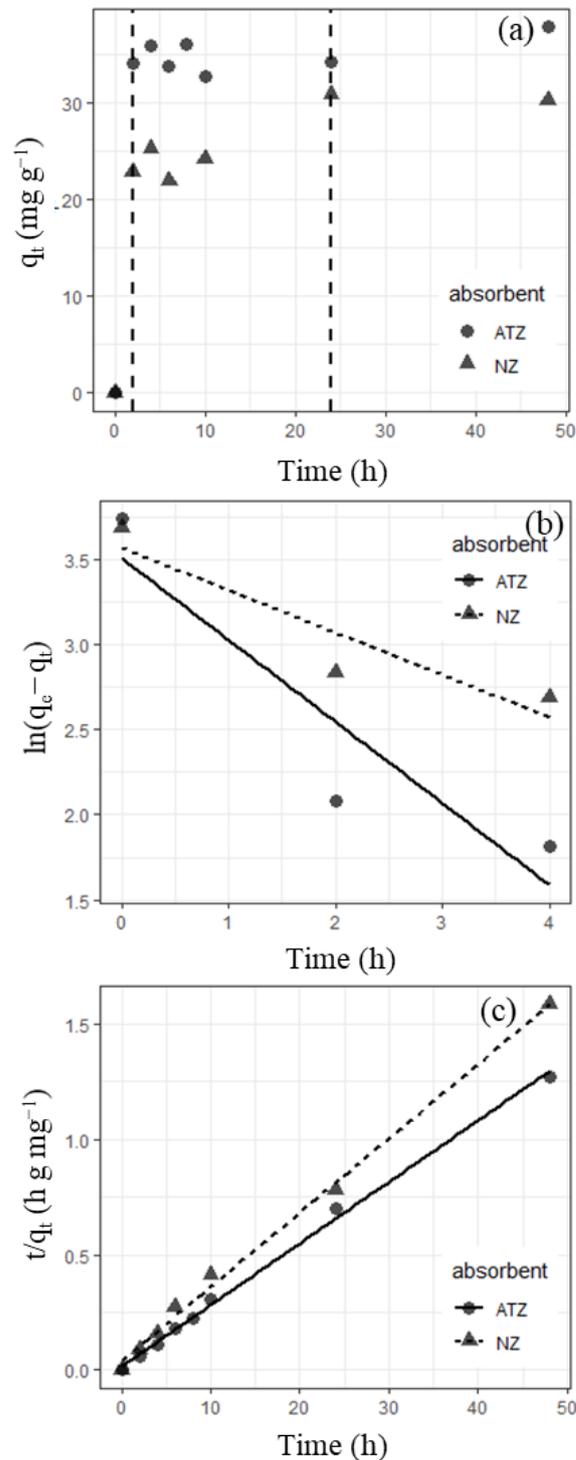


Figure 4. (a) Adsorbed amounts of potassium (K) on zeolite-based adsorbents with respect to time, (dashed line: the moments where each system reaches equilibrium); (b) the pseudo-first-order kinetics equation fitted to the 4 h K sorption data (solid line: ammonium acetate-treated zeolite, dashed line: natural zeolite); and (c) the pseudo-second-order kinetics equation fitted to the 72 h K sorption data (solid line: ammonium acetate-treated zeolite, dashed line: natural zeolite).

The K sorption was fitted to the pseudo-first-order kinetics equation (Equation (3)) and the pseudo-second-order kinetics equation (Equation (4)). The pseudo-first-order kinetics equation, written by Lagergren and modified by Na and Park, can demonstrate the relationship between adsorption amount at equilibrium and the reaction rate of adsorbents and adsorbate, in the aqueous solution [20,21]. The pseudo-second-order kinetics equation, written by Ho and McKay and modified by Na and Park, can represent surface adsorption including chemisorption [21–23]. The q_e values obtained in 3.1.1 were used in the kinetics equation.

For both the natural zeolite and the ammonium acetate-treated zeolite, not a single straight line could fit all the K sorption data over 48 h with the pseudo-first-order kinetics, since no further sorption was observed after 2 h. Thus, only the initial three data were fitted to the pseudo-first-order kinetics to derive the parameters (Figure 4b). This means that the pseudo-first-order kinetics are not suitable for predicting the K sorption on zeolite over the entire sorption period (i.e., 48 h). The pseudo-second-order kinetics equation could fit a straight line to the entire K sorption data over 48 h (Figure 4c). Moreover, the R^2 values indicate that pseudo-second-order kinetics are more suitable than pseudo-first-order kinetics for K sorption with both the natural zeolite and ammonium acetate treated-zeolite (Table 2). This suggests that the rate-controlling step during the K sorption reaction on zeolite was the chemical sorption [3]. Both the pseudo-first-order rates and the pseudo-second-order rates show that the K sorption on the ammonium acetate treated-zeolite was faster than that on the natural zeolite (Table 2).

Table 2. Parameters of kinetic models for K adsorption by natural zeolite and ammonium acetate-treated zeolite.

Adsorbent	Pseudo-First-Order			Pseudo-Second-Order			
	k_1 (h^{-1})	q_e (mg g^{-1})	R^2	k_2 ($\text{g mg}^{-1} \text{h}^{-1}$)	q_e (mg g^{-1})	h ($\text{mg g}^{-1} \text{h}^{-1}$)	R^2
Natural zeolite	0.249	39.9	0.857	0.0266	31.0	25.7	0.996
Ammonium acetate-treated zeolite	0.480	42.0	0.852	4.46	3.75	62.6	0.997

3.3. K Recovery from Seawater

K adsorption experiments using seawater were carried out to verify the effects of different K concentrations and pH conditions on K recovery from seawater using natural zeolite, ammonium acetate-treated zeolite, and manganese nodule. The K recovery on natural zeolite generally increased with increasing initial K concentration at pH 8.33 (Figure 5a). The K recovery from seawater by natural zeolite ranged 4–14% (Figure 5a). The ammonium acetate-treated zeolite also showed increasing K recovery with increasing K concentration from 23 mg L^{-1} to 50 mg L^{-1} at pH 8.33; however, further increase in the K concentration did not increase the K recovery (Figure 5b). The ammonium acetate-treated zeolite showed approximately 5–12% of K recovery. The manganese nodule showed a different trend with other adsorbents and had the highest recovery at the lowest concentration used at pH 8.33 (i.e., 23 mg L^{-1}) (Figure 5c). The manganese nodule had the K recovery of 0–22%, and the maximum recovery was observed with the diluted seawater sample (i.e., initial K concentration of 23 mg L^{-1}) at pH 8.33. Except for this condition (i.e., initial K concentration of 23 mg L^{-1} at pH 8.33), the zeolite-based adsorbents showed higher K recovery than the manganese nodule, and the K recovery was not affected by the pH conditions.

The results observed are similar to that observed with the KCl solutions (see Section 3.1.2). With the KCl solution, the zeolite-based adsorbent adsorbed more K than the manganese nodule at acidic pH condition, while the manganese nodule adsorbed more K at neutral pH condition (Figure 3a). With the seawater, regardless of the initial K concentrations, more K was recovered using the zeolite-based adsorbents at acidic pH condition (Figure 5).

At alkaline pH condition, the zeolite-based adsorbents were better for K recovery than the manganese nodule, except at the initial K concentration of 23 mg L^{-1} (Figure 5).

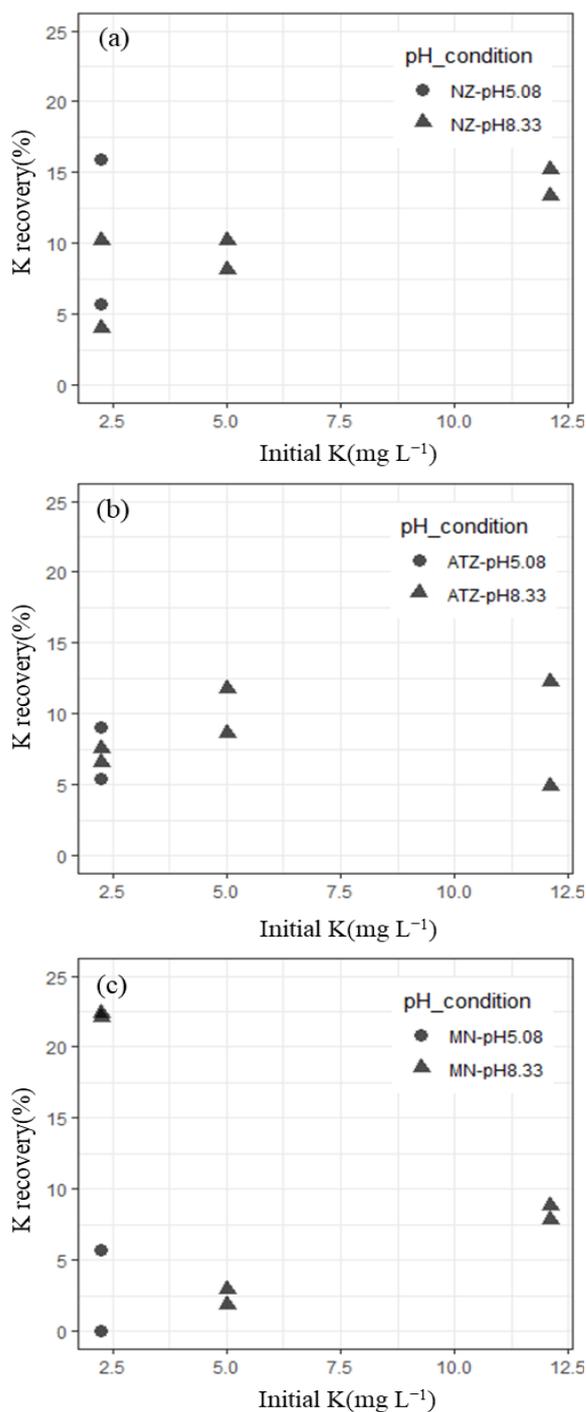


Figure 5. Recovery rate of potassium (K) by (a) natural zeolite (NZ), (b) ammonium acetate–treated zeolite (TZ), and (c) manganese nodule (MN) at various initial K concentrations (i.e., diluted seawater (23 mg L^{-1}), raw seawater (50 mg L^{-1}), and concentrated seawater (120 mg L^{-1})) at different pH conditions (i.e., $\text{pH } 5.08 \pm 0.04$ and $\text{pH } 8.33 \pm 0.15$).

Figure 6 compares the K sorption ability of three adsorbents in the KCl solutions and seawater. At low K concentrations (i.e., 23 mg L^{-1}), the K sorption was the greatest with the ammonium acetate-treated zeolite in the KCl solution at pH 4.57 (Figure 6a). However, with the KCl solution at pH 6.99 and seawater at pH 8.33, the manganese nodules generally

showed higher sorption capacities than the others (Figure 6a). At K concentrations of 50 and 120 mg L⁻¹, the zeolite-based adsorbents were more effective in K recovery from the acidic KCl solutions and seawater, while the manganese nodules were more effective for the neutral KCl solutions (Figure 6b,c). Except for the K recovery from the acidic KCl solution, the manganese nodules can be a comparable or better K adsorbent.

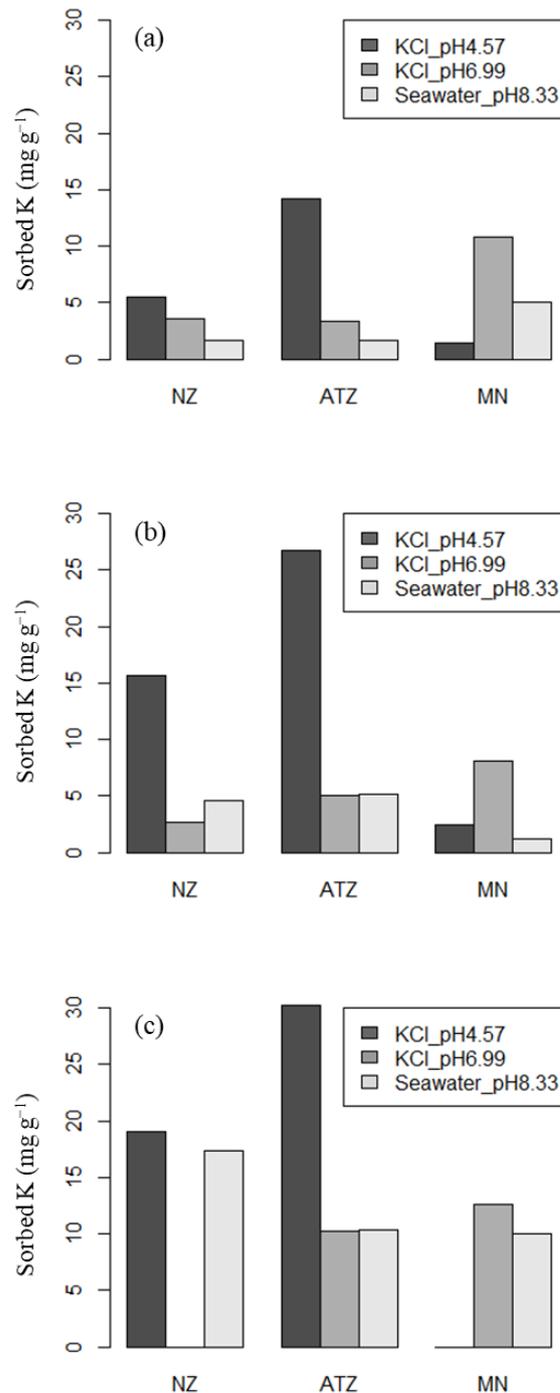


Figure 6. Sorption of potassium (K) on different adsorbents (i.e., natural zeolite (NZ), ammonium acetate-treated zeolite (ATZ), and manganese nodule (MN)) at average K concentration of (a) 23 mg L⁻¹, (b) 50 mg L⁻¹, and (c) 120 mg L⁻¹ at KCl pH 4.57, KCl pH 6.99, and seawater pH 8.33. Note that the absence of bar graphs in NZ and MN implies that there was no adsorption to those adsorbents.

Based on the K sorption on each adsorbent, the K recovery from the seawater was generally less than that from the KCl solutions (Figure 6). This could be attributed to the interference of other ions such as chlorine and Na, which account for more than 80% in seawater. As the K concentration in seawater increases, so do the other ions in seawater, and they will compete with K for adsorption. Considering such competition between mixtures of ions, K from waters and seawaters containing K and other ions can be more efficiently recovered using zeolite-based adsorbents than manganese nodule.

3.4. Regeneration Study with KCl Solutions

Figure 7 shows the changes in the amount of K sorbed on the natural zeolite and ammonium acetate-treated zeolite with respect to the number of repeated sorption tests. The average amounts of K sorbed on unit mass of both zeolites tend to decrease with the increasing number of repeated sorption tests (Figure 7). However, the reduction in the K sorption capacity was not statistically significant up to the third sorption test with the natural zeolite (Figure 7a), while the first and the fourth tests showed a statistically significant difference (p -value = 0.013). With the ammonium acetate-treated zeolite, the K sorption capacity of the first test was significantly greater than the following sorption tests (p -value < 0.05), but the K sorption capacities of the second and the third sorption tests and the third and the fourth tests were statistically similar (p -value > 0.05) (Figure 7b).

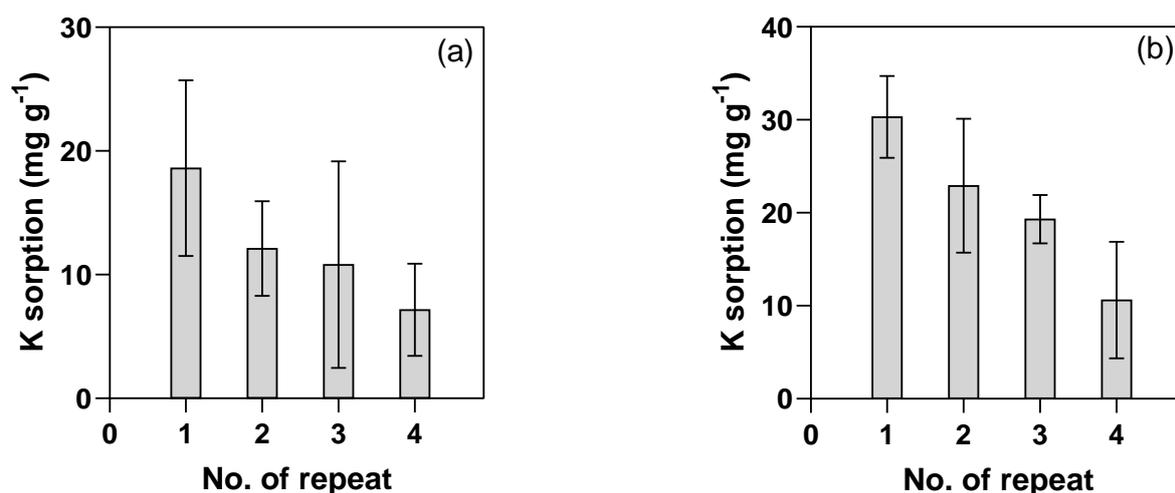


Figure 7. Changes in the potassium (K) sorption capacity with repeated sorption tests: (a) natural zeolite; (b) ammonium acetate-treated zeolite. The adsorbents were regenerated after each sorption test with 0.5 N HCl.

The decreasing trend in the average K sorption capacity may be explained by the partial desorption of K during the regeneration process [3]. The K sorption capacity was greater for the ammonium acetate-treated zeolite than the natural zeolite (Figure 7); however, the natural zeolite tends to maintain its K sorption capacity up to three times of reuses, while the ammonium acetate-treated zeolite tends to reduce its K sorption capacity after the first use. This may be due to the loss of the effect of ammonium acetate treatment after repeated regeneration processes.

4. Conclusions

The K sorption characteristics with three adsorbents, natural zeolite, ammonium acetate-treated zeolite, and manganese nodule, were studied and compared to see the potential use of manganese nodule as an alternative K adsorbent. The amounts of K adsorption with all three adsorbents increased with increasing initial K concentration. However, these three adsorbents showed different sorption characteristics depending on pH conditions. The manganese nodules show a comparable and, sometimes, better K recovery than the zeolite-based adsorbents under certain conditions; however, zeolite-

based adsorbents were generally still more suitable for K recovery considering competition between mixtures of ions in waters and seawaters. In particular, the natural zeolite can potentially be reused up to three times without losing its K sorption capacity. The K sorption capacity of the ammonium acetate-treated zeolite was higher than that of the natural zeolite, but the loss of K sorption capacity with the repeated uses was greater with the ammonium acetate-treated zeolite. Overall, the results show that the manganese nodule can potentially be used to recover K under certain conditions, but the zeolite-based adsorbents are generally better for K recovery from K-containing waters. This suggests that more studies on the K recovery using zeolite, including surface modified zeolite, are necessary to enhance the K recovery from seawater. Furthermore, studies on other alternative adsorbents are required.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/app11188660/s1>, Figure S1. SEM images of three adsorbents used in this study. (a) Natural zeolite, (b) ammonium acetate-treated zeolite, and (c) manganese nodule.

Author Contributions: S.S.: methodology, formal analysis, visualization, writing—original draft, writing—review and editing; E.H.J.: conceptualization, data curation; methodology; formal analysis; writing—original draft; writing—review and editing; visualization; supervision; project administration; funding acquisition; H.P.: conceptualization; methodology; writing—review and editing, funding acquisition; S.L.: conceptualization; methodology; writing—review and editing; J.H.K.: data curation; formal analysis; writing—review and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This study was funded by the National Research Foundation of Korea (NRF-2018R1C1B6002702; NRF-2020R1I1A1A01070853; NRF-2021R1A2C4001746).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available upon request from the corresponding author.

Acknowledgments: This study was funded by the National Research Foundation of Korea (NRF-2018R1C1B6002702; NRF-2020R1I1A1A01070853; NRF-2021R1A2C4001746). The authors also thank Moon Kyu Kim for helping with the preparation of the experiments.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Guo, X.-F.; Ji, Z.-Y.; Yuan, J.-S.; Zhao, Y.-Y.; Liu, J. Recovery of K⁺ from concentrates from brackish and seawater desalination with modified clinoptilolite. *Desalin. Water Treat.* **2015**, *57*, 6829–6837. [\[CrossRef\]](#)
2. Loganathan, P.; Naidu, G.; Vigneswaran, S. Mining valuable minerals from seawater: A critical review. *Environ. Sci. Water Res. Technol.* **2016**, *3*, 37–53. [\[CrossRef\]](#)
3. Park, H.; Singhal, N.; Jho, E.H. Lithium sorption properties of HMnO in seawater and wastewater. *Water Res.* **2015**, *87*, 320–327. [\[CrossRef\]](#)
4. Hou, J.; Yuan, J.; Shang, R. Synthesis and characterization of zeolite W and its ion-exchange properties to K⁺ in seawater. *Powder Technol.* **2012**, *226*, 222–224. [\[CrossRef\]](#)
5. Yuan, J.; Zhao, Y.; Li, Q.; Ji, Z.; Guo, X. Preparation of potassium ionic sieve membrane and its application on extracting potash from seawater. *Sep. Purif. Technol.* **2012**, *99*, 55–60. [\[CrossRef\]](#)
6. Epstein, J.; Altaras, D.; Feist, E.; Rosenzweig, J. The recovery of potassium chloride from Dead Sea brines by precipitation and solvent extraction. *Hydrometall.* **1975**, *1*, 39–50. [\[CrossRef\]](#)
7. Ghara, K.K.; Korat, N.; Bhalodia, D.; Solanki, J.; Maiti, P.; Ghosh, P.K. Production of pure potassium salts directly from sea bitter employing tartaric acid as a benign and recyclable K⁺ precipitant. *RSC Adv.* **2014**, *4*, 34706–34711. [\[CrossRef\]](#)
8. Naidu, G.; Jeong, S.; Johir, A.H.; Fane, A.G.; Kandasamy, J.; Vigneswaran, S. Rubidium extraction from seawater brine by an integrated membrane distillation-selective sorption system. *Water Res.* **2017**, *123*, 321–331. [\[CrossRef\]](#)
9. Guo, H.; Peng, C.; Kou, C.-J.; Jiang, J.-Y.; Zhang, F.; Yuan, H.-T. Adsorption mechanism of recovering potassium from seawater by modified-clinoptilolite using microwave. *J. Water Reuse Desalin.* **2017**, *8*, 102–110. [\[CrossRef\]](#)
10. Santiago, O.; Walsh, K.; Kele, B.; Gardner, E.; Chapman, J. Novel pre-treatment of zeolite materials for the removal of sodium ions: Potential materials for coal seam gas co-produced wastewater. *SpringerPlus* **2016**, *5*, 571. [\[CrossRef\]](#)

11. Warner, T.E.; Klokke, M.G.; Nielsen, U.G. Synthesis and Characterization of Zeolite Na-Y and Its Conversion to the Solid Acid Zeolite H-Y. *J. Chem. Educ.* **2017**, *94*, 781–785. [[CrossRef](#)]
12. Agrawal, A.; Sahu, K. Kinetic and isotherm studies of cadmium adsorption on manganese nodule residue. *J. Hazard. Mater.* **2006**, *137*, 915–924. [[CrossRef](#)]
13. Mallick, S.; Dash, S.; Parida, K. Adsorption of hexavalent chromium on manganese nodule leached residue obtained from NH₃-SO₂ leaching. *J. Colloid Interface Sci.* **2006**, *297*, 419–425. [[CrossRef](#)]
14. Pan, L.; Zhang, A.-B.; Sun, J.; Ye, Y.; Chen, X.-G.; Xia, M.-S. Application of ocean manganese nodules for the adsorption of potassium ions from seawater. *Miner. Eng.* **2013**, *49*, 121–127. [[CrossRef](#)]
15. Park, K.-H.; Nam, C.-W.; Kim, H.-I.; Park, J.-T. Treatment of metal wastes with manganese nodules. *J. Korean Inst. Res. Recycl.* **2005**, *14*, 17–21.
16. Kabwadza-Corner, P.; Johan, E.; Matsue, N. pH Dependence of Lead Adsorption on Zeolites. *J. Environ. Prot.* **2015**, *06*, 45–53. [[CrossRef](#)]
17. Kithome, M.; Paul, J.W.; Lavkulich, L.M.; Bomke, A.A. Effect of pH on ammonium adsorption by natural Zeolite clinoptilolite. *Commun. Soil Sci. Plant Anal.* **1999**, *30*, 1417–1430. [[CrossRef](#)]
18. Kyziol-Komosinska, J.; Rosik-Dulewska, C.; Franus, M.; Antoszczyszyn-Szpicka, P.; Czupiol, J.; Krzyżewska, I. Sorption Capacities of Natural and Synthetic Zeolites for Cu (II) Ions. *Pol. J. Environ. Stud.* **2015**, *24*, 1111–1123. [[CrossRef](#)]
19. Tong, Y.; Yuan, D.; Zhang, W.; Wei, Y.; Liu, Z.; Xu, Y. Selective exchange of alkali metal ions on EAB zeolite. *J. Energy Chem.* **2021**, *58*, 41–47. [[CrossRef](#)]
20. Lagergren, S. About the theory of so-called adsorption of soluble substances. *Kungl. Svenska. Ventenskapskad. Handl.* **1898**, *24*, 1–39.
21. Na, C.-K.; Han, M.-Y.; Park, H.-J. Applicability of Theoretical Adsorption Models for Studies on Adsorption Properties of Adsorbents (1). *J. Korean Soc. Environ. Eng.* **2011**, *33*, 606–616. [[CrossRef](#)]
22. Ho, Y.S.; McKay, G. A Comparison of Chemisorption Kinetic Models Applied to Pollutant Removal on Various Sorbents. *Process. Saf. Environ. Prot.* **1998**, *76*, 332–340. [[CrossRef](#)]
23. Robati, D. Pseudo-second-order kinetic equations for modeling adsorption systems for removal of lead ions using multi-walled carbon nanotube. *J. Nanostruct. Chem.* **2013**, *3*, 55. [[CrossRef](#)]