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Study on Heavy Metal Removal Rates According to Lithium Content in Post-Use Induction Top Plate Comminuted Powder

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Abstract: This study investigated the liquid-phase adsorption reactions of heavy metal ions (Pb, Cd, Cr^{6+}, Hg) in wastewater using post-use Li_2O-Al_2O_3-SiO_2 crystalline glass derived from induction top plate materials. The heavy metal ion adsorption characteristics were compared using samples before and after the Li removal process in LAS sample. The amount of zeolite used as an adsorbent, adsorption time, concentration of heavy metal elements, and pH were examined for their effects on adsorption capacity. Lithium-removed zeolite demonstrated an average improvement of 30% in heavy metal adsorption ability compared to conventional LAS zeolite. As the amount of zeolite added increased, the heavy metal adsorption removal rate also increased. Adsorption reaction time significantly influenced adsorption characteristics, with a notable improvement in the removal rate of Cd. Additionally, the adsorption removal rate of Cd increased with increasing pH, while that of Pb and Cr^{6+} decreased. The adsorption characteristics of Hg were not significantly affected by pH.

Keywords: Lithium, Zeolite, LAS, Metal Adsorption

1. INTRODUCTION

Zeolite, an industrial mineral with various potential values, is defined as a crystalline hydrated aluminosilicate with a robust three-dimensional structure. Pure zeolite possesses a specific gravity of approximately 2.0-2.3 and a refractive index of around 1.44-1.52, featuring uniform micropores of approximately 3-20 Å. Currently, over 200 types of zeolites with diverse pore structures are known, including approximately 50 natural zeolites and 150 synthetic zeolites for specialized industrial applications, such as industrial catalysts and synthetic detergent promoters [1-4].

The fundamental structure of all zeolites consists of a (Si, Al)O_4 framework structure surrounded by cavities (surface pores) occupied by relatively large cations and water molecules, which are interconnected by shared oxygen atoms in pairs of tetrahedra. The negative charge of the AlO_4 unit is balanced by the presence of exchangeable cations. These ions can be readily replaced by other substances, such as heavy metals or ammonium ions. This phenomenon is called cation exchange, which allows zeolites to possess properties such as cation exchangeability and reversible dehydration property by enabling free activity of cations, such as sodium, potassium, calcium, and some incidental cations like magnesium, barium, strontium, and iron, as well as water within the structure. The porous framework structure of zeolite enables molecular sieve reactions for the separation of molecular mixtures depending on the size and shape of the molecular compounds. Clinoptilolite, a type of zeolite with a relatively high cation exchange capacity, is well-known as a powerful adsorbent for toxic gases such as hydrogen sulfide (H_2S) and sulfur dioxide (SO_2) [5-10].

Major application areas where the unique selective ion exchange and adsorption properties of zeolite can be utilized include the treatment of livestock and agricultural wastewater, domestic sewage treatment, industrial wastewater treatment, drinking water quality improvement, radioactive waste treatment and prevention of radioactive contamination, and removal of soil-contaminating components during waste disposal and incineration processes. Loizidou and Townsend mentioned that not only the selective ion exchange properties of natural zeolite for the removal of heavy metals from aqueous solutions but also the recyclability of zeolite is essential. They suggested that natural ferrierite and mordenite exhibit lower exchange capacity for lead compared to clinoptilolite but are useful for removing lead from wastewater [11]. Studies by Semmens and Seyfarth showed that natural clinoptilolite (especially when pretreated with concentrated NaCl) exhibits very high selectivity for heavy metal removal from wastewater. In particular, research on the treatment of multi-metal-contaminated wastewater showed that using clinoptilolite treated with 2N NaCl, 90% of heavy metals were removed within 15 minutes of contact time. Their studies revealed that the selectivity of clinoptilolite follows the order $Pb^{2+}>Cu^{2+}>Cd^{2+}>Zn^{2+}>Cr^{3+}>Co^{2+}>Ni^{2+}$ [12]. Blachard et al. conducted a study on a purification process using a bed made of clinoptilolite to remove ammonium ions and heavy metals, thus purifying drinking water. They reported that a Na-clinoptilolite layer exhibited selectivity for contaminants, including heavy metals, in the order of $Pb^{2+} > NH^{4+} > Cd^{2+}$, Cu^{2+}, $Sr^{2+} > Zn^{2+} > Co^{2+}$ [5]. Typically, the maximum purification effect can be easily achieved by combining chemical precipitation, activated carbon columns, anion exchange materials, and clinoptilolite [13]. Such a method results in the removal efficiency of ammonium at 90%, phosphorus at 90-99%, suspended solids at 99%, and organic matter at 94%. Kayablai and Kezer suggested that using natural zeolite instead of typical clay in landfills reduces the required thickness of liners and decreases groundwater damage caused by leachate [14].

In this study, liquid-phase adsorption experiments were conducted on heavy metal ions (Pb, Cd, Cr^{6+}, Hg) present in wastewater using post-use Li_2O-Al_2O_3-SiO_2 crystalline glass derived from induction top plate materials. The removal rate of heavy metal elements in industrial wastewater was compared using zeolite after the removal of lithium. The changes in adsorption capacity were investigated depending on the adsorption reaction conditions, such as the amount of zeolite used as an adsorbent, adsorption time, concentration of heavy metal elements, and pH.

2. MATERIALS AND METHODS

2.1 Materials

The Lithium Aluminum Silicate (LAS) sample used in this study was a powder obtained by comminuting and recovering induction top plates. XRD analysis revealed that LAS is composed of a mixture of (Li, Mg, Zn)1.7$Al_2O_4SiO_6O_{12}$ and $ZrTiO_4$ as shown in Figure **1**. SEM-EDS measurement results are shown in Figure **2**.

The LAS sample was subjected to liberation using ball mills and planetary mills. When a ball mill was used, the comminuted LAS contained approximately 87.3% 100 mesh oversize, 8.1% 100-270 mesh size, and 270 mesh under-size. When a planetary mill was used, the comminuted LAS contained approximately 13.3% 100 mesh oversize 24% 100-270 mesh size, and 62.7% 270 mesh under-size. In this experiment, the 270 under size LAS sample comminuted using planetary and ball mills was used. XRF and ICP measurement results based on mesh size are shown in Table **1**. The LAS sample contained valuable metals such as Li (1.56%), Zn (1.20%), Mg (0.26%), Fe (0.24%), Al (9.37%), Ti (1.36%), Zr (1.33%), and Si (28.9%). When converted to oxides, this corresponds to Li_2O (3.35%), ZnO (1.5%), MgO (0.44%), Fe_2O_3 (0.34%), Al_2O_3 (17.7%), TiO_2 (2.27%), ZrO_2 (1.8%), and SiO_2 (62%).

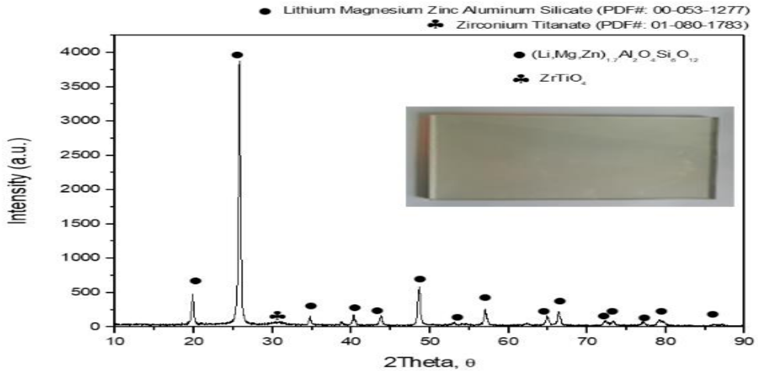


Figure 1: Raw LAS sample (top) and XRD analysis results of the raw LAS sample (bottom).

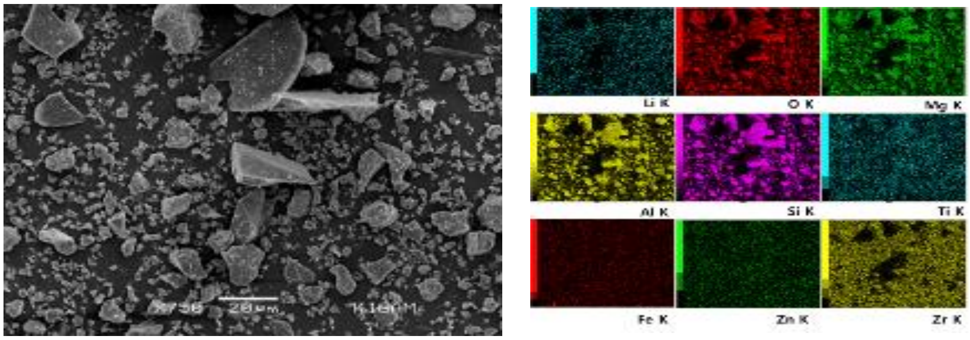


Figure 2: SEM analysis of the raw LAS sample (left) and mapping analysis results of the raw LAS sample (right).

Table 1: Distribution of valuable metals in LAS by liberation

Unit: wt.%

Mesh	Li	Zn	Mg	Fe	Al	Ti	Zr	Si
6 over	1.55	1.25	0.27	0.22	9.90	1.35	1.29	28.20
6-12	1.50	1.23	0.33	0.23	9.15	1.21	1.19	26.00
12-18	1.65	1.17	0.26	0.25	9.55	1.36	1.33	26.95
18-40	1.55	1.24	0.27	0.26	9.25	1.34	1.35	27.30
40-60	1.50	1.22	0.28	0.24	8.80	1.36	1.33	30.30
60-100	1.57	1.21	0.25	0.30	9.58	1.51	1.41	31.20
100-270	1.61	1.11	0.26	0.15	9.21	1.46	1.35	29.50
270-325	1.57	1.21	0.22	0.25	9.36	1.35	1.44	29.60
325 under	1.51	1.20	0.24	0.26	9.56	1.34	1.33	31.40

2.2 EXPERIMENTAL METHODS

2.2.1. Lithium Removal Method

Lithium was removed from the induction top plate comminuted powder through a mixed sulfuric acid thermal reaction. First, the LAS sample was mixed with sulfuric acid (95%) at a 1:2 mass ratio and placed in an alumina crucible. Subsequently, a thermal reaction was conducted in an electric furnace under an Ar atmosphere to induce phase transformation of Li in the LAS. The optimal conditions were determined by conducting the experiment at reaction temperatures of 300, 400, and 500℃ and a reaction time of 1 hour. The samples, after completing the thermal reactions, were mixed with 1L of distilled water and stirred for 30 minutes to leach lithium sulfate and remove impurities. To recover only the zeolite, a vacuum filter was used to separate the liquid and solid phases. The recovered zeolite was dried for more than 24 hours in a 95℃ oven to remove moisture. The zeolite was analyzed for phase content using an X-ray diffractometer (XRD) and the residual lithium content was measured using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES).

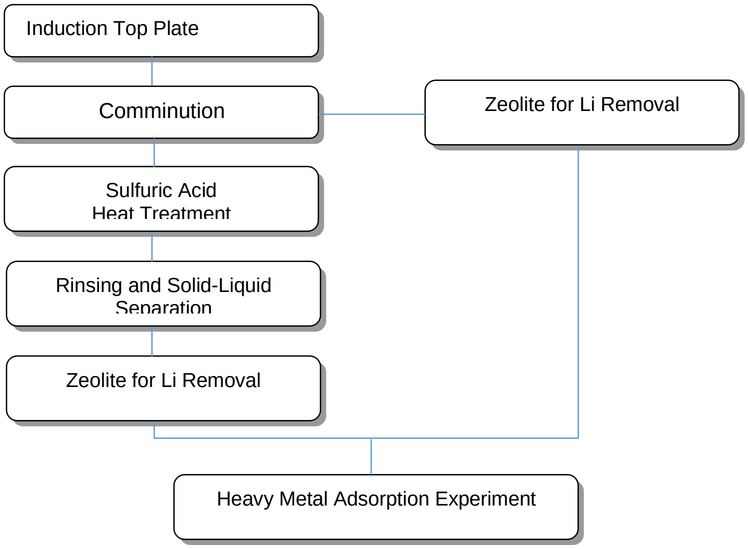


Figure 3: Overall experimental process diagram.

2.2.2. Heavy Metal Adsorption Process

Optimal conditions for the adsorption characteristics of four heavy metal elements (Pb, Cd, Cr6+, Hg) using zeolite were investigated. LAS zeolite recovered by comminuting induction top plates and lithium-removed zeolite were used in the experiment. A 1.000 ppm standard solution from KANTO was used as the standard solution for investigating the adsorption characteristics of heavy metal elements. Acetic acid (99.0% purity) and ammonia solution (25% purity) were used as reagents for pH adjustment. Experiments were conducted to investigate the effects of zeolite addition on heavy metal solutions, the influence of stirring time, the influence of concentration changes, and the influence of pH changes. After the experiments, the remaining amounts of the four heavy metal elements in the liquid phase were measured to calculate the adsorption removal rate. The measurements of the four heavy metal elements remaining in the liquid phase after adsorption was performed using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES).

3. RESULTS AND DISCUSSION

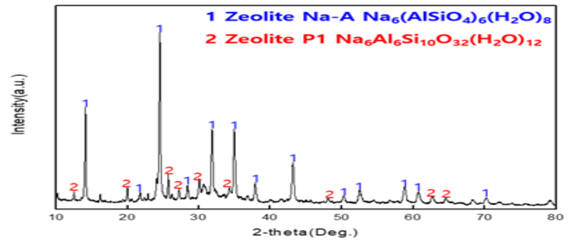
3.1 Lithium Removal Using Sulfuric Acid (Temperature, Concentration)

A mixture of 5 g LAS sample and 10 ml sulfuric acid was placed in an alumina crucible. Thermal reactions were conducted at temperatures of 300, 400, and 500℃ in an Ar atmosphere in an electric furnace, maintaining a reaction time of 1 hour. The following is the expected reaction formula between lithium compounds in the LAS sample and sulfuric acid:

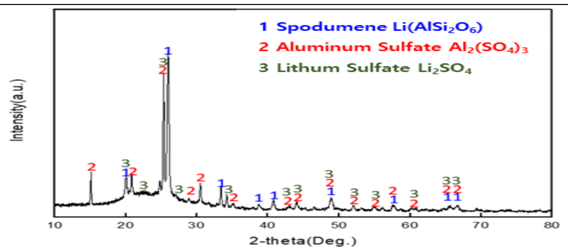
$$2LiAlSi_2O_6(s) + H_2SO_4(l) = Li_2SO_4(aq) + Al_2O_3(s) + 4SiO_2(s) + H_2O \qquad (1)$$

After the thermal reaction, the samples were rinsed with distilled water to remove lithium sulfate and impurities. Since lithium sulfate has a solubility in water and zeolite does not, the difference in solubility was utilized to separate the phases. The thermal reaction products were mixed with 1L of distilled water and stirred for 30 minutes. After stirring, a vacuum filter was used to separate the liquid and solid phases. The recovered zeolite was then dried for more than 24 hours in a 95℃ oven to remove internal moisture. As residual moisture in the zeolite can affect the heavy metal removal rate, it was thoroughly dried to remove moisture.

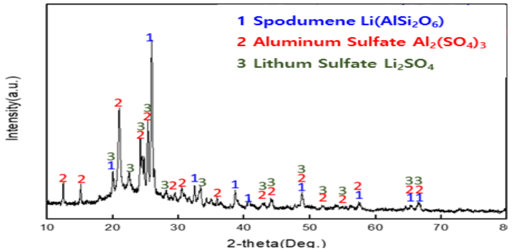
The experimental results are summarized in Figure **4**, and phase transformations of Li compounds were confirmed in all temperature ranges. At 300℃, no residual lithium compound phases were observed in the XRD analysis, and a 96.47% lithium removal rate was confirmed.



300℃



400℃

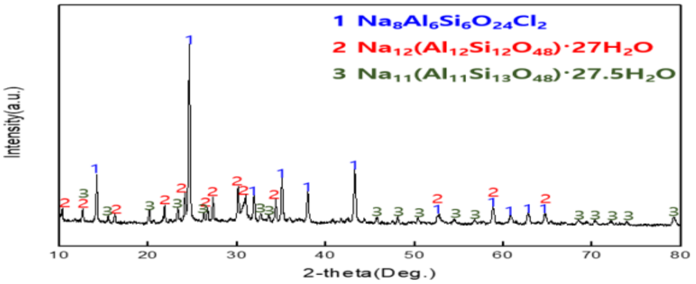


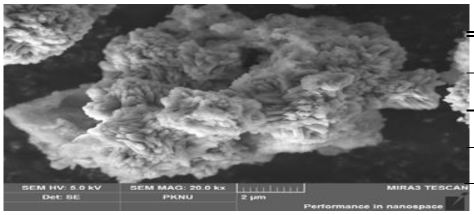
500℃

Sample Name	Raw Material Li Content (wt%)	Zeolite Li Content (wt%)	Li Removal Rate (%)
300℃	1.56	0.055	96.47
400℃		0.146	90.64
500℃		0.193	87.63

Figure 4: Results of lithium removal thermal reaction experiment using sulfuric acid (XRD).

After the lithium removal process, the zeolite structure was decomposed and an additional synthesis process was carried out to synthesize the zeolite phase. Using 50 wt.% 50 ml NaOH solution, 5 g of the thermal reaction product from the sulfuric acid lithium removal was mixed and sintered at 90℃ to produce Na-type zeolite. Additionally, the zeolite was analyzed by XRD, SEM, and XRF, and the results are shown in Figure **5**.





Element and Content (wt.%)			
Si	Al	Na	Ti
50.5	24.1	10.1	5.0
Zn	Mg	Zr	Fe
2.9	1.9	1.4	0.2

Figure 5: Analysis results of lithium-removed zeolite LAS.

3.2 Influence of the Amount of Zeolite Added

The heavy metal adsorption performance depending on the amount of LAS zeolite and lithium-removed zeolite added was measured. 1, 2, 3, 4, and 5 g of zeolite samples were each added to 200 mL beakers containing 50 mL of Pb, Cd, Cr^{6+}, and Hg heavy metal solutions at 100 ppm, and stirred for 30 minutes at a speed of 300 rpm. After stirring, the liquid phase was separated and the remaining four heavy metal elements in the liquid phase were measured. Adsorption by adsorbents, such as zeolites, occurs in three stages. The first stage involves the transport and diffusion of organic materials through water to the solid-liquid interface. In the second stage, the organic material is dispersed through the pores of the adsorbent. Lastly, the diffused organic material is adsorbed onto the surface of the micropores of the particles. The adsorbable surface area includes both the outer surface of the particles and the pore surface. In fact, the pore surface area is much larger than the particle surface area, and most adsorption occurs on the pore surface.

The amount of substance adsorbed onto the adsorbent depends on the amount and properties of the adsorbate, as well as the temperature. The total amount of adsorbed substance is determined by the function of concentration at a constant temperature, which is called the isothermal adsorption equation. The Freundlich, Langmuir, and BET equations are examples of isothermal adsorption equations, with the Freundlich equation being most commonly used in constant or wastewater treatment plant water conditions. The Freundlich equation is an empirical adsorption equation defined by $\frac{X}{M} = KC^{1/n}$, where X is the amount of adsorbate (mg) adsorbed, M is the adsorbent concentration, C is the adsorbate concentration after adsorption, K is the Freundlich capacity coefficient, and 1/n is the Freundlich sensitivity variable. In this study, heavy metal removal experiments were conducted under identical concentration and temperature conditions, and heavy metal concentrations in the solution before and after the experiment were measured to calculate the heavy metal adsorption removal rate using the following equation:

$$Adsorption\ Removal\ Rate = \frac{c_i - c_f}{c_i} \times 100(\%) \qquad (2)$$

Using the equation with C_i representing the initial concentration (ppm) and C_f representing the solution concentration after the adsorption experiment (ppm), the heavy metal removal rate was calculated. The results, as shown in Table **2**, confirmed that the removal rate of heavy metals increased as the amount of zeolite added to the solution with the same concentration of heavy metals increased. After adding 2 g of zeolite, most heavy metal concentrations did not change significantly, indicating that the best condition for this specific heavy metal solution is to add 2 g of zeolite.

Table 2: Heavy Metal Concentration and Removal Rates after Experiment Depending on the Amount of Zeolite Added

LAS Zeolite					**Lithium-removed Zeolite**				
Zeolite (g)	**Residual Concentration (ppm)**				**Zeolite (g)**	**Residual Concentration (ppm)**			
	Pb	Cd	Cr6+	Hg		Pb	Cd	Cr6+	Hg
1	0.41	79.31	97.15	94.48	1	0.42	6.38	91.12	57.55
2	0.35	70.06	95.12	92.85	2	0.34	5.77	94.14	55.59
3	0.34	54.22	92.23	96.34	3	0.32	2.35	90.22	51.58
4	0.36	43.17	92.45	95.25	4	0.25	0.92	96.26	50.45
5	0.24	30.02	81.57	96.12	5	0.25	0.61	93.28	46.14
Zeolite (g)	**Heavy Metal Removal Rate (%)**				**Zeolite (g)**	**Heavy Metal Removal Rate (%)**			
	Pb	Cd	Cr6+	Hg		Pb	Cd	Cr6+	Hg
1	99.59	20.69	2.85	5.52	1	99.58	93.62	8.88	42.45
2	99.65	29.94	4.88	7.15	2	99.66	94.23	5.86	44.41
3	99.66	45.78	7.77	3.66	3	99.68	97.65	9.78	48.42
4	99.64	56.83	7.55	4.75	4	99.75	99.08	3.74	49.55

5	99.76	69.98	18.43	3.88	5	99.75	99.39	6.72	53.86

Both LAS zeolite and lithium-removed zeolite showed no significant changes in heavy metal removal rates from the results with 2g or more of the added amount. Overall, it was confirmed that the heavy metal removal rate improved as the amount of zeolite added increased. In the case of lithium-removed zeolite, the heavy metal removal rate of Cd and Hg increased compared to the original LAS zeolite, but it was not effective in removing Cr^{6+}.

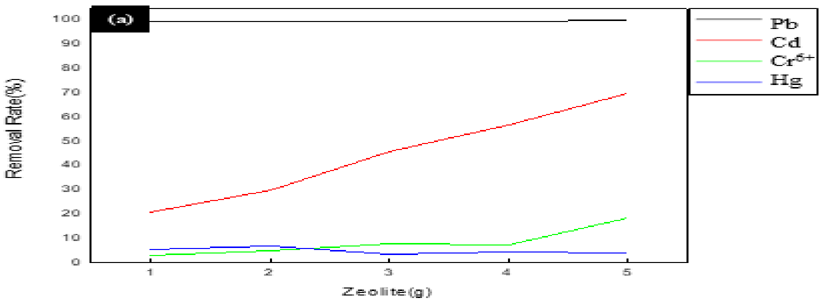


Figure 6: Influence of Zeolite Addition Amount on Heavy Metal Removal Rate (a) LAS Zeolite / (b) Lithium-removed Zeolite.

3.3 Influence of Stirring Time

2 g of zeolite powder was mixed with 100 ppm 50 ml heavy metal solution. The stirring speed was maintained at 300 rpm. To investigate the changes in heavy metal removal rates depending on the stirring time, the stirring time was changed to 10, 30, 60, 90, and 120 minutes. The concentration of heavy metal solution before and after the heavy metal removal experiment was measured using ICP-OES. The experimental results are shown in Table **3**. The heavy metal removal rate was calculated according to Equation (1) using the measured heavy metal solution concentration and is represented in Table **3** and Figure **7**.

It was confirmed that the heavy metal removal rate increased as the stirring time increased in all zeolite and heavy metal solution experimental conditions. In all results, it was confirmed that the heavy metal concentration decreased as the stirring time increased.

Table 3: Heavy Metal Concentration and Removal Rates after Experiment Depending on Stirring Time

LAS Zeolite					**Lithium-removed Zeolite**				
Time (min)	**Residual Concentration(ppm)**				**Tine (min)**	**Residual Concentration(ppm)**			
	Pb	**Cd**	**Cr6+**	**Hg**		**Pb**	**Cd**	**Cr6+**	**Hg**
10	0.61	78.48	95.45	94.47	**10**	0.49	6.47	90.14	57.39
30	0.52	69.78	92.78	92.48	**30**	0.38	5.09	87.45	56.33
60	0.47	55.59	92.48	92.41	**60**	0.37	2.68	88.25	57.24
90	0.41	42.47	81.15	91.12	**90**	0.24	0.85	87.23	53.23
120	0.28	28.52	77.15	90.31	**120**	0.23	0.41	87.64	53.12
Time (min)	**Heavy Metal Removal Rate (%)**				**Time (min)**	**Heavy Metal Removal Rate (%)**			
	Pb	**Cd**	**Cr6+**	**Hg**		**Pb**	**Cd**	**Cr6+**	**Hg**
10	99.39	21.52	4.55	5.53	**10**	99.51	93.53	9.86	42.61
30	99.48	30.22	7.22	7.52	**30**	99.62	94.91	12.55	43.67
60	99.53	44.41	7.52	7.59	**60**	99.63	97.32	11.75	42.76
90	99.59	57.53	18.85	8.88	**90**	99.76	99.15	12.77	46.77
120	99.72	71.48	22.85	9.69	**120**	99.77	99.59	12.36	46.88

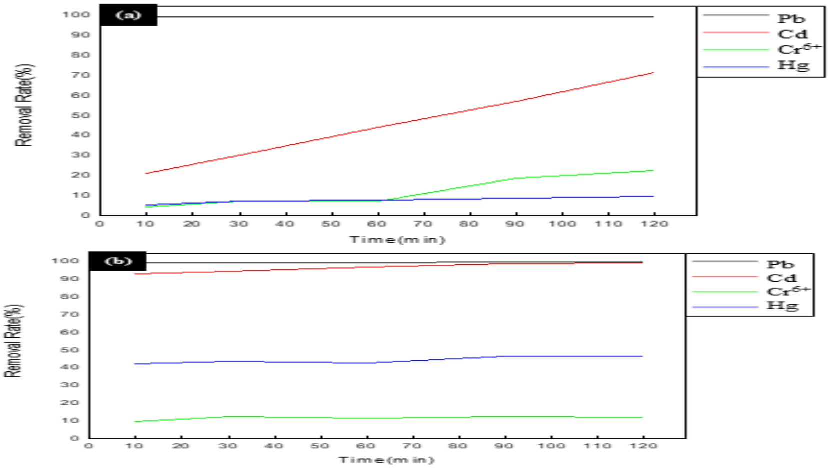


Figure 7: Influence of Stirring Time on Heavy Metal Removal Rate (a) LAS Zeolite / (b) Lithium-removed Zeolite.

In the case of Pb, as shown in Figure **7** and Table **3**, the heavy metal removal rate was very high, averaging over 99%. The removal rates of the remaining heavy metal elements, excluding Pb, increased with the stirring time but were not sufficiently removed. The heavy metal removal rate was in the order of Pb> Cd> $Cr^{6+} \geq$ Hg under the same conditions. Moreover, the lithium-removed zeolite showed a higher heavy metal removal rate than the original LAS zeolite.

Adsorbents such as zeolites have different adsorption characteristics depending on various conditions, including the size of the internal cavity, crystal structure, composition, and surface properties. Ion adsorption by adsorbents occurs rapidly at the active sites where ions can attach to the adsorbent surface. Then, it slowly diffuses into the internal cavity and reaches equilibrium, no longer showing adsorption performance. It is presumed that in the case of the two zeolites used in the experiment, most of Pb was adsorbed in the initial surface adsorption characteristics, showing a removal rate of over 99%. Cr6+ and Hg have research results showing poor adsorption characteristics with Na-zeolite used in the study, and similar results were obtained [12, 13].

In the Cd removal experiment results, the heavy metal removal rate increased linearly as the reaction time increased. Lithium-removed zeolite showed a higher average Cd removal rate than LAS zeolite, and the linear increase in removal rate over time was similarly confirmed. These results indicate that the zeolite used in the study is capable of sufficiently removing Cd, not only through the adsorption stage on the zeolite surface but also through the diffusion process into the internal cavity of the zeolite.

3.3 Effect of Concentration Change

A heavy metal removal experiment was conducted by mixing 2 g of zeolite powder and 50 ml of four types of heavy metal solutions. To examine the effect of initial heavy metal solution concentration, removal experiments were performed under five conditions with initial solution concentrations of 10, 30, 50, 70, and 100 ppm. The stirring speed was maintained at the same 300 rpm as before, and the stirring time was set to 30 minutes. The results are shown in Table **4** and Figure **8.**

Table 4: Residual heavy metal content and heavy metal removal rate after the experiment, depending on the initial heavy metal concentration

LAS Zeolite					Lithium-removed Zeolite				
Original Solution (ppm)	**Residual Concentration(ppm)**				**Original Solution (ppm)**	**Residual Concentration (ppm)**			
	Pb	**Cd**	**Cr6+**	**Hg**		**Pb**	**Cd**	**Cr6+**	**Hg**
10	0.51	3.20	8.20	9.12	**Figure 6:**	0.52	0.59	9.00	3.82
30	0.42	9.21	25.01	28.20	**Figure 6:**	0.43	1.71	26.45	12.21

50	0.30	16.14	41.23	44.01	**Figure 6:**	0.30	3.42	44.11	29.14
70	0.32	20.65	54.14	63.70	**Figure 6:**	0.32	3.22	62.12	35.15
100	0.29	31.41	81.41	89.01	**Figure 6:**	0.41	4.25	89.35	49.47
Original Solution (ppm)	**Heavy Metal Removal Rate (%)**				**Original Solution (ppm)**	**Heavy Metal Removal Rate (%)**			
	Pb	**Cd**	**Cr6+**	**Hg**		**Pb**	**Cd**	**Cr6+**	**Hg**
10	94.90	68.00	18.00	8.80	**Figure 6:**	94.80	94.10	10.00	61.80
30	98.60	69.30	16.63	6.00	**Figure 6:**	98.57	94.30	11.83	59.30
50	99.40	67.72	17.54	11.98	**Figure 6:**	99.40	93.16	11.78	41.72
70	99.54	70.50	22.66	9.00	**Figure 6:**	99.54	95.40	11.26	49.79
100	99.71	68.59	18.59	10.99	**Figure 6:**	99.59	95.75	10.65	50.53

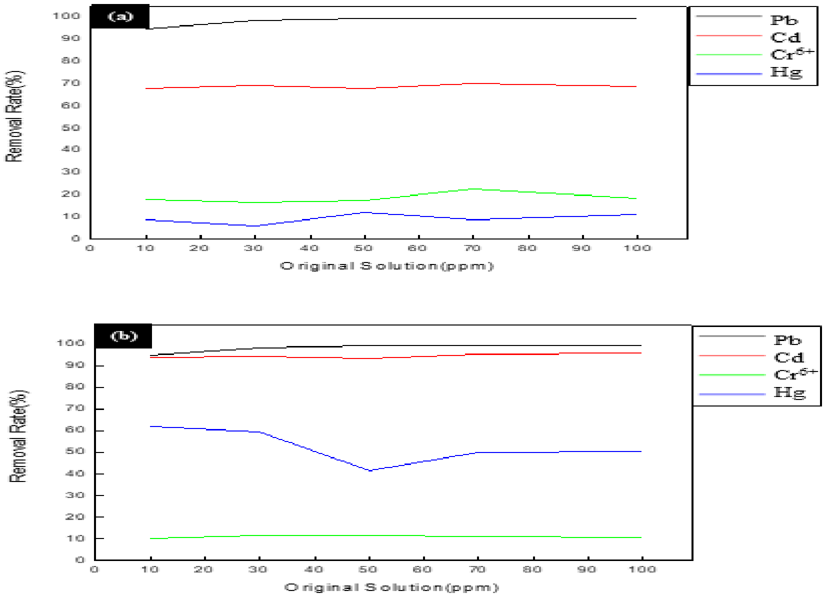


Figure 8: The influence of initial heavy metal solution pH on heavy metal removal rate (a) LAS Zeolite, (b) Lithium-removed Zeolite.

As shown in the experimental results, the initial solution concentration did not significantly affect the removal rate of heavy metal elements, except for Pb, in both zeolites. For Cd, a similar heavy metal removal rate was observed as in the previous 30-minute stirring time effect experiment, and there was no influence of the initial heavy metal solution concentration on Cd in particular. Only for Pb was a linear improvement in heavy metal removal rate observed depending on the initial heavy metal solution concentration. Considering this result along with the stirring time effect experiment, it is inferred that the zeolites used in the experiment mainly removed Pb through surface adsorption.

3.4 Effect of pH Change

2 g of zeolite powder was mixed with 50 ml of four types of heavy metal solutions with a concentration of 100 ppm. The stirring speed was maintained at 300 rpm, and the stirring time was set to 30 minutes. Experiments were conducted to determine the effect of heavy metal solution pH on heavy metal removal rate. Acetic acid and ammonia were used for pH adjustment of the solution, as they do not cause phase changes in the zeolite. A 1M solution of each was prepared for pH adjustment. Adsorption experiments were conducted at pH conditions of 3, 5, 7, 9, and 11.

First, the effect of zeolite mixed with distilled water on the pH of the solution was investigated. When 2 g of zeolite was mixed with 50 ml of distilled water, the initial pH of LAS zeolite was found to be between 7 and 7.2, maintaining neutrality. Lithium-removed zeolite was also measured to have a pH of 6.5 to 7.7. Thus, it was confirmed that zeolite does not significantly affect the pH of the solution. The results of heavy metal adsorption experiments depending on pH are shown in Table **5** and Figure **9**.

Table 5: Residual heavy metal content and heavy metal removal rate after the experiment, depending on pH

LAS Zeolite					**Lithium-removed Zeolite**				
pH	**Residual Concentration(ppm)**				**pH**	**Residual Concentration(ppm)**			
	Pb	**Cd**	**Cr6+**	**Hg**		**Pb**	**Cd**	**Cr6+**	**Hg**
3	0.15	78.02	76.18	89.01	**3**	0.15	3.25	78.12	56.12
5	0.22	69.04	82.68	90.23	**5**	0.21	2.18	84.15	54.17
7	0.30	55.51	84.54	87.89	**7**	0.31	1.19	87.48	54.98
9	0.52	42.12	89.12	91.25	**9**	0.48	0.71	87.68	55.94
11	0.64	38.23	90.11	89.21	**11**	0.61	0.62	91.14	48.48
pH	**Heavy Metal Removal Rate (%)**				**pH**	**Heavy Metal Removal Rate (%)**			
	Pb	**Cd**	**Cr6+**	**Hg**		**Pb**	**Cd**	**Cr6+**	**Hg**
3	99.85	21.98	23.82	10.99	**3**	99.85	96.75	21.88	43.88
5	99.78	30.96	17.32	9.77	**5**	99.79	97.82	15.85	45.83
7	99.70	44.49	15.46	12.11	**7**	99.69	98.81	12.52	45.02
9	99.48	57.88	10.88	8.75	**9**	99.52	99.29	12.32	44.06
11	99.36	61.77	9.89	10.79	**11**	99.39	99.38	8.86	51.52

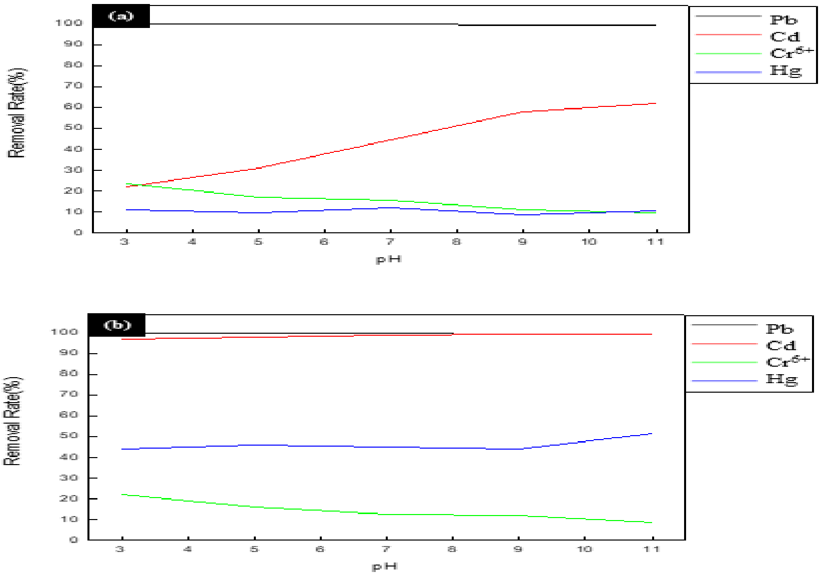


Figure 9: The influence of initial heavy metal solution concentration on heavy metal removal rate (a) LAS Zeolite, (b) Lithium-removed Zeolite.

As shown in Table **5** and Figure **9**, the removal rate of Pb and Cr^{6+} decreased with increasing pH, while the removal rate of Cd increased. The removal rate of Hg was not significantly affected by pH changes. It has been reported that generally, zeolites, activated carbon, and adsorbents tend to show a decrease in metal element adsorption capacity at low pH. This is because adsorbents tend to combine with hydrogen ions instead of metal adsorption, and this competition leads to a decrease in the adsorption rate. Also, as the pH of the solution increases, the surface of mineral substances like zeolite increases its negative charge. This dehydrogenation reaction increases the negative charge on the surface, which acts as an active site for element adsorption and promotes the adsorption reaction of heavy metal species. However, the experimental results showed that the heavy metal removal rate of Pb and Cr6+ decreased with increasing pH. It seems that the ammonia used for controlling the pH of the solution was adsorbed on the zeolite instead of heavy metal ions, resulting in a decreased heavy metal removal rate. For Cd, the heavy metal removal rate linearly increased as the pH increased. After the heavy metal adsorption experiment for Cd, it was observed that the amount of recovered zeolite material increased compared to the original 2 g. It appears that the formation of hydroxides or solid precipitates due to the increase in pH improved the heavy metal removal rate.

CONCLUSION

Based on the experiments conducted using synthetic zeolites for the removal of heavy metals Pb, Cd, Cr^{6+}, and Hg, the following conclusions were drawn:

1. Under the same heavy metal solution concentration, stirring time, and pH conditions, the heavy metal removal rate increased as the amount of zeolite added increased.

2. The lithium-removed zeolite showed improved heavy metal removal performance compared to the original LAS zeolite, with a particularly increased removal rate for Cd and Hg.

3. An increase in stirring time under the same initial solution concentration, pH, and zeolite addition conditions significantly affected heavy metal removal. In particular, the heavy metal removal rate for Cd linearly increased as the stirring time increased.

4. No significant changes in the heavy metal removal rate were observed when the initial heavy metal solution concentration was the same, and other experimental conditions were identical.

5. As the pH increased, the heavy metal removal rate for Cd increased, while the removal rate for Pb and Cr^{6+} decreased. The pH of the initial heavy metal solution did not affect the removal rate of Hg.

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