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Study on Heavy Metal Adsorption Capacity According to Modification Conditions with Ca-Zeolite

Jei-Pil Wang[1*], Tserendejid bayarmaa[2]

[1]*College of Engineering, Pukyong National University, Busan, Republic of Korea.*

[2]*Department of Engineering, School of Technology in Darkhan, Mongolian University of Science and Technology, Mongolia, *Corresponding author: jpwang@pknu.ac.kr*

Abstracts: 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 in which Li had been removed through a sulfuric acid heat reaction. Two types of zeolites, before and after Ca^{2+} modification, were used for heavy metal adsorption. 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. Ca-zeolite showed an average adsorption removal rate improvement of 54.5% for Cr^{6+} and 79.5% for Hg compared to the original lithium-removed 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: Ca-Zeolite, Heavy Metal Adsorption, lithium Sulfate.

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 an (Si,Al)O4 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 AlO4 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 (H2S) and sulfur dioxide (SO2) [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 2+>Cu2+>Cd2+>Zn2+>Cr3+>Co2+>Ni2+

[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 Pb2+>NH4+>Cd2+,Cu2+, Sr2+>Zn2+>Co2+ [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, Cr6+, Hg) present in wastewater using post-use Li2O-Al2O3-SiO2 crystalline glass derived from induction top plate materials. Two samples were compared for the removal rates of heavy metal elements in industrial wastewater: zeolites prepared by removing Li from the LAS materials and zeolites modified with a CaCl2 solution. Additionally, the changes in adsorption capacity were investigated according to adsorption reaction conditions, including 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)1.7Al2O4SiO6O12 and ZrTiO4 (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 over size, 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 over size, 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 Li2O (3.35%), ZnO (1.5%), MgO (0.44%), Fe2O3 (0.34%), Al2O3 (17.7%), TiO2 (2.27%), ZrO2 (1.8%), and SiO2 (62%).

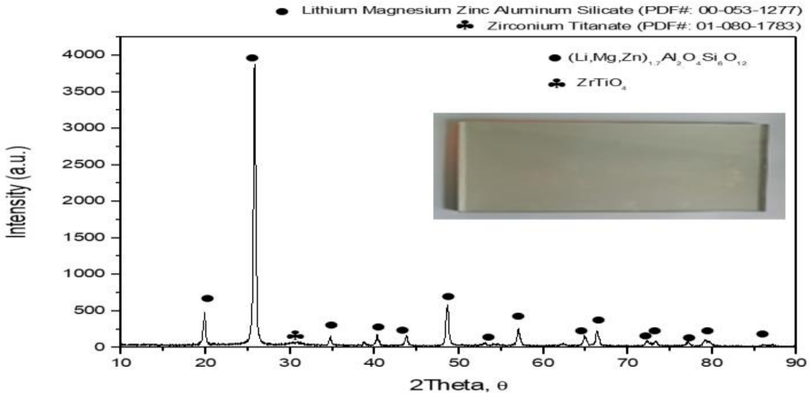


Figure 1: Raw LAS sample (top) and XRD analysis results of the raw LAS sample (bottom).

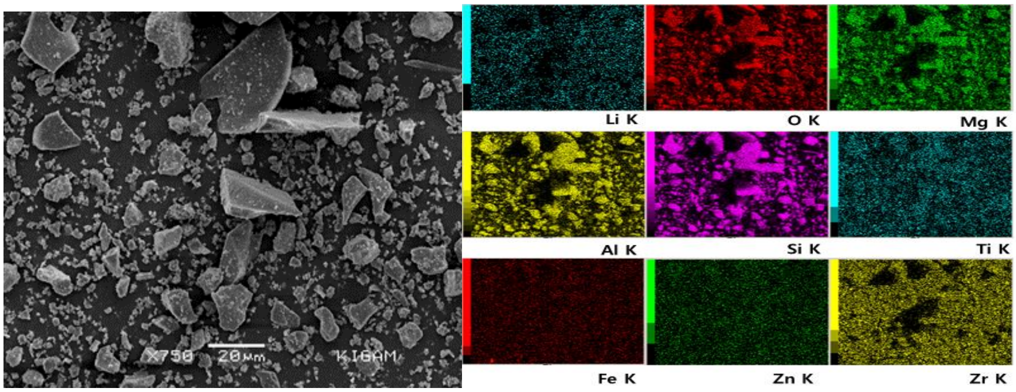


Figure 2: SEM analysis of the raw LAS sample (left) and mapping analysis results of the raw LAS sample (right)

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. Then, a thermal reaction was conducted in an electric furnace under an Ar atmosphere. The reaction temperature was set at 300, 400, and 500°C, with a reaction time of 1 hour. After the thermal reaction, the sample was mixed with distilled water and stirred for 30 minutes to remove lithium sulfate and other impurities. This process was repeated three times. Afterward, the zeolite recovered through the separation of liquid and solid phases was dried in a 95°C oven for more than 24 hours. 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).

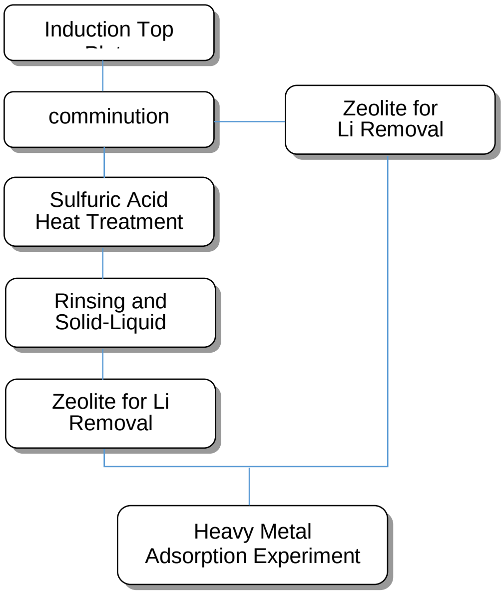


Figure 3: Overall experimental process diagram

2.2.2. Heavy Metal Adsorption Process

Ca-zeolite was prepared through the following process Lithium-removed zeolite obtained from the lithium removal process in LAS was utilized for the preparation of Ca-modified zeolite. After the lithium removal process, Ca-zeolite was synthesized through an ion-exchange process with a cationic solution containing dissolved Ca ions and Na-A type zeolite. First, the zeolite was dried in a dryer at a temperature above 90°C for 24 hours to remove all moisture inside the zeolite. Residual moisture in the zeolite's pore structure could affect the cation exchange process. CaCl2 (99%) was used to convert Na in the zeolite to the Ca form. A 1M CaCl2 solution was prepared for use. 10 g of zeolite was added to 1L of CaCl2 solution in a 1L beaker, and the mixture was stirred at 300 rpm for 24 hours. To replenish the decreased Ca ion concentration after 24 hours, the reacted solution was discarded and replaced with a fresh solution. This process was repeated three times to ensure that all Na-type zeolites underwent ion exchange. The modified zeolite was then mixed with 1L of distilled water and stirred at 300 rpm for 30 minutes, followed by filtration and drying at a temperature above 90°C for more than 24 hours to remove moisture. The Ca-form zeolite was confirmed for cation exchange by XRD analysis.

2.2.3. Heavy Metal Adsorption Process

Optimal conditions for the adsorption characteristics of four heavy metal elements (Pb, Cd, Cr6+, Hg) using zeolite were investigated. The experiments compared lithium-removed zeolite obtained from the comminuted induction top plate material (LAS) and Ca-form zeolite prepared using CaCl2 solution through cation exchange. The heavy metal removal rates were compared between Na-type zeolite and Ca-type zeolite to evaluate the impact of the main cationic material in the zeolite. 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 were performed using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES).

3.RESULTS AND DISCUSSION

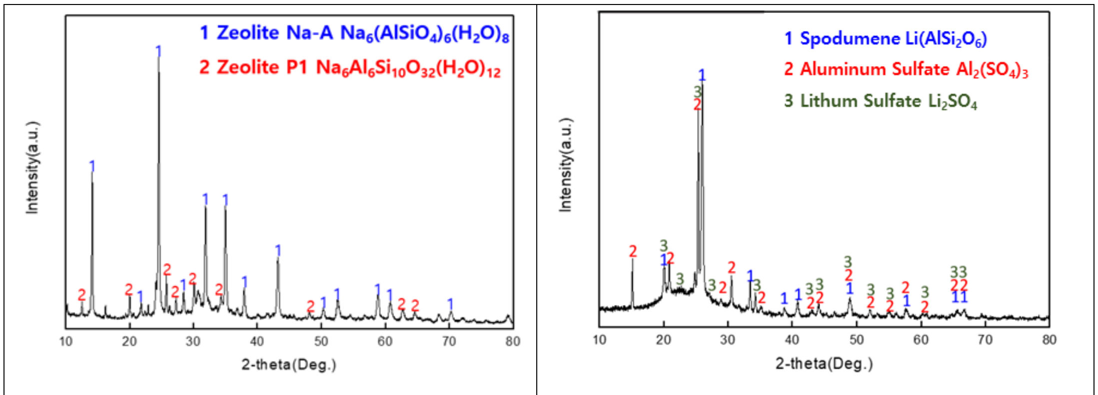
3.1 Lithium Removal Using Sulfuric Acid (Temperature, Concentration)

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:

$$2LiAlSi2O6(s) + H2SO4(l) = Li2SO4(aq) + Al2O3(s) + 4SiO2(s) + H2O \qquad (1)$$

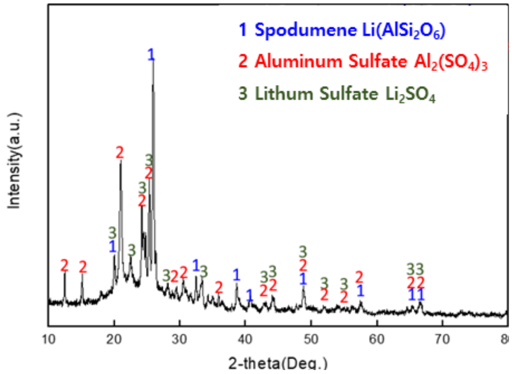
Lithium compounds in the LAS samples reacted with sulfuric acid to form lithium sulfate, which was subsequently removed during the following washing process. The reacted samples were mixed with 1L of distilled water and stirred for 30 minutes to remove lithium sulfate and other impurities. This process was repeated three times. Afterward, the recovered zeolite was then separated by filtration and dried at 95°C in an oven for more than 24 hours 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. Additionally, the 300°C zeolite was analyzed using SEM and XRF, as shown in Figure 5.



300 ℃

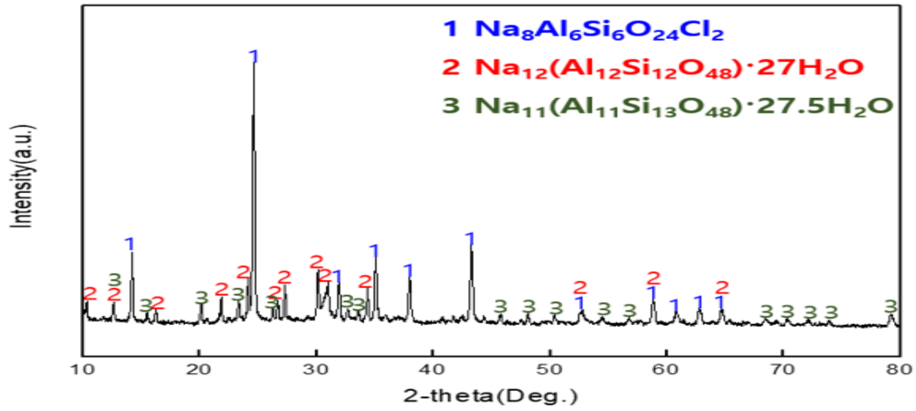
400℃

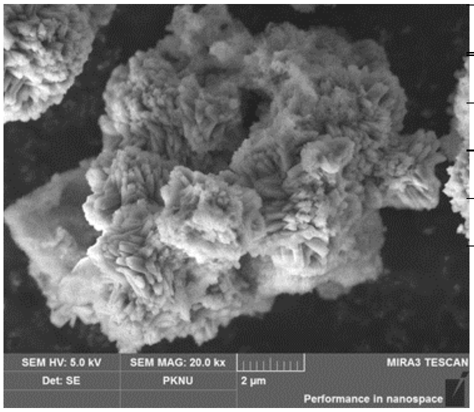


500℃

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).



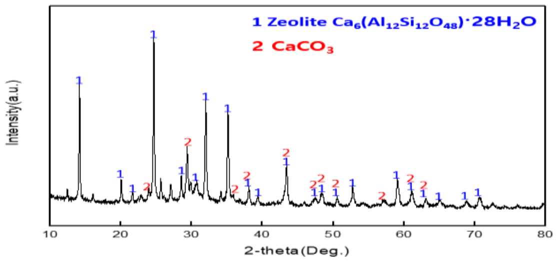


Element and Content (wt.%)			
Si	Al	Na	Ti
50.5	24.1	10.1	5.0
Zn	Mg	Zr	Fe
2.9	1.9	1.4	0.2

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

3.2 Results of Na-zeolite CaCl2 Modification Experiment

10 g of Li-removed zeolite and 1L of 1M CaCl2 were placed in a beaker and stirred at room temperature for 24 hours at 300 rpm. After 24 hours, an equal volume of the same concentration solution was replaced to recover the Ca ion concentration in the solution. This process was repeated three times to ensure the complete modification of Na-type zeolite to Ca-type zeolite. The reacted zeolite was separated from the solution, mixed with 1L of distilled water, and stirred at 300 rpm for 30 minutes. Then, the zeolite was recovered by vacuum filtration. The recovered zeolite was left in a dryer at 90°C or higher for over 24 hours to remove all moisture. The manufactured Ca-type zeolite was analyzed by XRD and XRF to confirm cation modification. It was confirmed that the original Na-type zeolite changed to Ca-type zeolite. The Na+ ions in the original zeolite were replaced with Ca2+, forming Ca-A type zeolite in the form of Ca6(Al12Si12O48)·28H2O from Na6(AlSiO4)6·(H2O)8.



Element and Content (wt.%)			
Si	Ca	Al	Na
29.84	25.15	24.46	8.6
Ti	Zn	Mg	Ba
5.41	1.98	1.58	1.47
Zr	K	Fe	
1.11	0.26	0.18	

Figure 5: Results of Na-zeolite CaCl2 Modification Experiment (XRD/XRF).

3.3 Influence of the Amount of Zeolite Added

The heavy metal adsorption performance depending on the zeolite addition amount was measured using Li-removed zeolite and CaCl2 modified zeolite. 1, 2, 3, 4, and 5 g of zeolite samples were each added to 200 mL beakers containing 50 mL of Pb, Cd, Cr6+, and Hg heavy metal solutions at 100 ppm, and stirred for 30 minutes at a speed of 300 rpm. The heavy metal solution concentration before and after stirring was measured by ICP-OES to determine the change in concentration. 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 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 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=(C_i-C_f)/C_i ×100(%)   (2)

Here; Ci is the initial concentration (ppm), and Cf is the solution concentration (ppm) after the adsorption experiment.

The heavy metal removal rate was calculated using this equation. The experimental results are shown in Table 2 and Figure 6, and it was confirmed that the heavy metal removal capacity improved as the addition amount of both zeolites increased in solutions with the same heavy metal concentration. However, the change was not significant when the addition amount was more than 2 g.

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

Lithium-removed Zeolite					**(a) Li-removed zeolite / (b) Ca-zeolite**				
Zeolite (g)	**Residual Concentration (ppm)**				**Zeolite (g)**	**Residual Concentration (ppm)**			
	Pb	Cd	Cr6+	Hg		Pb	Cd	Cr6+	Hg
1	0.42	6.38	91.12	57.55	**1**	0.42	0.91	45.45	12.34
2	0.34	5.77	94.14	55.59	**2**	0.33	0.74	43.42	12.24
3	0.32	2.35	90.22	51.58	**3**	0.25	0.72	40.12	9.79
4	0.25	0.92	96.26	50.45	**4**	0.19	0.73	41.02	10.98
5	0.25	0.61	93.28	46.14	**5**	0.17	0.72	42.45	10.97
Zeolite (g)	**Heavy Metal Removal Rate (%)**				**Zeolite (g)**	**Heavy Metal Removal Rate (%)**			
	Pb	**Cd**	**Cr6+**	**Hg**		**Pb**	**Cd**	**Cr6+**	**Hg**
1	99.58	93.62	8.88	42.45	**1**	99.58	99.09	54.55	87.66
2	99.66	94.23	5.86	44.41	**2**	99.67	99.26	56.58	87.76
3	99.68	97.65	9.78	48.42	**3**	99.75	99.28	59.88	90.21
4	99.75	99.08	3.74	49.55	**4**	99.81	99.27	58.98	89.02
5	99.75	99.39	6.72	53.86	**5**	99.83	99.28	57.55	89.03

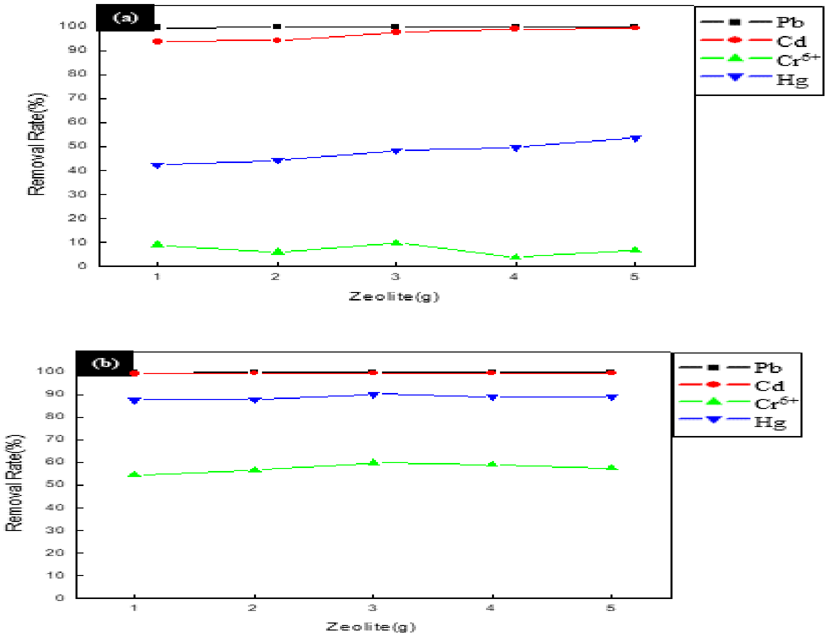


Figure 6: Influence of Zeolite Addition Amount on Heavy Metal Removal Rate (a) Li-removed zeolite, (b) Ca-zeolite.

Ca-zeolite also showed a similar trend in heavy metal removal rates as Li-removed zeolite. The adsorption capacity of Cr6+ and Hg in the Ca-zeolite adsorption experiment improved compared to Li-removed zeolite.

3.4 Effects of Stirring Time

Heavy metal removal experiments were conducted using 2 g each of Li-removed zeolite and Ca-zeolite. The heavy metal solution of 100 ppm 50 ml and 2 g of zeolite were mixed and stirred at 300 rpm. To check the removal ability according to the heavy metal removal time, stirring was performed for 10, 30, 60, 90, and 120 minutes. The heavy metal solution concentration before and after the experiment was measured using ICP-OES to calculate the change in heavy metal concentration. The measured heavy metal concentrations are shown in Table 3.

In all results, it was found that the heavy metal concentration decreased as the stirring time increased. In particular, it was observed that the heavy metal concentration of Cd decreased significantly as the stirring time increased.

Table 3: Heavy metal content and removal rate in the solution after the experiment depending on the stirring time

Lithium-removed Zeolite					(a) Li-removed zeolite / (b) Ca-zeolite				
Time (min)	**Residual Concentration (ppm)**				**Time (min)**	**Residual Concentration (ppm)**			
	Pb	**Cd**	**Cr6+**	**Hg**		**Pb**	**Cd**	**Cr6+**	**Hg**
10	0.49	6.47	90.14	57.39	**10**	0.42	0.98	45.12	12.01
30	0.38	5.09	87.45	56.33	**30**	0.35	0.79	43.12	11.12
60	0.37	2.68	88.25	57.24	**60**	0.24	0.78	42.55	10.15
90	0.24	0.85	87.23	53.23	**90**	0.17	0.65	41.68	9.54
120	0.23	0.41	87.64	53.12	**120**	0.13	0.52	41.69	10.12
Time (min)	**Heavy Metal Removal Rate (%)**				**Time (min)**	**Heavy Metal Removal Rate (%)**			
	Pb	**Cd**	**Cr6+**	**Hg**		**Pb**	**Cd**	**Cr6+**	**Hg**
10	99.51	93.53	9.86	42.61	**10**	99.58	99.02	54.88	87.99
30	99.62	94.91	12.55	43.67	**30**	99.65	99.21	56.88	88.88
60	99.63	97.32	11.75	42.76	**60**	99.76	99.22	57.45	89.85
90	99.76	99.15	12.77	46.77	**90**	99.83	99.35	58.32	90.46
120	99.77	99.59	12.36	46.88	**120**	99.87	99.48	58.31	89.88

The heavy metal removal rate calculated using equation (2) is shown in Table 3 and Figure 7. In all four heavy metal solutions, it was confirmed that the heavy metal removal rate increased as the stirring time increased.

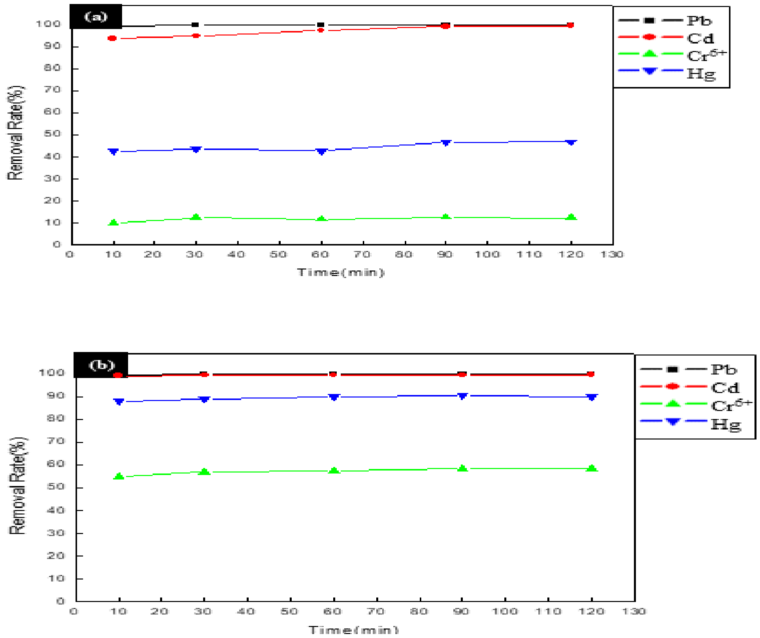


Figure 7: Influence of Stirring Time on Heavy Metal Removal Rate (a) Li-removed zeolite, (b) Ca-zeolite

As shown in Figure 7 and Table 3, both zeolites showed a very high average Pb removal rate of 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> Cr6+≥ Hg under the same conditions. Ca-zeolite, modified with CaCl2, showed an overall improvement in heavy metal removal rate compared to Li-removed zeolite. In particular, as seen in Figure 7, the removal rate of Cr6+ and Hg, which were not well removed in the original zeolite, has greatly improved. 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].

The removal rates of all four heavy metal elements improved with the increase of stirring time, but the effect of time on the removal of Cd was most significant. As shown in Figure 7, the removal rate of Cd exhibited a linear increase with time. In the mechanism of adsorbents like zeolites, it was found that Cd was not effectively removed during the surface adsorption stage. It seems that the removal effect of Cd is more significant as it diffuses into the zeolite structure. This was confirmed by the linear increase in the removal rate with the increase of time.

3.5 Effect of Concentration Change

2 g of zeolite powder was mixed with 50 ml of four heavy metal solutions at concentrations of 10, 30, 50, 70, and 100 ppm in a 200 ml beaker. The experiment was conducted to compare heavy metal removal rates depending on the initial heavy metal solution concentration, with the same zeolite addition amount. The stirring speed was maintained at 300rpm, and the stirring time was set at 30 minutes. The adsorption experiment results are shown in Table 4, and the calculated adsorption removal rates are shown in Figure 8.

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

Lithium-removed Zeolite					**(a) Li-removed zeolite / (b) Ca-zeolite**				
Original Solution (ppm)	**Residual Concentration (ppm)**				**Original Solution (ppm)**	**Residual Concentration (ppm)**			
	Pb	**Cd**	**Cr6+**	**Hg**		**Pb**	**Cd**	**Cr6+**	**Hg**
10	0.52	0.59	9.00	3.82	**10**	0.42	0.48	5.2	2.8
30	0.43	1.71	26.45	12.21	**30**	0.38	0.9	15.1	8.4
50	0.30	3.42	44.11	29.14	**50**	0.28	2.4	24.8	14.9
70	0.32	3.22	62.12	35.15	**70**	0.27	2.7	33.7	19.5
100	0.41	4.25	89.35	49.47	**100**	0.32	3.7	49.1	28
Original Solution (ppm)	**Heavy Metal Removal Rate (%)**				**Original Solution (ppm)**	**Heavy Metal Removal Rate (%)**			
	Pb	**Cd**	**Cr6+**	**Hg**		**Pb**	**Cd**	**Cr6+**	**Hg**
10	94.80	94.10	10.00	61.80	**10**	95.80	95.20	48.00	72.00
30	98.57	94.30	11.83	59.30	**30**	98.73	97.00	49.67	72.00
50	99.40	93.16	11.78	41.72	**50**	99.44	95.20	50.40	70.20
70	99.54	95.40	11.26	49.79	**70**	99.61	96.14	51.86	72.14
100	99.59	95.75	10.65	50.53	**100**	99.68	96.30	50.90	72.00

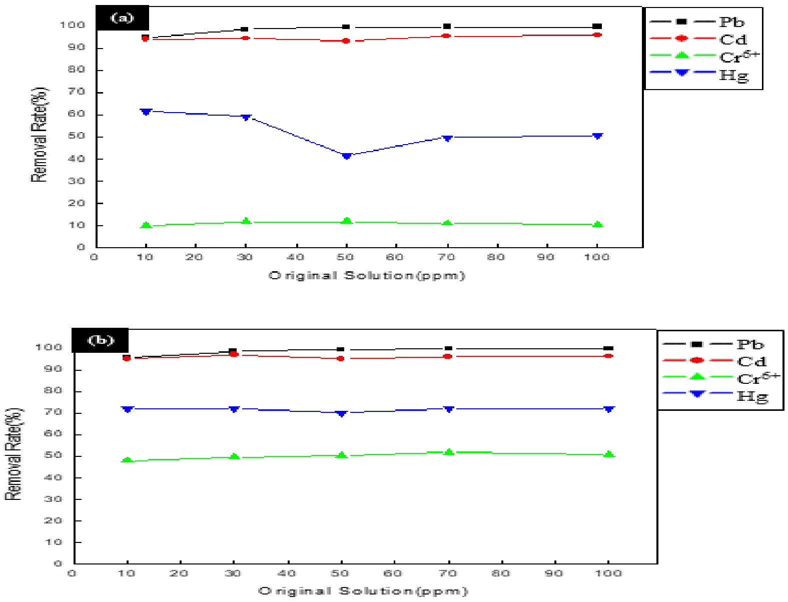


Figure 8: Influence of Stirring Time on Heavy Metal Removal Rate (a) Li-removed zeolite, (b) Ca-zeolite

As shown in Figure 8, both zeolites did not exhibit a significant effect on the heavy metal removal rates based on the initial heavy metal solution concentration. Only Pb showed a change in heavy metal removal rates depending on the initial heavy metal solution concentration. This is believed to be due to the fact that the adsorption of Pb is mostly removed by the surface adsorption characteristics of zeolite. Pb showed almost the same heavy metal removal rate regardless of the influence of time, and it seems that if the heavy metal concentration in the initial solution is low, the amount of adsorption decreases, resulting in a lower heavy metal removal rate. In the case of Cd, the same result was obtained as the heavy metal removal rate at the 30-minute condition when considering the effect of stirring time experiment. This shows that the removal mechanism of Cd is not only through surface adsorption characteristics but also through the diffusion inside the zeolite, which is consistent with the results obtained from the effect of stirring time experiment. In particular, Ca-zeolite modified with CaCl2 was more effective in removing Cr6+ and Hg than the original zeolite. In the case of Hg, the heavy metal removal rate improved by about 10% compared to lithium zeolite, and the removal rate of Cr6+ increased by more than 30%.

3.6 Effect of pH Change

2 g of zeolite powder was mixed with 50ml of four heavy metal solutions with a concentration of 100 ppm in a 200 ml beaker. 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 initial 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 initial pH was measured by mixing 2 g of zeolite with 50 ml of distilled water. Both types of zeolites had a pH of 6.5 to 7.7, which did not exceed the neutral solution range. Thus, it was confirmed that zeolite does not significantly affect the pH of the solution. The results of heavy metal adsorption experiments with zeolite depending on pH are shown in Table 7 and Figure 8.

Table 5: Residual heavy metal content and heavy metal removal rate after the experiment.

Li-removed zeolite					Ca-zeolite				
pH	Residual Concentration (ppm)				pH	Residual Concentration (ppm)			
	Pb	Cd	Cr^{6+}	Hg		Pb	Cd	Cr^{6+}	Hg
3	0.15	3.25	78.12	56.12	**3**	0.13	1.12	55.45	27.12
5	0.21	2.18	84.15	54.17	**5**	0.18	1.01	56.36	28.85
7	0.31	1.19	87.48	54.98	**7**	0.18	0.85	56.25	28.14

9	0.48	0.71	87.68	55.94	**9**	0.34	0.84	58.12	30.16
11	0.61	0.62	91.14	48.48	**11**	0.47	0.64	58.02	30.22
pH	**Heavy Metal Removal Rate (%)**				**pH**	**Heavy Metal Removal Rate (%)**			
	Pb	**Cd**	**Cr^{6+}**	**Hg**		**Pb**	**Cd**	**Cr^{6+}**	**Hg**
3	99.85	96.75	21.88	43.88	**3**	99.87	98.88	44.55	72.88
5	99.79	97.82	15.85	45.83	**5**	99.82	98.99	43.64	71.15
7	99.69	98.81	12.52	45.02	**7**	99.82	99.15	43.75	71.86
9	99.52	99.29	12.32	44.06	**9**	99.66	99.16	41.88	69.84
11	99.39	99.38	8.86	51.52	**11**	99.53	99.36	41.98	69.78

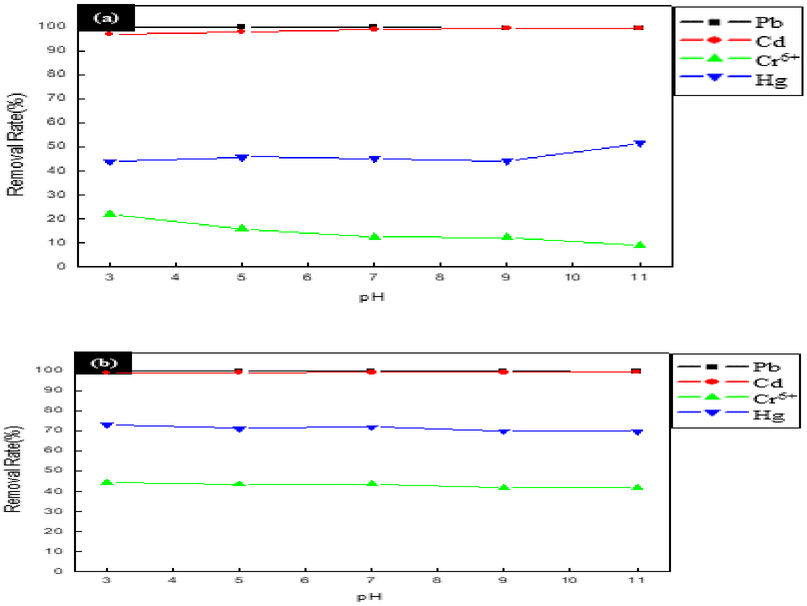


Figure 9: Effect of pH on heavy metal removal rate (a) Li-removed zeolite, (b) Ca-zeolite.

Table 5 and Figure 9 show the heavy metal removal rates of the zeolites depending on the initial pH of the heavy metal solution. For both zeolites, the removal rates of Pb and Cr6+ decreased with increasing pH. Although the change in heavy metal removal rate for Pb and Cr6+ was not significant depending on the pH, it showed a consistent decreasing trend. In the case of Cd, the heavy metal removal rate increased linearly with increasing pH. In the case of Hg, a nearly constant heavy metal removal rate was measured regardless of the pH change, confirming that pH does not affect the removal of Hg. 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 active sites 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.

CONCLUSION

Based on the experiments conducted using synthetic zeolites for the removal of heavy metals Pb, Cd, Cr6+, and Hg, the following conclusions were drawn;

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

2. Ca-zeolite, which was modified with CaCl2, showed improved overall heavy metal removal performance compared to the original zeolite produced by removing Li from LAS material, particularly for the removal of Cd and Hg, which were difficult to remove with the original zeolite.

3. It was confirmed that the stirring time had a significant impact on the heavy metal removal performance of zeolite, and the heavy metal removal rate increased with increasing time. However, the effect varied depending on the mechanism by which zeolite removed heavy metal elements.

4. The initial heavy metal concentration did not have a significant effect on the heavy metal removal rate of zeolite.

5. With the change in pH, the heavy metal removal rate of Cd increased as the pH increased. In contrast, Pb and Cr6+ removal rates decreased. Hg removal rate remained constant regardless of the initial heavy metal solution pH.

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