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

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**Abstracts:** In this study, synthetic zeolites were prepared using a sample obtained by removing Li from used LAS ($Li_2O$-$Al_2O_3$-$SiO_2$) crystallized glass, which is a material for induction top plates, through a sulfuric acid heat reaction. The removal experiment of heavy metals (Pb, Cd, $Cr^{6+}$, Hg) ions present in wastewater was conducted. Two types of zeolites were used for heavy metal adsorption: before and after $K^+$ modification. The changes in the amount of heavy metal adsorption 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. K-zeolite showed an average improvement of 54.5% for $Cr^{6+}$ and 79.5% for Hg compared to the conventional lithium removal zeolite. According to the experimental results of heavy metal removal under various conditions, the heavy metal adsorption removal rate increased as the amount of zeolite added increased. It was confirmed that the adsorption reaction time had a significant impact on the adsorption characteristics, and in particular, the removal rate of Cd greatly improved. For Cd, the removal rate improved as the pH increased, while for Pb and $Cr^{6+}$, the removal rate improved as the pH decreased. The removal rate of Hg was found to be similar across the entire pH range.

**Keywords:** K-Zeolite, LAS, 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 3-20Å. 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 zeolites for the removal of heavy metals from aqueous solutions are important, but also the possibility of zeolite regeneration and reuse. They suggested that natural ferrierite and mordenite, although showing a lower exchange capacity for lead compared to clinoptilolite, could be useful for removing lead from wastewater. In the study by Semmens and Seyfarth, it was shown that natural clinoptilolite (especially when pre-treated with concentrated NaCl) has very high selectivity for the removal of heavy metals 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. According to their research, the selectivity of clinoptilolite follows the order of Pb2+>Cu2+>Cd2+>Zn2+>Cr3+>Co2+>Ni2+. Blachard et al. studied the treatment process of purifying drinking water by removing ammonium ions and heavy metals using a bed of clinoptilolite. They found that the Na-clinoptilolite bed showed selectivity towards contaminants, including heavy metals, in the order of Pb2+>NH4+>Cd2+, Cu2+, Sr2+>Zn2+>Co2+.

Generally, the maximum purification effect can be easily achieved by combining clinoptilolite with other methods such as chemical precipitation, activated carbon columns, and anion exchange materials. The removal efficiency of pollutants through these methods is about 90% for ammonium, 90-99% for phosphorus, 99% for suspended solids, and 94% for organic matter. 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 to remove heavy metal ions (Pb, Cd, Cr6+, Hg) present in wastewater using zeolite synthesized from Li2O-Al2O3-SiO2 crystallized glass used as an induction top plate material. Two samples, zeolite produced by removing Li from the LAS material and zeolite modified with KCl solution, were used to compare the removal rates of heavy metal elements in industrial wastewater. 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.

## 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%).

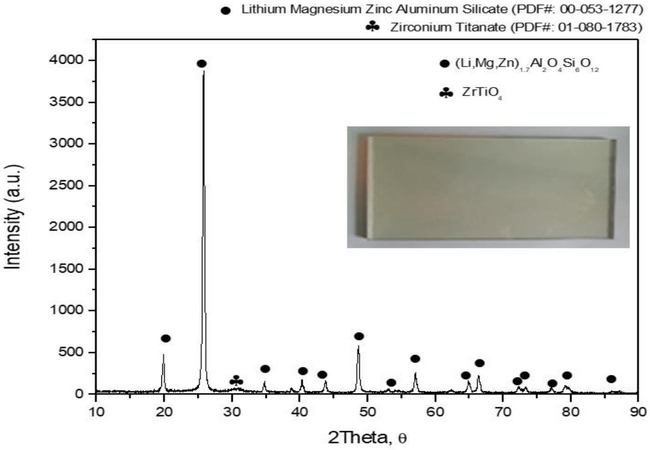


**Figure 1:** Raw LAS sample (top) and XRD analysis results of the raw LAS sample (bottom)

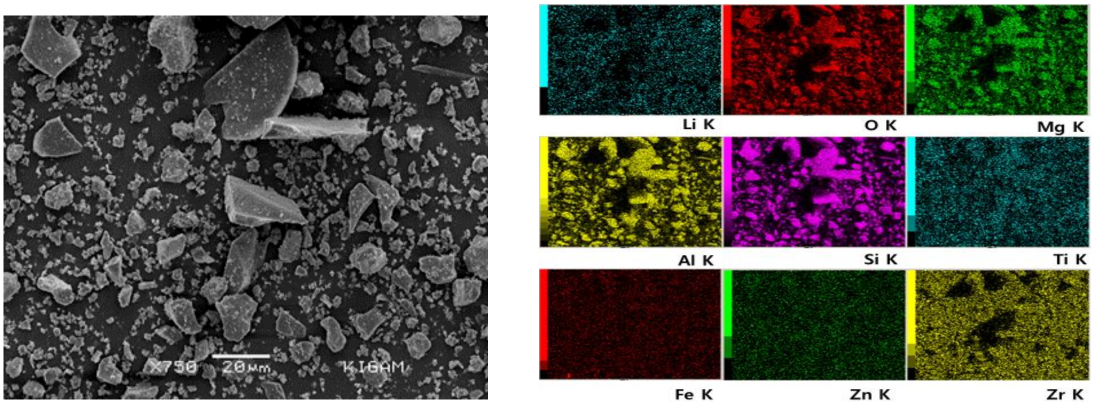


**Figure 2**: SEM analysis of the raw LAS sample (left) and mapping analysis results of the raw LAS sample (right).

**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. The thermal reaction was then carried out in an electric furnace under an Ar atmosphere. The reaction temperature was set at 300, 400, and 500℃, with a reaction time of 1 hour. After the thermal reaction, the sample was mixed with distilled water for 30 minutes to remove lithium sulfate and other impurities. Distilled water (1L) was used, and this process was repeated three times to ensure sufficient removal of lithium sulfate and impurities. The zeolite sample was separated from the liquid using a vacuum filtration system, and the recovered zeolite was dried for more than 24 hours at 95℃ in a dryer to remove all residual moisture. The zeolite was analyzed by X-ray diffraction (XRD), and the residual lithium content was measured by inductively coupled plasma optical emission spectrometry (ICP-OES).

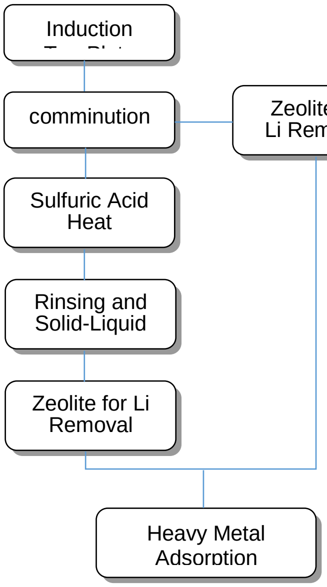


**Figure 3**: Overall experimental process diagram.

### 2.2.2. KCl modification method

K-zeolite was prepared according to the following process. The zeolite with lithium removed was used to prepare the K-modified zeolite. After the lithium removal process, the zeolite was converted to K-type zeolite through an ion-exchange process with a cationic solution using Na-A type zeolite. The zeolite was first dried at a temperature above 90℃ for 24 hours in a dryer to remove all moisture from the zeolite, as residual moisture in the zeolite's pore structure could affect the cation exchange process. KCl (99%) was used to convert the Na+ in the zeolite to K+. A 1M concentration of KCl was prepared and used. 1L of KCl solution and 10 g of zeolite were placed in a 1L beaker, stirred at 300 rpm for 24 hours. After 24 hours, the reacted solution was discarded, and a new solution was replaced to recover the decreased K+ ion concentration. This process was repeated three times to ensure all Na-type zeolite could undergo ion exchange. After the modification process, the zeolite was mixed with 1L of distilled water and stirred at 300 rpm for 30 minutes, then filtered and dried at a temperature above 90℃ for more than 24 hours to remove moisture.

### 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. In the experiment, zeolite with lithium removed from the LAS material obtained by crushing induction top plates and K-type zeolite produced through cation exchange using KCl solution were compared. 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).

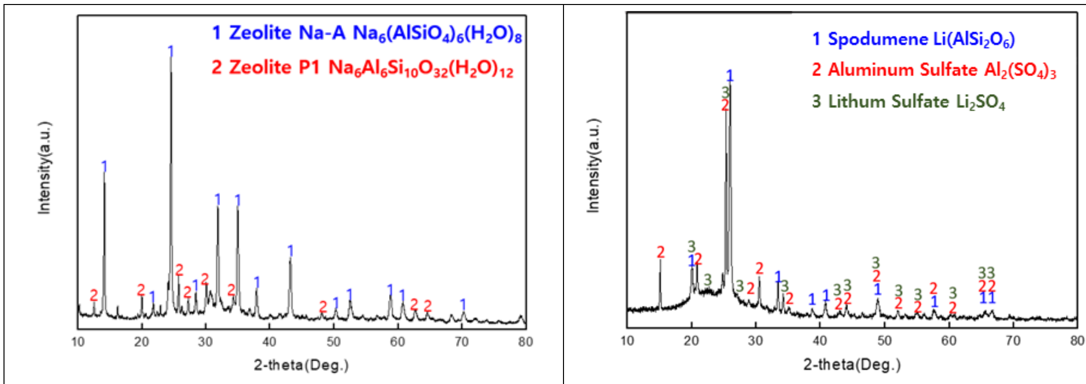
## 3. RESULTS AND DISCUSSION

### 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:

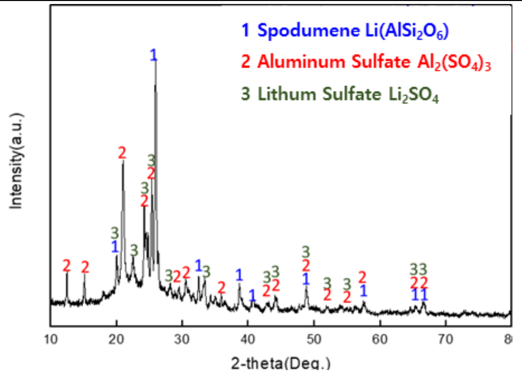
$$2LiAlSi2O6(s) + H2SO4(l) = Li2SO4(aq) + Al2O3(s) + 4SiO2(s) + H2O \qquad (1)$$

Lithium compounds in the LAS sample reacted with sulfuric acid to form lithium sulfate, which was then removed in the subsequent washing process. The reacted sample was 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 zeolite recovered through the separation of liquid and solid phases was dried in a 95°C oven for more than 24 hours. 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 zeolite was analyzed by XRD, SEM, and XRF, and the results are shown in Figure 4.



300 ℃

400 ℃



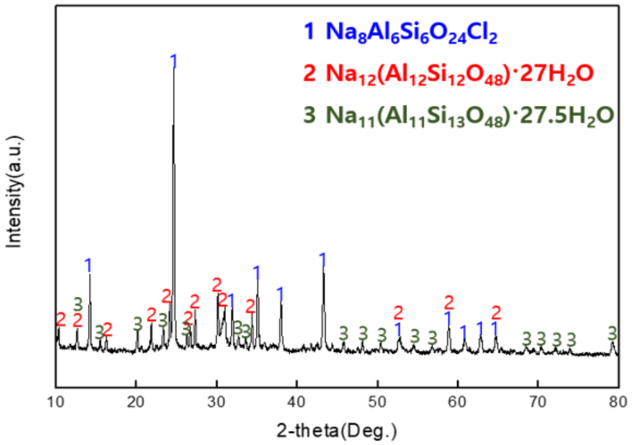
500 ℃

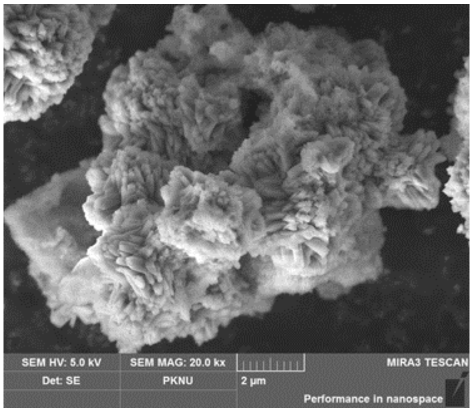
| Sample Name | Raw Material (wt%) | Zeolite (wt%) | Li Removal Rate (%) (%) |
|---|---|---|---|
| 300 ℃ | 1.56 | 0.055 | 96.47 |
| 400 ℃ |  | 0.146 | 90.64 |
| 500 ℃ |  | 0.193 | 87.63 |

**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.



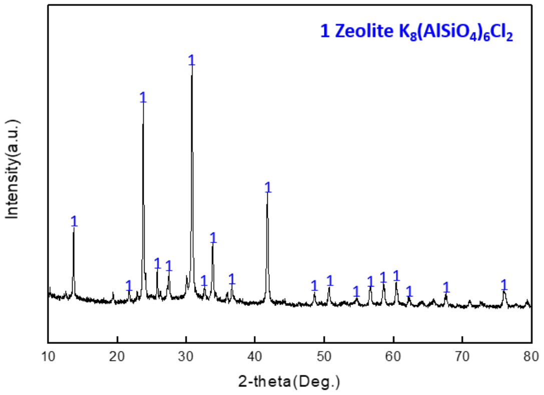


| Element and Content (wt.%) | | | |
|---|---|---|---|
| Si | Al | Na | Ti |
| 50.5 | 24.1 | 10.1 | 5.0 |
| Zn | Mg | Zr | Fe |
| 2.9 | 1.9 | 1.4 | 0.2 |

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

### 3.2 Na-Zeolite Kcl Modification Experiment Results

10 g of zeolite with Li removed was placed in a 1L beaker with 1M KCl 1L and stirred at room temperature for 24 hours at 300 rpm. After 24 hours, the solution was discarded to increase the K+ ion concentration in the solution and replaced with the same 1M 1L solution. This process was repeated three times to induce all Na-type zeolites to become K-type zeolites. After all the processes were completed, the zeolite was mixed with 1L of distilled water, stirred at 300 rpm for 30 minutes, and then vacuum-filtered to separate the solution and zeolite. The prepared zeolite was dried at 90℃ or higher for more than 24 hours to remove moisture and was then analyzed using XRD and XRF. The analysis confirmed that all the original Na-type zeolites had changed to K-type zeolites. It was observed that the original Na+ ions in the zeolite were replaced by K+ ions, resulting in the formation of K-type zeolite with the structure K8(AlSiO4)6Cl2 from Na6(AlSiO4)6·(H2O)8.



| Element and Content (wt.%) | | | |
|---|---|---|---|
| K | Si | Al | Ti |
| 39.03 | 27.04 | 20.73 | 4.58 |
| Zn | Ba | Zr | Mg |
| 2.43 | 1.84 | 1.73 | 1.37 |
| Na | Ca | Fe | |
| | 0.40 | 0.21 | |

**Figure 6**: XRD/XRF results of KCl-modified Na-zeolite experiment.

### 3.3 Influence of the Amount of Zeolite Added

The adsorption performance of heavy metals was measured according to the amount of zeolite added, using both lithium-removed zeolite and KCl-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 concentration of heavy metal solutions before and after stirring was measured using ICP-OES to confirm the changes in concentration, and the heavy metal removal rate was calculated using these measurements. 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 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. Using this formula, the heavy metal removal rate was calculated. The experimental results are shown in Table 2, and it was confirmed that the heavy metal removal ability improved as the amount of both zeolites added increased from the same concentration of heavy metal solution. However, the change was not significant for addition amounts of 2 g or more.

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

| Lithium-removed Zeolite | | | | | K-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 | 0.89 | 44.01 | 11.53 |
| **2** | 0.34 | 5.77 | 94.14 | 55.59 | **2** | 0.35 | 0.78 | 42.25 | 11.00 |
| **3** | 0.32 | 2.35 | 90.22 | 51.58 | **3** | 0.21 | 0.85 | 41.52 | 9.87 |
| **4** | 0.25 | 0.92 | 96.26 | 50.45 | **4** | 0.15 | 0.86 | 41.12 | 9.88 |
| **5** | 0.25 | 0.61 | 93.28 | 46.14 | **5** | 0.14 | 0.76 | 42.15 | 10.01 |
| | | | | | | | | | |
| **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 | 99.11 | 55.99 | 88.47 |
| **2** | 99.66 | 94.23 | 5.86 | 44.41 | **2** | 99.65 | 99.22 | 57.75 | 89.00 |
| **3** | 99.68 | 97.65 | 9.78 | 48.42 | **3** | 99.79 | 99.15 | 58.48 | 90.13 |
| **4** | 99.75 | 99.08 | 3.74 | 49.55 | **4** | 99.85 | 99.14 | 58.88 | 90.12 |
| **5** | 99.75 | 99.39 | 6.72 | 53.86 | **5** | 99.86 | 99.24 | 57.85 | 89.99 |

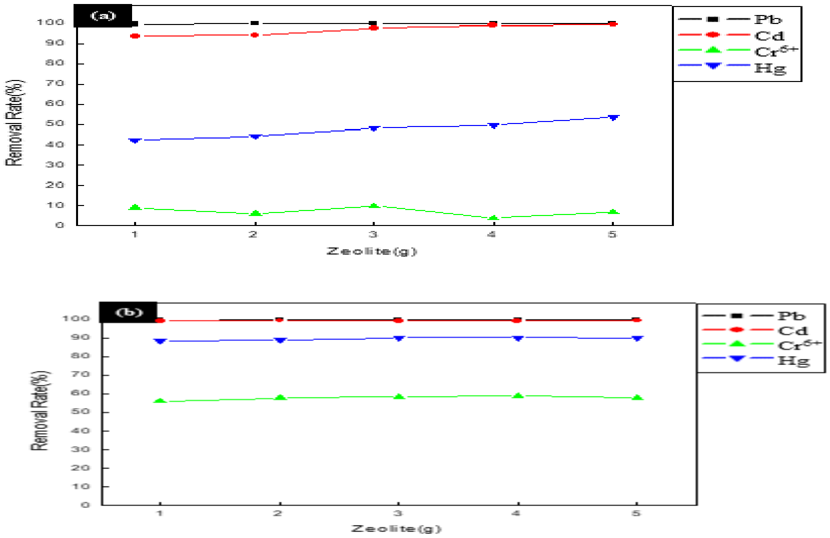


**Figure 6**: Influence of Zeolite Addition Amount on Heavy Metal Removal Rate (a) Li-removed zeolite, (b) K-zeolite

K-zeolite also showed a similar trend in heavy metal removal rates as Li-removed zeolite. The adsorption capacity of Cr6+ and Hg in the K-zeolite adsorption experiment improved compared to Li-removed zeolite. K-zeolite also showed a similar trend in heavy metal removal rates as Li-removed zeolite. K-zeolite adsorption experiment results showed improved adsorption capacity, especially for Cr6+ and Hg, compared to Li-removed zeolite. The adsorption removal rate increased by an average of 50.8% for Cr6+ and 41.6% for Hg.

### 3.4 Effects of Stirring Time

Heavy metal removal experiments were conducted using 2 g each of Li-removed zeolite and K-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, the heavy metal removal rate increased as the stirring time increased. Especially for Cd, the heavy metal concentration decreased significantly as the stirring time increased, and a similar removal rate was observed from the 90-minute condition.

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

| Lithium-removed Zeolite | | | | | K-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 | 0.91 | 44.01 | 11.32 |
| **30** | 0.38 | 5.09 | 87.45 | 56.33 | **30** | 0.35 | 0.72 | 43.02 | 11.12 |
| **60** | 0.37 | 2.68 | 88.25 | 57.24 | **60** | 0.22 | 0.62 | 41.04 | 10.25 |
| **90** | 0.24 | 0.85 | 87.23 | 53.23 | **90** | 0.14 | 0.55 | 39.51 | 9.12 |
| **120** | 0.23 | 0.41 | 87.64 | 53.12 | **120** | 0.13 | 0.41 | 39.50 | 10.01 |
| | | | | | | | | | |
| 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 | 99.09 | 55.99 | 88.68 |
| **30** | 99.62 | 94.91 | 12.55 | 43.67 | **30** | 99.65 | 99.28 | 56.98 | 88.88 |
| **60** | 99.63 | 97.32 | 11.75 | 42.76 | **60** | 99.78 | 99.38 | 58.96 | 89.75 |
| **90** | 99.76 | 99.15 | 12.77 | 46.77 | **90** | 99.86 | 99.45 | 60.49 | 90.88 |
| **120** | 99.77 | 99.59 | 12.36 | 46.88 | **120** | 99.87 | 99.59 | 60.50 | 89.99 |

The heavy metal adsorption removal rate was calculated using the formula (2) and is shown in Figure 6. It was confirmed that the heavy metal removal rate increased for all four heavy metal solutions as the stirring time increased.

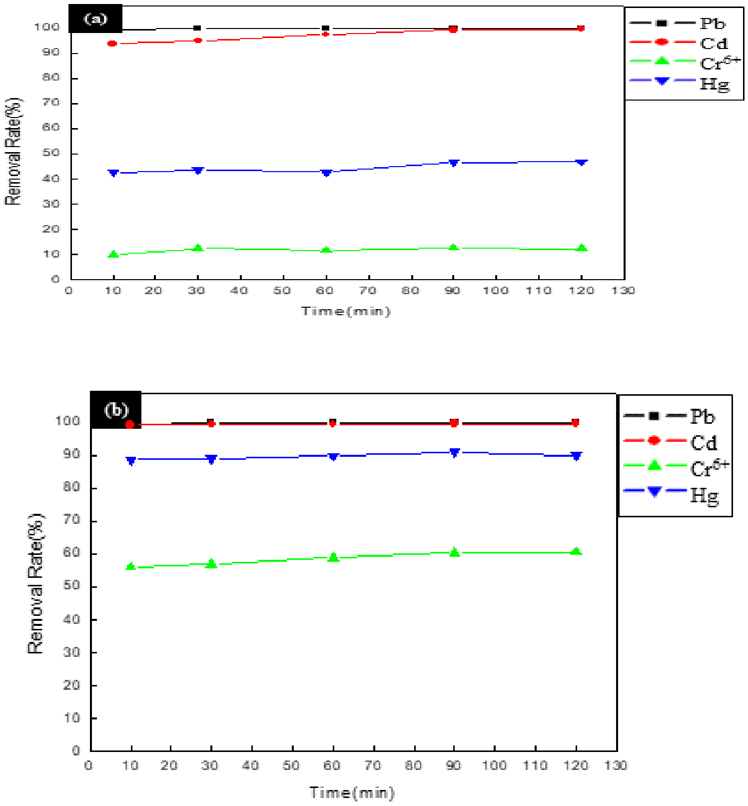


**Figure 7**: Effect of pH on heavy metal removal rate (a) Li-removed zeolite, (b) K-zeolite.

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> Cr6+≥ Hg under the same conditions. Unlike Li-removed zeolite, K-zeolite modified with KCl generally showed improved heavy metal removal rates. In particular, Figure 7 shows a significant improvement in the removal rates of Cr6+ and Hg, which were not effectively removed in the original 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]. Although the removal rate of all four heavy metal elements improved as the stirring time increased, the effect of time was most significant in the Cd removal experiment. As seen in Figure 7, the removal rate of Cd showed a tendency to increase linearly over time. It was found that the mechanism of adsorbents like zeolite is not very effective in removing Cd at the surface adsorption stage. It seems that the effect of removing Cd by diffusion into the zeolite structure is greater. This was confirmed by the linear increase in the removal rate as time increased.

### 3.5 Effect of Concentration Change

2 g of each zeolite powder was added to 200 ml beakers and mixed with 50 ml of four heavy metal solutions with concentrations of 10, 30, 50, 70, and 100 ppm. The same amount of zeolite was used to compare the heavy metal removal rates depending on the initial heavy metal solution concentration. The stirring speed was maintained at 300 rpm, and the stirring time was set to 30 minutes. The adsorption experiment results are shown in Table 4, and the calculated adsorption removal rates based on the results are shown in Figure 7.

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

| Lithium-removed Zeolite | | | | | K-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** | 0.40 | 0.41 | 5.10 | 2.75 |
| **30** | 0.43 | 1.71 | 26.45 | 12.21 | **30** | 0.37 | 0.72 | 14.11 | 8.33 |
| **50** | 0.30 | 3.42 | 44.11 | 29.14 | **50** | 0.27 | 2.21 | 22.91 | 13.91 |
| **70** | 0.32 | 3.22 | 62.12 | 35.15 | **70** | 0.26 | 2.41 | 32.42 | 17.52 |
| **100** | 0.41 | 4.25 | 89.35 | 49.47 | **100** | 0.30 | 3.51 | 47.12 | 27.21 |
| | | | | | | | | | |
| **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** | 96.00 | 95.90 | 49.00 | 72.50 |
| **30** | 98.57 | 94.30 | 11.83 | 59.30 | **30** | 98.77 | 97.60 | 52.97 | 72.23 |
| **50** | 99.40 | 93.16 | 11.78 | 41.72 | **50** | 99.46 | 95.58 | 54.18 | 72.18 |
| **70** | 99.54 | 95.40 | 11.26 | 49.79 | **70** | 99.63 | 96.56 | 53.69 | 74.97 |
| **100** | 99.59 | 95.75 | 10.65 | 50.53 | **100** | 99.70 | 96.49 | 52.88 | 72.79 |

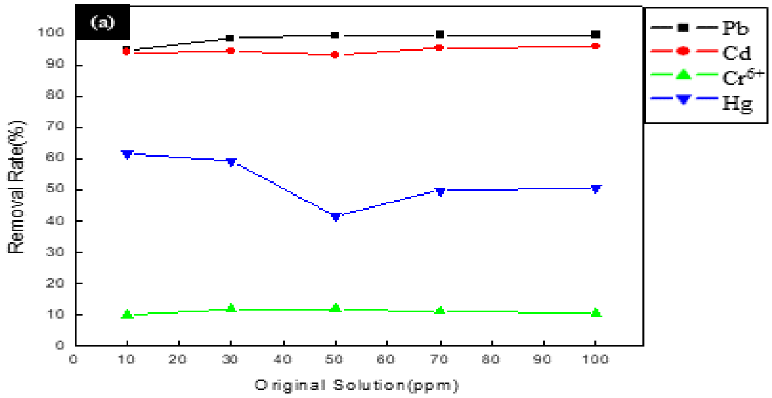


**Figure 8.** The influence of initial heavy metal solution on heavy metal removal rates (a) Li-removed zeolite, (b) K-zeolite

As shown in Figure 8, the initial heavy metal solution concentration did not greatly affect the heavy metal removal rates for both zeolites. For Pb, only the heavy metal removal rate changed depending on the initial heavy metal solution concentration. This is thought to be because, when considering the results of the effect of stirring time, most of the Pb adsorption occurs due to surface adsorption characteristics of the zeolite, resulting in a large amount of removal. In the case of Pb, it showed almost the same heavy metal removal rate regardless of the influence of time, and it seems that the heavy metal removal rate was low when the concentration of heavy metals in the initial solution was low, as the amount of adsorption decreased. In the case of Cd, similar result values were obtained when compared with the heavy metal removal rate under the 30-minute condition in the influence of stirring time. This shows that the removal mechanism of Cd is not only due to surface adsorption characteristics, as derived from the influence of stirring time, but also due to the greater amount of removal at the mechanism stages, such as diffusion inside the zeolite. In particular, K-zeolite modified with KCl was more effective in removing Cr6+ and Hg than the existing zeolite. In the case of Hg, the heavy metal removal rate improved by about 10% compared to lithium zeolite, and for Cr6+, the heavy metal removal rate improved by more than 30%.

### 3.4 Effect of pH Change

2 g of zeolite powder was added to a 200 ml beaker and mixed with 50 ml of four 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. 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 checked by mixing 2 g of zeolite with 50 ml of distilled water and measuring the pH. Both types of zeolite had a pH of 6.5~7.7, 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 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**

| **Lithium-removed Zeolite** | | | | | **K-Zeolite** | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **pH** | **Residual Concentration (ppm)** | | | | **pH** | **Residual Concentration (ppm)** | | | |
| | **Pb** | **Cd** | **Cr6+** | **Hg** | | **Pb** | **Cd** | **Cr6+** | **Hg** |
| **3** | 0.15 | 3.25 | 78.12 | 56.12 | **3** | 0.12 | 1.42 | 57.39 | 27.12 |
| **5** | 0.21 | 2.18 | 84.15 | 54.17 | **5** | 0.17 | 1.11 | 58.54 | 26.25 |
| **7** | 0.31 | 1.19 | 87.48 | 54.98 | **7** | 0.18 | 0.91 | 58.47 | 28.45 |
| **9** | 0.48 | 0.71 | 87.68 | 55.94 | **9** | 0.37 | 0.77 | 61.67 | 30.17 |
| **11** | 0.61 | 0.62 | 91.14 | 48.48 | **11** | 0.49 | 0.58 | 62.10 | 30.38 |
| | | | | | | | | | |
| **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** | 99.88 | 98.58 | 42.61 | 72.88 |
| **5** | 99.79 | 97.82 | 15.85 | 45.83 | **5** | 99.83 | 98.89 | 41.46 | 73.75 |
| **7** | 99.69 | 98.81 | 12.52 | 45.02 | **7** | 99.82 | 99.09 | 41.53 | 71.55 |
| **9** | 99.52 | 99.29 | 12.32 | 44.06 | **9** | 99.63 | 99.23 | 38.33 | 69.83 |
| **11** | 99.39 | 99.38 | 8.86 | 51.52 | **11** | 99.51 | 99.42 | 37.90 | 69.62 |

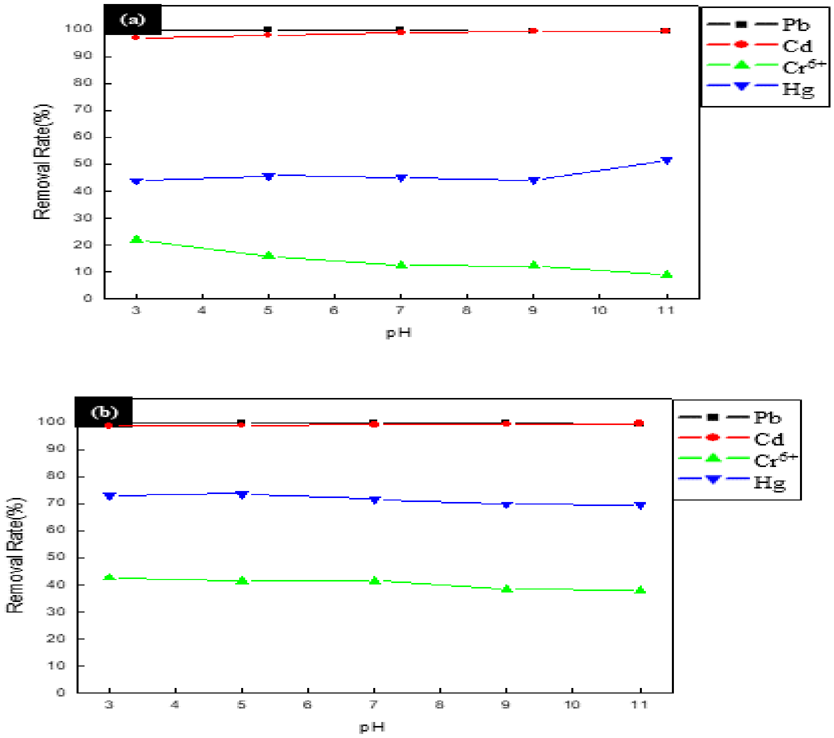


**Figure 9**: Effect of pH on heavy metal removal rate (a) Li-removed zeolite, (b) K-zeolite.

Table 5 and Figure 9 show the heavy metal removal rates of zeolites depending on the pH of the initial 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 pH changes, and it was confirmed that pH does not affect Hg removal. 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. Under the same conditions of stirring time, initial solution concentration, and pH, the heavy metal removal rate increased as the amount of zeolite added increased.

2. K-zeolite, modified with KCl, showed overall improved heavy metal removal performance compared to the zeolite manufactured by removing Li from the existing LAS materials. In particular, the removal performance of Cd and Hg, which were difficult to remove with the existing zeolite, improved.

3. It was confirmed that stirring time has a significant effect on heavy metal removal performance in the zeolite heavy metal removal process, and the heavy metal removal rate increased as time increased. However, the effect varied depending on the mechanism by which zeolite removes heavy metal elements.

4. The initial heavy metal concentration did not greatly affect the heavy metal removal rate of the zeolite.

5. As pH changed, Cd showed an increased heavy metal removal rate with increasing pH. In contrast, Pb and Cr6+ decreased.  Hg showed a constant heavy metal removal rate regardless of the pH of the initial heavy metal solution.

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