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SYNTHESIS OF ANALCIME ZEOLITE USING Al AND Si FROM WASTE RESOURCES FOR THE REMOVAL OF Pb/Cd IONS FROM AQUEOUS SOLUTION

Zeolites, minerals with the formula $M_x/n[AlO_2]_x(SiO_2)_y \cdot zH_2O$, are environmentally friendly materials used as water treatment adsorbents, gas adsorbents, and petrochemical catalysts. This study used a mixture of aluminum black dross and waste glass to synthesize zeolites via a hydrothermal synthesis and analyzed the effects of varying reaction time on phase changes under different synthesis conditions. With increased reaction times, a phase change from zeolite Na-P1 to analcime was observed; on employing hydrothermal synthesis at 150°C for 96 h, the majority of the crystalline structures changed into analcime. Heavy metal cation adsorption was tested to assess the applicability of the synthesized analcime to water treatment. Zeolite adsorption of at least 95% was observed for both Pd and Cd ions. Although a higher level of adsorption was observed for Pb ion than Cd ion, Cd ion was demonstrated to undergo relatively faster adsorption when tested under optimal pulp density at the same level of adsorption (95%).

Keywords: Zeolite; Analcime; Waste resources; Recycling; Heavy metal removal

1. Introduction

Zeolites collectively refer to natural or artificial aluminosilicate minerals created via Al-Si-OH radial polymerization and are commonly expressed using the formula $M_x/n[AlO_2]_x(SiO_2)_y \cdot zH_2O$, where M can be K, Na, Ca, Mg, or other elements. There are approximately 30 structural types of naturally occurring zeolites, whereas millions of types of synthetic zeolites are available – most notably chabazite, sodalite, analcime as well as zeolites A, X, Y, and P – depending on reaction conditions. Different structural types are known to have a range of three-dimensional crystalline structures and characteristics (e.g., ion adsorption and gas adsorption properties) [1-3]. In the past, zeolites have mainly been used as detergents; however, increased knowledge of zeolites' ability to allow cations into their crystalline structure to selectively and strongly adsorb polar substances, as well as to catalyze heavy metal ion exchange, has prompted the use of zeolites as adsorbents for hazardous heavy metal ions in water treatment applications, as adsorbents for gases, and as catalysts in petrochemical applications [4-6].

More recently, zeolites have drawn attention as recycling materials, because they can be synthesized from raw materials

such as industrial waste. Numerous studies have reported the synthesis of zeolites from Al- or Si-containing wastes, including coal fly ash (CFA), paper sludge ash (PSA), and oil shale ash (OSA) [7-12]. Specifically, Anuwattana and Khummongkol successfully synthesized Na-A zeolite using cupola slag and aluminum sludge through hydrothermal synthesis [7] and Cardoso et al. reported the use of CFA to synthesize Na-P1 zeolite for waste water treatment, which confirmed the mineral's ability to catalyze heavy metal cation exchanges (As, Cu, Fe, Mg, Ni, Zn, etc.) [8]. Kim et al. reported that crushing and acid pickling of waste windshield glass, followed by the removal of organic compounds and the subsequent use of hydrothermal synthesis, led to successful synthesis of type-A zeolite and sodalite [9].

This study investigates new recycling materials for zeolite synthesis. The waste materials tested in this study are aluminum black dross (ABD), a principal by-product of the aluminum melting processes, and pulverized glass extracted from waste LCD panels. These materials were synthesized into Na-P zeolite and analcime. The ability of the synthesized zeolite to adsorb heavy metal ions was tested using Pb and Cd solutions and varying reaction times. The applicability of the synthesized zeolite to water treatment was then assessed.

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2. Materials and methods

2.1. Materials

The ABD used for zeolite synthesis was generated by melting used aluminum drink cans. For material preparation, a distilled water and ABD solution (10:1) was stirred (for 24 h, 200 RPM) to eliminate the water-soluble matter; potassium chloride (KCl, Sigma-Aldrich, 99.9%) and sodium chloride (NaCl, Sigma-Aldrich, 99.9%) were found in the dross. ABD powder, stripped of water-soluble matter, was mixed with a 1 M hydrochloric acid (HCl, DAEJUNG, 35%) solution and then stirred (for 2 h, 200 RPM) to remove remaining impurities. The resultant ABD powder was used as a precursor for zeolite synthesis. The glass powder was synthesized from waste glass recycled from waste LCD panels. Using an oscillation mill (Made by Korea Mechanical Engineering Co., Ltd.) and a cutting mill, organic films on the surface of the waste glass were removed prior to pulverization. The resultant glass powder was mixed with a 5 M hydrochloric acid solution and stirred (for 2 h, 200 RPM) to remove any remaining impurities. ABD powder and glass powder were mixed at a weight ratio of 0.3:1 (hereafter referred to as mixed powder) for synthesis. The mixed powder was processed in an oscillation mill at 1500 RPM for 30 min to complete the crushing and stirring prior to the experiments.

2.2. Zeolite synthesis

The mixed powder was combined with a 1 M sodium hydroxide (NaOH, Sigma-Aldrich, 99.9%) solution at a ratio of 1 g/20 mL and then stirred (for 1 h, 200 RPM). A 120 mL portion of the combined solution was added to a 200 mL hydrothermal synthesis reactor (autoclave). The charged autoclave was placed in a preheated oven at 150°C for heat treatment. Test times were varied from 4 h to 96 h (4, 7, 24, 48, 72h, 96h). The heat treatment was accompanied by stirring at 200 RPM to ensure consistent reaction throughout each mixture. Once the reaction was complete, the mixed powder was washed three times with distilled water and once with ethanol (C₂H₅OH, DAEJUNG, 99.9%). Centrifuge-enabled solid-liquid separation was used to separate the mixed powder. The collected powder was dried in an oven at 80°C for 24 h.

2.3. Pb/Cd ions removal

A test solution was prepared to evaluate the mixed powder's Pb/Cd ions adsorption characteristics. For the preparation reagents, lead(II) chloride (PbCl₂, Sigma-Aldrich, 99.9%) and cadmium chloride (CdCl₂, Sigma-Aldrich, 99.9%) were dissolved in distilled water to adjust the concentration of both Pb and Cd to 100 ppm each. Pulp density-based experiments were carried out to investigate the Pb/Cd ions adsorption characteristics of the synthesized zeolite.

Using a zeolite sample synthesized using a 96-h reaction time, pulp density was varied between 0.1 g/100 mL and 0.5 g/100 mL. The "pulp density" refers to the amount of synthetic zeolite loaded per unit waste simulated solution volume. Stirring at 400 RPM for 24 h was used to mix the solution. Subsequently, the solution was processed in a centrifuge (Hanil, Comvi R515) for solid-liquid separation (15000 RPM, 10 min). Only the recovered solvent was collected. To investigate the effect of reaction time on the Pb/Cd adsorption characteristics of the zeolite, pulp densities of 0.1 g/100 mL and 0.5 g/100 mL were adopted for Pb and Cd ions, respectively. Reaction time was varied from a minimum of 5 s to a maximum of 15 min. Changes in the extraction of metal ions from solution were observed.

2.4. Mineral characterization

The composition of the mixed powder was analyzed via X-ray fluorescence (XRF) (Shimadzu, XRF-1800). Phase analysis of the raw materials and the synthesized zeolite was conducted via X-ray diffraction (XRD) (Rigaku, ULTIMA IV) to reveal the crystalline structure of the mixed powder (Fig. 1). Microstructural analysis of the zeolite was performed using field emission scanning electron microscopy / energy dispersive x-ray spectroscopy (FE-SEM/EDX) (Tescan, MIRA 3). Inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Agilent, MP-AES 4200). was employed to evaluate the heavy metal (Cd/Pb) ion adsorption capacity of the synthesized zeolite. An Agilent Technologies analysis system was used to quantify the concentrations of metal ions that were present in the solution.

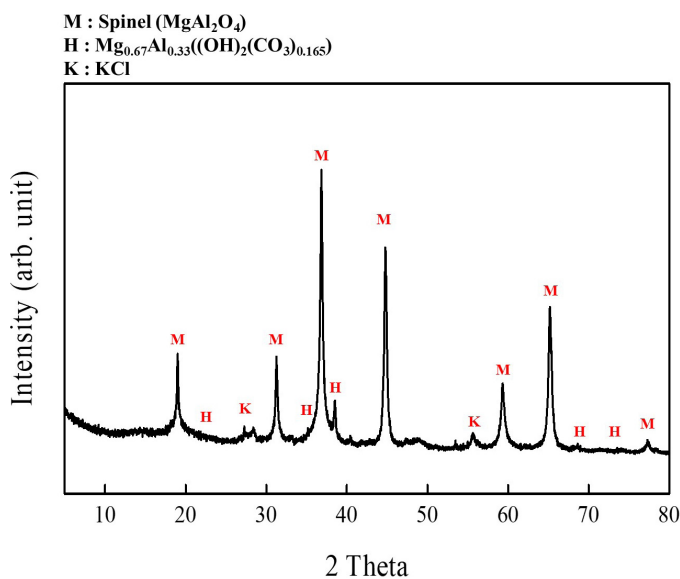


Fig. 1. Results of X-ray diffraction (XRD) analysis showing the composition of the aluminum black dross powder and glass powder mixed at a weight ratio of 0.3:1 ("Mixed Powder")

3. Results and discussion

Table 1 summarizes the results of the XRF compositional analysis performed on the mixed powder used for zeolite synthesis. The XRF results showed the presence of Si (75.4 wt.%) and Al (19.15 wt.%). The content of Mg, an element known to impede zeolite crystallization, was found to be low (2.59 wt.%). These results confirmed the suitability of the mixed powder as a raw material for chemical zeolite synthesis [13]. XRD patterns were absent in the waste glass, which is a noncrystalline form of SiO₂. The crystalline structure was confirmed to include spinel (found in ABD) and aluminum and magnesium hydroxides. These findings are consistent with the results of the XRF analysis. The mixed powder was repeatedly confirmed to have appropriate mixes of the elements required in zeolite synthesis.

TABLE 1

Composition of the Mixed Powder, comprising aluminum black dross powder and waste glass powder (dross:glass = 0.3:1)

Element	Si	Al	Mg	K	Cl
Wt.%	75.4	19.2	2.6	0.9	1.9

During zeolite synthesis, several variables can be manipulated (e.g., Al/Si ratio, reaction temperature, and reaction time) to instigate phase changes. In the hydrothermal synthesis of zeolites, referred to as hydrogel formation or clay conversion, zeolites are synthesized from Al and Si source materials at temperature ranges that do not exceed 200°C [14-16]. In these processes, varying reaction time is known to significantly influence core formation and crystalline phase transformations in the synthesized zeolites. Therefore, a fixed Al-Si ratio and reaction temperature were used, and reaction times varied from 4 h to 96 h. Figure 2 shows the XRD patterns for the various reaction times of the hydrothermally synthesized zeolite. The

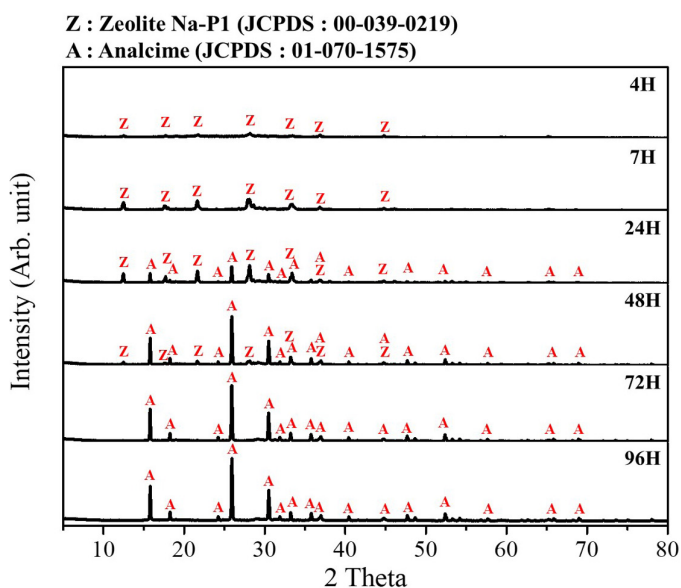


Fig. 2. Results of the XRD analysis according to the reaction time of hydrothermally synthesized zeolite

XRD patterns data base of zeolite Na-P1 and analcime was referring to the related paper [17]. Under the 4-h reaction time condition, the XRD patterns have a peak confirmed as type-P zeolite, although its intensity is extremely low compared to that at other reaction times. It was, therefore, difficult to make a clear judgment. Similarly, the 7-h reaction time condition confirms the presence of type-P zeolite, with a higher intensity and clearer pattern compared to the 4-h condition. Under the 24-h reaction time condition, both type-P and analcime zeolite peaks were observed for the first time. As the reaction time increased, the intensity of the type-P zeolite gradually decreased after peaking at the 24-h point, whereas the intensity of analcime (zeolite) continued to increase.

When determining the degree of crystallization achieved by each zeolite structure, the intensity of the main peak cannot be taken as an absolute value, but can still be used as a relative value for comparison purposes [18-21]. Figure 3 compares the measured changes in the XRD patterns of the main peaks of the type-P zeolite ($2\theta = 28.1^\circ$) and analcime ($\theta = 25.9^\circ$). Azizi and Ehsani Tilami have studied the crystallization behavior of type-P zeolite and analcime, experimentally confirming the crystallization process of the zeolites by using D-methionine as a structure-directing agent [22]. Previous studies have also described the crystallization behavior of type-P and analcime zeolites under 60-h reaction times at 100-130°C during heat treatment [23]. Additionally, Oleksiak and Rimer observed that, in general, the shorter the synthesis time and the lower the temperature, the lower the framework density. This study also reported that, as the temperature or time increased under high Si-content conditions, phase transitions of Linde Type A (LTA)-FAU (Faujasite)-GIS (Glismondine)-ANA (Analcime) took place. Molar volumes of the type-P zeolite and analcime were reported to be 36.7 cm³/mol and 31.4 cm³/mol and theoretical density were reported to be the type-P zeolite and analcime 2.59g/cm³ and 2.27g/cm³, respectively. This study also confirmed the previous finding that as reaction time increased, a phase change towards a denser

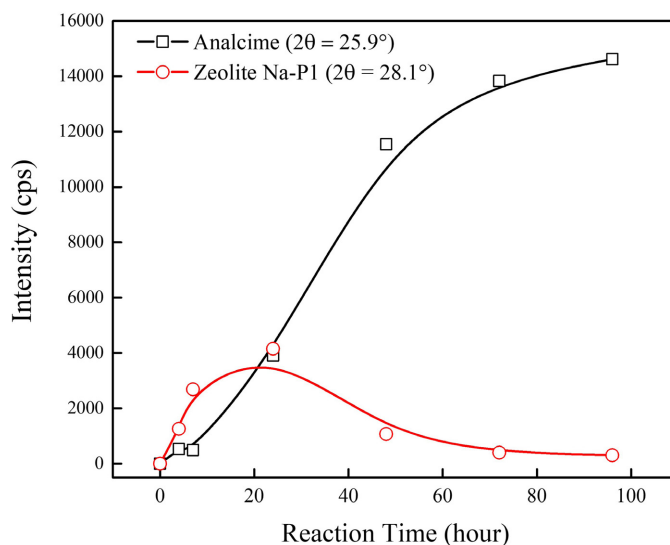


Fig. 3. Differences in intensity of the main XRD peak values according to reaction time (type-P zeolite vs. analcime)

framework occurred (type-P zeolite \rightarrow analcime) [17, 25]. This is believed to have contributed to the predominance of analcime observed under the 96-h heat treatment condition, the longest of all reaction time conditions tested.

Figure 4 shows the SEM images of the raw material powder used for zeolite synthesis and the synthesized zeolites at different reaction times (4–96 h). Type-P zeolite is generally known to form condensed polyhedron crystalline structures (μm), whereas analcime (zeolite) commonly takes the form of a 24-faceted coarse crystalline structure [26,27]. In Figure 4a, the images of the mixed powder confirm an irregular, mixed distribution of the relatively small (1–10 μm) ABD particles and relatively large (10–100 μm) crushed particles of waste glass. Figures 4b and 4c show the condensation of irregularly shaped particles, whose form is attributed to a relatively short time (4 h or 7 h) for crystal growth. Figure 4d shows the condensation and distribution of a large number of polyhedron structures, i.e., the principal struc-

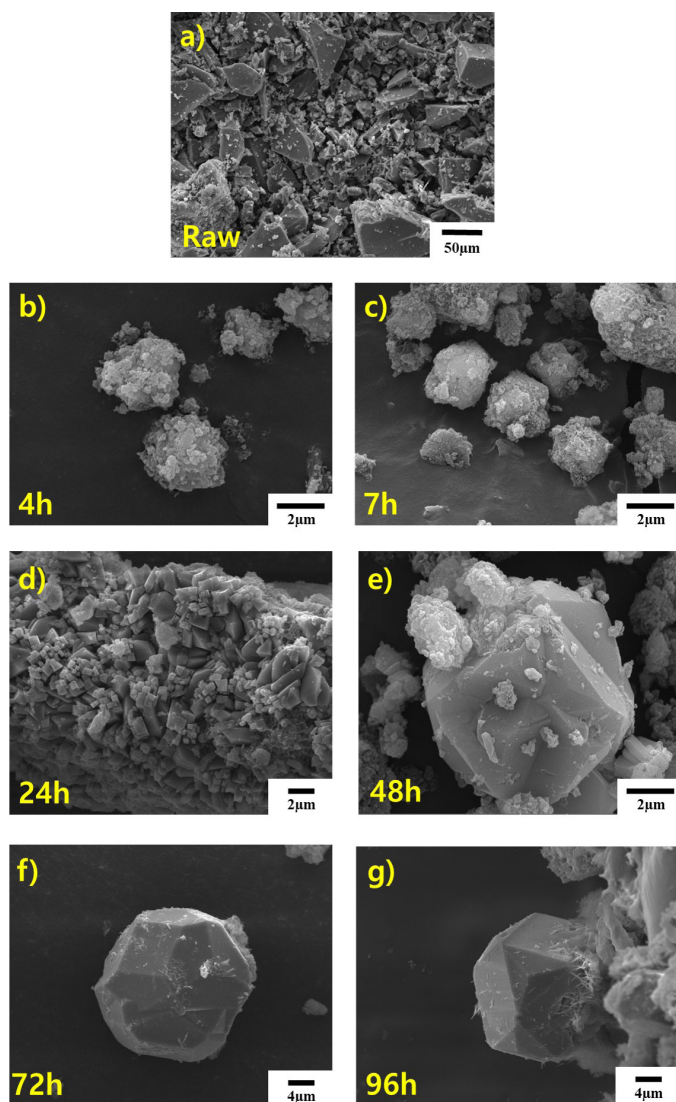


Fig. 4. Scanning electron microscopy (SEM) images comparing the two types of synthesized zeolites according to reaction time. a) shows the mixed powder; b) 4 h, c) 7 h: irregularly shaped particles; d) 24 h: hundreds number of polyhedron structures, i.e., type-P zeolite; e–g) 48, 72, and 96 h, respectively: 24-faceted coarse crystalline form of analcime

ture of the type-P zeolite, which occurred using a reaction time of 24 h. Figures 4e–g show the characteristic 24-faceted coarse crystalline form of analcime. These results reflect the patterns observed in the XRD analysis, i.e., the longer reaction times lead to enhanced crystal growth. The 96-h reaction time condition resulted in the creation of a single-phase analcime structure with a high degree of crystallization.

Figure 5 shows the results of SEM/EDX analysis of zeolite Na-P1 and Analcime found under 96h condition. It can be confirmed that the content of aluminum, silicon, and sodium is very similar in both crystal phases, and it can be deduced that the zeolite Na-P1 and analcime may be chemically closely related.

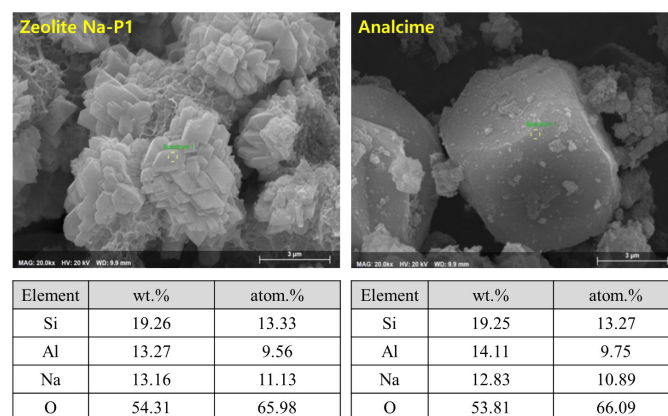
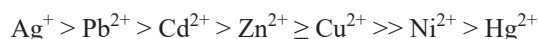


Fig. 5. The results of scanning electron microscopy (SEM) images / energy dispersive x-ray spectroscopy (EDX) of zeolite Na-P1 and Analcime (at 96h condition)

Figure 6 shows the heavy metal (Pb and Cd) adsorption characteristics of the synthesized zeolites (from the 96-h condition) against pulp density and time. The zeolites were determined to adsorb at least 95% of Pb when the pulp density was approximately 0.1 g/100 mL (100 ppm) or greater. Cd adsorption was determined to reach a minimum of 95% with a pulp density of at least 0.5 g/100 mL. The differences in Pb and Cd adsorption are attributable to the different cation exchange characteristics that are associated with the heavy metal ion selectivity of the zeolites. Heavy metal ion selectivity is known to result from differences in the hydrate radius and hydration energy of metal ions. According to the existing literature, a smaller hydrate radius and greater hydration energy generally contribute to a greater difference in polarity, which in turn contributes to higher degrees of ion exchange. The results of this study are in line with such findings. The element-specific ion exchange trend under different hydrate radius and hydration energy variables are as follows [10, 28–30]:



The heavy metal ion adsorption behavior of zeolites can be explained as the substitution of the metal cations Na^+ and K^+ , which are attached to surface structures of the zeolites by weak covalent bonds, with heavy metal ions that exist in the solution.

This study measured the concentrations of Na^+ ions contained in the heavy metal solution before and after the adsorption of heavy metal ions by the zeolites. The pre-adsorption Na^+ ion concentration was 1.98 ppm, which increased to 69.11 ppm following adsorption. This result is indicative of the aforementioned behavior of heavy metal substitution.

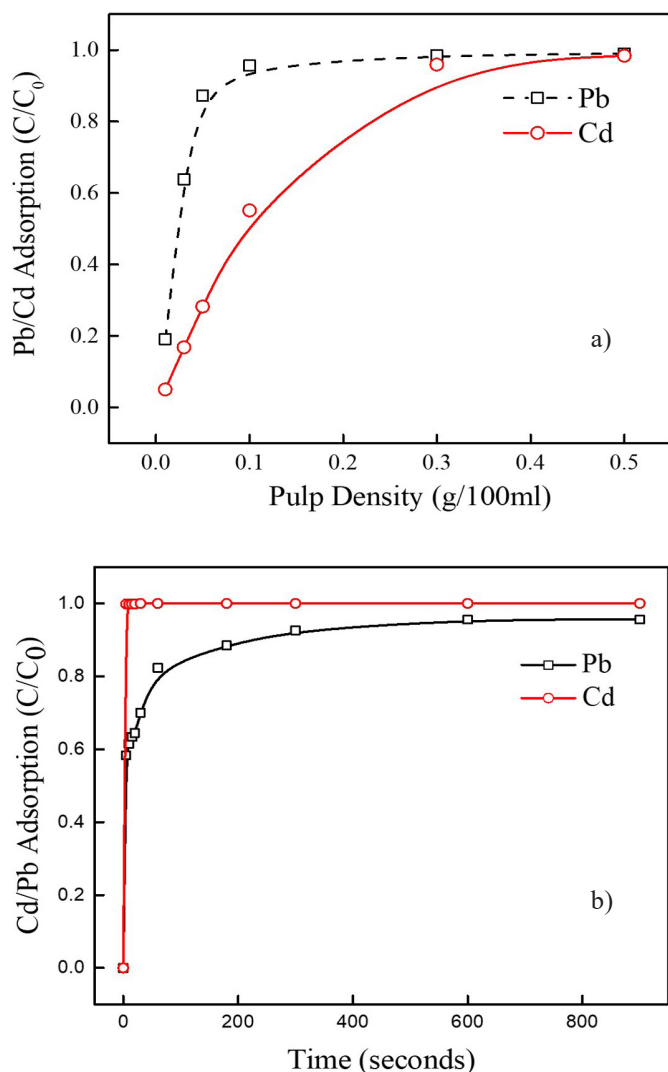


Fig. 6. Evaluation of Pb/Cd adsorption of the synthesized zeolites (synthesized for 96 h), according to a) pulp density and b) adsorption time

Zeolites were also added to the Pb and Cd solutions at concentrations of 0.1 g/100 mL and 0.5 g/100 mL, respectively, according to the ideal pulp density obtained from the 95% Pb/Cd ion removal rate in the initial experiments. Then, time-based adsorption rates were evaluated. The Pb solution required approximately 600 s to achieve 95% adsorption, whereas the Cd solution took approximately 5 s. For Pb, whose ion selectivity is higher than that of Cd, ion adsorption was about 5 times higher than that of Cd per unit mass of zeolites. Time-based heavy metal adsorption was found to be quicker with Cd than Pb. These findings indicate that the heavy metal adsorption speed of zeolites is influenced substantially by the concentration of zeolites in the solution.

4. Conclusions

In this study, a mixture of aluminum black dross powder (waste material) and waste glass (“mixed”) powder was fabricated and used to synthesize zeolites. A simulated waste solution containing Pb and Cd was prepared to evaluate the adsorption behavior of the synthesized zeolites. Zeolite synthesis was performed using varying reaction times, resulting in the development of a single-phase analcime zeolite at a reaction temperature of 150°C and a 96-h reaction time condition, using the process of hydrothermal synthesis. The synthesized zeolites were added to the simulated solutions containing Pb and Cd (100 ppm) and their adsorption capacity was evaluated by varying pulp density and reaction time. Due to the different ion selectivity associated with Pb and Cd, zeolite adsorption capacity was also confirmed to vary. A pulp density of approximately 0.1 g/100 mL or greater (100 ppm) was found to be associated with a minimum of 95% Pb adsorption; and a pulp density of at least 0.5 g/100 mL was confirmed to have resulted in a minimum of 95% Cd adsorption. The results of this study indicate that, for identical adsorption times, zeolite concentration in solution plays a larger role in adsorption than ion selectivity.

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