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Fabrication of K-PHI Zeolite Coated Alumina Hollow Fiber Membrane and Study on Removal Characteristics of Metal Ions in Lignin Wastewater

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Abstract – Recently, hybrid coal research is underway to upgrade low-grade coal. The hybrid coal is made by mixing low-grade coal with bioliquids such as molasses, sugar cane, and lignin. In the case of lignin used here, a large amount of lignin is included in the wastewater of the papermaking process, and thus, research on hybrid coal production using the same is attracting attention. However, since a large amount of metal ions are contained in the lignin wastewater from the papermaking process, substances that corrode the generator are generated during combustion, and the amount of fly ash is increased. To solve this problem, it is essential to remove metal ions in the lignin wastewater. In this study, metal ions were removed by ion exchange with a alumina hollow fiber membrane coated with K-Phillipsite (K-PHI) zeolite. The alumina hollow fiber membrane used as the support was prepared by the nonsolvent induced phase separation (NIPS) method, and K-PHI seeds were prepared by hydrothermal synthesis. The prepared K-PHI seed was seeded on the surface of the support and coated by secondary growth hydrothermal synthesis. The characteristic of prepared coating membrane was analyzed by Scanning Electron Microscope (SEM), X-Ray Diffraction (XRD), Energy Dispersive Spectroscopy (EDX), and the concentration of metal ions before and after ion exchange was measured by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). The extraction amount of K^+ is 86 mg/kg, and the extraction amount of Na^+ is 54.9 mg/kg. Therefore, K-PHI zeolite membrane has the potential to remove potassium and sodium ions from the solution and can be used in acidic lignin wastewater.

Key words: Ion exchange, K-PHI zeolite, Alumina hollow fiber membrane, Hydrothermal synthesis coating, Lignin wastewater

1. Introduction

Biological liquids can be used to develop biological mixed coal technology. But alkaline mineral components (sorghum, lignin, sugar extracted from biomass) are a problem in the combustion of biological liquids. During the combustion process of the mixed coal, the ash becomes gaseous, and then slagging is induced by the alkaline substance, after the ash fusion of the silicate melt, agglomerates, corrodes, and re-assembles through the use of the ash Causes boiler blockage in the boiler. Although the amount of metal oxides in the biological liquid is small, they will accumulate in the boiler and form scale during the combustion process. In order to remove the metal ions from the bio-liquid before the bio-liquid is introduced into the coal, and to produce high-quality bio-coal, it is necessary to conduct research to remove the metal ions. At present, Japan, South Korea, China and other countries are studying the process of manufacturing the removal of alkaline metal ions from clean coal. In Japan, the production process of ashless coal that removes ash by using organic solvents for high temperature and high pressure (250 °C~400 °C, about 10 bar) solvent extraction and drying of plastic components is being studied [1-5].

In recent years, with the development and innovation of separation technology using separation membranes, it is becoming an eco-friendly and efficient separation technology. Organic membranes are made of polymers in the form of membranes. Because they exhibit high separation efficiency in liquid separation and can be easily manufactured by various methods, they have been widely used in many fields. However, due to the nature of the polymer, its thermal stability and chemical stability are low, and the use of polymer membranes under high pressure conditions is limited, making it difficult to use under harsh conditions. Especially when the lignin extract is discharged at a temperature of 180 °C or higher, and a high alkaline condition with a pH of 13 or higher, when the polymer membrane is used as the separation membrane, the separation membrane is easily deformed or damaged, resulting in The separation performance deteriorates, making long-term use difficult.

Carbides, etc. are used as separation membranes for inorganic membrane materials. Inorganic material membranes have the advantages of high thermal stability and chemical stability, so that even under harsh conditions, they can also have the advantages of separation membranes for efficient separation. Therefore, in recent years, zeolite, metal oxides, and alloys are often used as separation membrane materials. Among them, zeolite is a material that can perform ion exchange, and the cations in its structure can be replaced by other cations, so it is often used to make molecular sieves to extract the required ions [6-8].

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Since zeolite molecular sieve cannot achieve continuous extraction effect when extracting alkaline ions, the combination of zeolite and ceramic membrane is used to extract alkaline ions from seawater, so as to achieve the effect of continuously extracting alkaline metal ions from seawater [9-12].

In this research, the development of a zeolite-coated ceramic hollow fiber membrane for alkali metal removal technology is ongoing. This technology removes alkali metal ions from the lignin extract discharged from the pulp and paper process to recover lignin and fiber. And organic matter to improve the thermal efficiency and quality of the mixed coal.

2. Experiment

2-1. Material

The materials of α-Al_2O_3 hollow fiber membrane used 1-Methyl-2-pyrrolidinone anhydrous (NMP, 99.5%, SAMCHUN), α-Al_2O_3 powder (< 0.5 μm, Kceracell), Polyethersulfone (PESf, Ultrason®), Polyvinylpyrrolidone (PVP, 99.5%, Sigma). The materials of K-PHI zeolite used sodium aluminate ($NaAlO_2$, Extra Pure, JUNSEI), Sodium silicate (Na_2SiO_3, powder, SiO_2 50% ~ 55%, Na_2O 23% ~ 27%, SAMCHUN), Potassium Hydroxide (KOH, 95%, Extra Pure, SAMCHUN), Tetrapropylammoniumbromide (TPABr, 98%, SIGMA) and Ammonia solution (NH_4OH, Extrapure, JUNSEI).

2-2. Production of hollow fiber membrane support

201 g of NMP and 36 g of PESf were mixed at room temperature during 24 hours. Then 3 g of PVP and 360 g of α-Al_2O_3 powder were added the PESf solution. And mixed for 24 hours at a speed of 300 rpm to prepare a solution. After that, the solution was placed in a stainless steel reactor for 1 hour in a vacuum of 0.8 bar for degassing. The spinning conditions are set as the air gap distance is 10 cm, the nitrogen pressure is 3 MPa, and the water flow rate is 10 ml/min. After spinning, manufactured green body put into water for 24 hours to remove residual organic solvent. Then, the green body is dried at 90 °C oven for overnight. The dried hollow fiber membrane was sintered in a furnace at heating rate of 3 °C/min to 1300 °C and was maintained at the temperature for 3 hours.

2-3. Synthesis of K-PHI zeolite seeds

The K-PHI zeolite coated alumina membrane was prepared starting from a K-PHI zeolite seeds. first, 15.72 g of distilled water and 42.53 g of Na_2SiO_3 mixed at 250 rpm for 3 hours for prepared water glass solution. And then, 3.11 g of $NaAlO_2$ and 16.34 g of distilled water mixed at 250 rpm for 3 hours for prepared $NaAlO_2$ solution. Then, the two solutions were mixed and stirred for 3 hours to form a colloid. After that, 7.44 g of KOH and 1.55 g of TBABr at the colloid solution were added and stirred for 3 hours. The K-PHI mother solution was placed in the Teflon vessel within the stainless steel hydrothermal synthesis reactor. The solution was aged for 1 hour, and then the reactor was placed in the oven at 150 °C for 24 hours of hydrothermal synthesis reaction. After the reaction was completed, the synthesized solution was filtered through a filtration device and washed 3 times. Finally, the filtered K-PHI zeolite seeds were dried in the oven at 90 °C for overnight.

2-4. Vacuum seeding process

The 2 wt% seed solution was made with mixed the previously produced seed crystals and distilled water. And one end of the alumina hollow fiber support was sealed with Teflon tape and the other end was connected to a vacuum pump. Next, The prepared support was put in the seed solution and carried out seeding at a vacuum pressure of -0.5 bar for 30 seconds. After the above seeding process was repeated 3 times, the seeding membrane was calcined in the furnace at 500 °C for 4 hours with heating rate of 1 °C/min for removal the organic template.

2-5. Coating on the K-PHI zeolite seeded support

The K-PHI zeolite coating solution was fabricated with $NaSiO_3$, Na_2AlO_3, KOH, TBABr, and distilled water. The first, 118.75 g of $NaSiO_3$ and 190.40 g of distilled water were stirred at 250 rpm for 3 hours to prepare water glass solution. The second, the 8.20 g of Na_2AlO_3 and 95.18 g of distilled water were stirred at 250 rpm for 3 hours to prepare $NaSiO_3$ solution. Then the above two solutions were mixed and stirred for 3 hours to form a colloid. After that 39.45 g of KOH and 12.54 g of TBABr were added and stirred for 3 hours. Next, the colloid solution was put in hydrothermal synthesis reactor and for 1 hour to age the colloid solution. And then both ends of the prepared seeding membrane were sealed with Teflon tape. The membrane was put into a hydrothermal synthesis reactor, and reacted in oven at 150 °C for 24 hours for hydrothermal synthesis. After the reaction was completed, the K-PHI zeolite coated membrane was washed 3 times with distilled water, and the coated membrane was calcined in the furnace at 500 °C for 4 hours for removal the organic template. The heating rate is the same as the vacuum seeding process.

2-6. Characterize K-PHI zeolite membranes

The mean pore size of hollow fiber membrane for support is evaluated by the gas permeation test [13,14]. The nitrogen gas is flowed to the shell side of the hollow fiber membrane, and then permeation gas into the lumen side of hollow fiber membrane is measured the flow rate through a primary flow calibrator (SENSIDYNE®, Gilian Gilibrator). The effective area of the hollow fiber membrane was calculated by the following equation:

$$A_{HFM} = l_{OD} \times l_{HFM} \quad (1)$$

A_{HFM} is the effective area of the hollow fiber membrane. l_{OD} is the outer diameter of the hollow fiber membrane, and l_{HFM} is the length of the hollow fiber membrane.

The permeability is calculated from the measured permeation flow rate and the effective area of the hollow fiber membrane. The permeability is determined using the following formula:

$$Q = \frac{q_{per}}{A_{HFM} \times P_{per}} \quad (2)$$

Q is the permeability of the nitrogen gas permeated the hollow fiber membrane. q_{per} is the permeation flow rate of the nitrogen gas, and P_{per} is the permeation pressure. Next, a graph is made with the permeability and the permeation pressure of the hollow fiber membrane. The slope (S_0) and the intersection (I_0) were used to evaluate the mean pore size of the hollow fiber membrane. And calculate the average pore size of the hollow fiber membrane by the following formula:

$$d_p = \frac{32}{3}\frac{S_0}{I_0}\left(\frac{8RT}{\pi M}\right)^{0.5}\mu \quad (3)$$

Where d_P is the mean pore size. R is the gas constant of nitrogen and the T is the temperature. The M is the molecular weight of nitrogen gas, and μ is the gas viscosity of nitrogen.

The scanning electron microscope (SEM, NNS-450, FEI Company) and energy dispersive spectrometer (EDS, NNS-450, FEI Company) analysis were performed to confirm whether the K-PHI zeolite was coated on the surface of the alumina support. The cross section of the coating membrane was analyzed using an electron beam of 15.00 kV. And Na, Si, and K elements were confirmed by EDS analysis. In addition, the crystal peak was confirmed through X-ray diffraction (XRD, Dmax-2500pc, Rigaku) analysis to confirm whether the component of the coated material was K-PHI zeolite. The light source used for the analysis was a Cu Kα1 light source (λ=1.54041 Å), and the analysis was set in the range of 5-80°.

2-7. Metal ion removal in lignin wastewater

The experiment process of metal ion removal is shown in the Fig. 1. The used solution for the experiment is the lignin waste water from the pulp factory. An experiment was performed to remove potassium and sodium ions from lignin wastewater using the K-PHI zeolite coating hollow fiber membrane prepared above. The lignin wastewater flows from the membrane module to the shell side of the hollow fiber membrane at a flow rate of 1 ml/min, and the ammonia solution flows to the lumen side of the hollow fiber membrane at a flow rate of 1 ml/min. The mechanism of metal ions is shown in Fig. 2. The ammonia ion is exchanged K^+ ion in the K-PHI zeolite layer coated on the hollow fiber membrane surface. Then, the ammonia ion in the zeolite layer exchange with K^+ and Na^+ ions in the lignin wastewater again. Thus, K^+ and Na^+ ions in the lignin wastewater are ion-exchanged with ammonia ions in ammonia solution to remove K^+ and Na^+ ions in the lignin wastewater. At this time, the concentration of ammonia solution is used 0.15 mol/L.

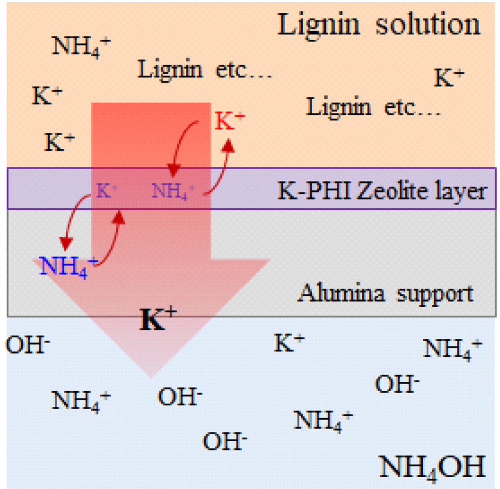

Fig. 2. Mechanism of metal ion exchange.

3. Result

3-1. Structure characteristics of K-PHI zeolite membrane

The Fig. 3 is a cross section and surface SEM image of alumina hollow fiber membrane and alumina hollow fiber membrane coated

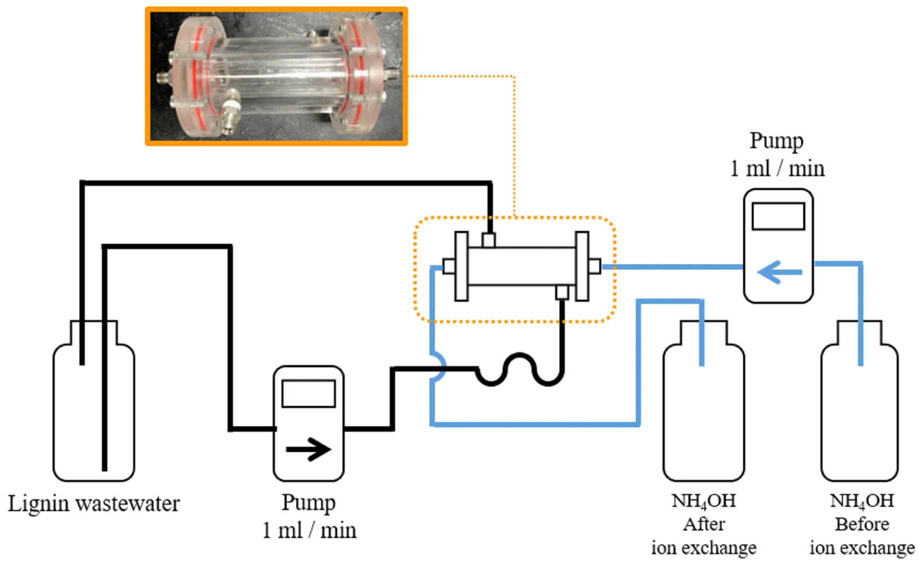

Fig. 1. Diagram of potassium and sodium ion exchange device.

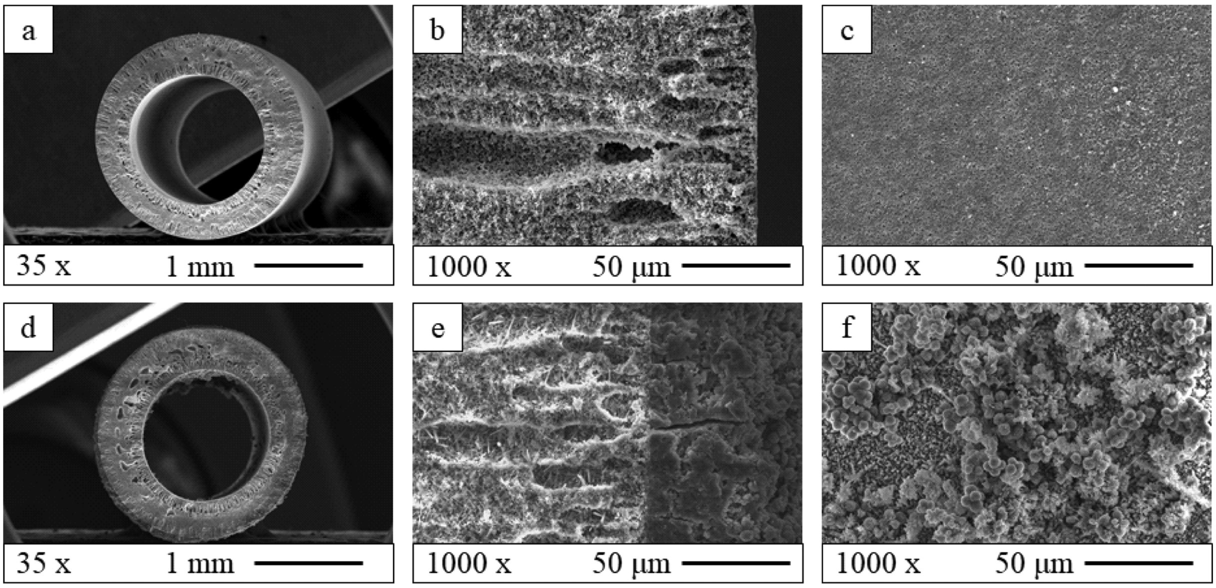

Fig. 3. Cross section SEM of alumina hollow fiber membrane before and after coating (a, b, c: Non coated on support, d, e, f: Zeolite coated on support).

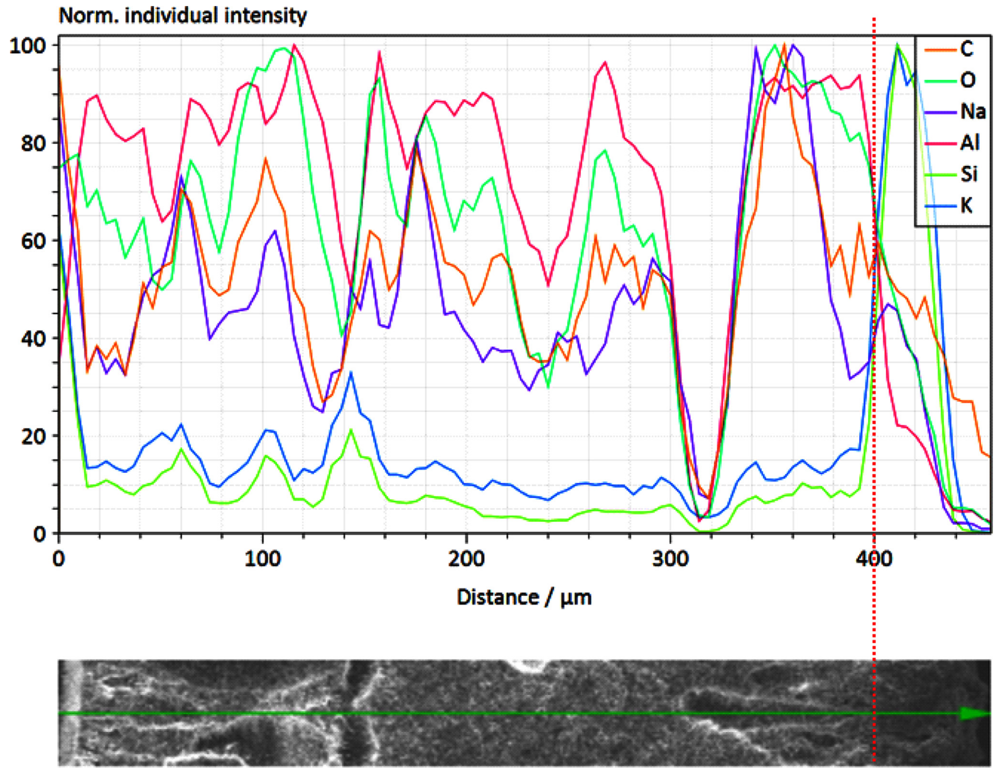

Fig. 4. Cross section EDS of zeolite coated on support.

with K-PHI zeolite. As shown in Fig. 3(b, e), it can be seen that a new coating layer was formed on the surface of the alumina hollow fiber membrane after coating K-PHI zeolite. In addition, as shown in Fig. 3(c, f), it is confirmed that zeolite crystals were formed on the surface of the hollow fiber membrane after K-PHI zeolite was coated. Looking at the results of the EDS analysis in Fig. 4, the ratio of Al element was high until 400 μm for the alumina hollow fiber membrane support, and then gradually decreased. However, it can be seen that the ratio of the Si and K elements, which are constituent elements of the K-PHI zeolite, rapidly increases after 400 μm. The K-PHI zeolite coated on the alumina hollow fiber membrane can be confirmed from the XRD results in Fig. 5. As seen in Fig. 5, the crystal peak of the alumina support and the crystal peak of K-PHI zeolite are mixed. The K-PHI zeolite coated on the alumina hollow fiber membrane is confirmed from the result.

The weight of alumina hollow fiber membrane before and after

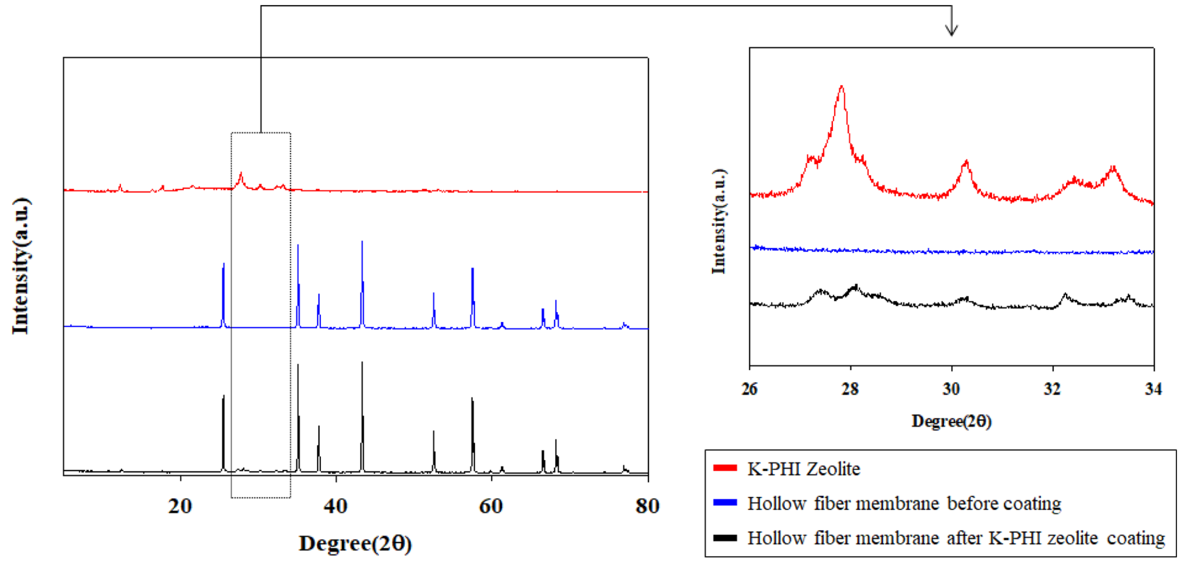

Fig. 5. XRD of Zeolite membrane, K-PHI zeolite, and Support.

Table 1. K-PHI zeolite content on zeolite coated on alumina hollow fiber membrane

Membrane length 12 cm		
Before coating (g)	After coating (g)	K-PHI zeolite content (g)
0.396	0.445	0.049

coating were measured, and the results are shown in Table 1. The weight of membrane before coating is 0.396 g. And the weight of membrane after coating is 0.445 g. So, the weight of coated K-PHI zeolite is 0.049 g.

3-2. The metal ion removal performance of K-PHI zeolite membrane

As seen in Fig. 6, when lignin wastewater was filtered with an non-coated alumina hollow fiber membrane, the K^+ ions increased by 2 mg/kg and the Na^+ ions decreased by 2.4 mg/kg. This is determined that the non-coated hollow fiber membrane filtration cannot be removed K^+ ions and Na^+ ions.

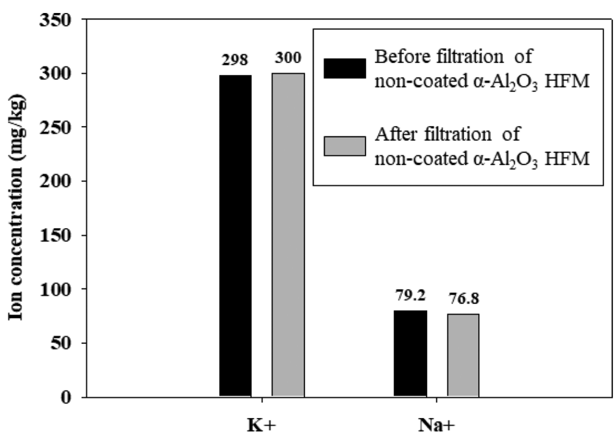

Fig. 6. ICP-OES analysis result before and after filtration of non-coated α-Al_2O_3 hollow fiber membrane.

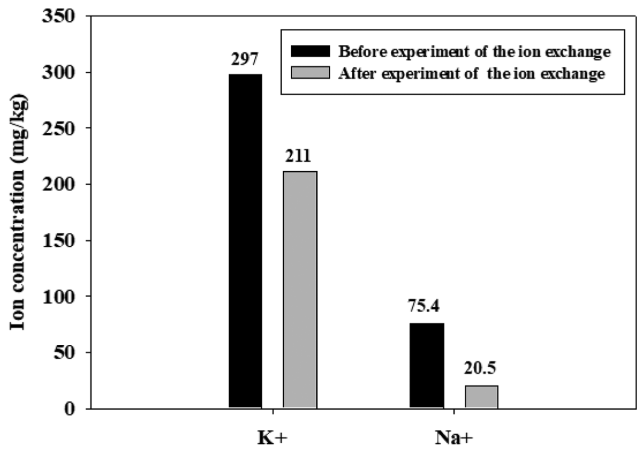

Fig. 7. ICP-OES analysis result before and after ion exchange experiment.

To analyze the metal ion removal performance of the K-PHI zeolite coated hollow fiber membrane, the solution before and after ion exchange was analyzed by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, OPTIMA 8300, PerkinElmer, Inc.). As shown in Fig. 7, The initial lignin wastewater was contained 297 mg/kg of K^+ ions and 75.4 mg/kg of Na^+ ions, respectively. However, after conducting an ion exchange experiment with a membrane coated with K-PHI zeolite, K^+ ions decreased by 29.0% to 211 mg/kg, and Na^+ ions decreased by 72.8% to 20.5 mg/kg.

4. Conclusion

An experiment was conducted to remove K^+ ions and Na^+ ions from lignin wastewater using a K-PHI zeolite coated alumina hollow fiber. The principle of K^+ and Na^+ ion removal was achieved through ion exchange between K^+ ions contained in the K-PHI zeolite structure and NH_4^+ ions contained in ammonia water flowing to the lumen side of the membrane. The above experiment was performed using only one of hollow fiber coated with K-PHI zeolite. As a result, K^+ ions decreased by 29.0% and Na^+ ions decreased by 72.8%.

In order to manufacture the 'Two-in-One Hybrid Coal' from the previous study [15], 90% of metal ions must be removed from the lignin wastewater. Therefore, based on the above experimental results, it is considered that at least 3 of hollow fiber membrane coated with k-phi zeolite are required.

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