A Hybrid Ion-Exchange Fabric/Ceramic Membrane System to Remove As(V), Zn(II), and Turbidity from Wastewater

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Abstract: Ceramic membranes and ion exchangers are effective at removing turbidity and ionic contaminants from water, respectively. In this study, we demonstrate the performance of a hybrid ion-exchange fabric/ceramic membrane system to treat metal ions and turbidity at the same time in synthetic wastewater. The removal rate of As(V) and Zn(II) by the ceramic membrane increased with solution pH, while turbidity was completely removed regardless of the solution pH. The main reaction of As(V) removal was adsorption at solution pH 6 and precipitation at solution pH 8, whereas phase-change was the predominant reaction for Zn(II) removal at both solution pH values. The removal efficiency of the ion-exchange fabric was affected by the solution pH, with the maximum removal capacity of As(V) occurring at solution pH 4. The As(V) adsorption capacity of the ion-exchange fabric reached equilibrium within 120 min. The ion-exchange capacity of the ion-exchange fabric was compared with commercial ion-exchange fibers. The regeneration efficiency of the ion-exchange fabric using 0.1 M NaCl solution was around 95% on average and decreased slightly as the number of regeneration cycles was increased. Over 80% of As(V) and Zn(II) were steadily removed at solution pH 6 by the hybrid ion-exchange fabric/ceramic membrane system. Reduced flow rate and removal capacity were recovered through a backwashing process during continuous treatment with the hybrid ion-exchange fabric/ceramic membrane system.

Keywords: ion-exchange fabric; ceramic membrane; Zn(II) removal; As(V) removal; turbidity removal

1. Introduction

Recently, interest in ceramic membranes has skyrocketed due to their superior thermal and chemical stability compared to polymer membranes [1]. They have a hydrophilic surface that makes them more durable and resistant to failure due to less membrane contamination [2]. In addition, ceramic membranes are attractive in industrial wastewater treatment because they are low-pressure-driven membranes that effectively remove colloidal and suspended particles and require a small footprint [3]. However, low-pressure-driven membranes are not effective at removing ionic contaminants such as heavy metals [4], and thus many physicochemical strategies have been proposed to increase their ionic removal efficiency. The deposition of nanoscale inorganic adsorbents such as iron oxide and zirconium dioxide on ceramic membrane pores is the most common modification method [5–7], with coating the top layer with different types of polymers such as chitosan and cellulose acetate over the ceramic
support being an alternative [8,9]. The development of hybrid processes combining ceramic membranes with ozone or ion-exchange processes has also been reported [10–12].

Ion-exchange processes are well-known for their effectiveness in removing ionic contaminants during water treatment. Recent studies have been conducted actively on ion-exchange processes using ion-exchange fibers due to the advantages of the fibrous form [13–16]. The fibers have a faster adsorption/desorption rate than ion-exchange resins due to the short transit distance of the ions and a better absorption capacity due to the large number of functional groups present along the fibers. Furthermore, the compact configuration of the treatment module is easy to fabricate and relatively free from head loss. Most ion-exchange fiber contact systems for wastewater treatment processes involve the production of a fixed-bed columns or filters made by grafting on nonwoven fabric [17–19].

To remove turbidity and ionic contaminants simultaneously, in this study, a hybrid system was prepared by combining the ceramic membrane and ion-exchange fabric in the reactor rather than separating each process. The performances of both the prepared ceramic membrane and the ion-exchange fabric were evaluated under various solution pH conditions, and the removal mechanisms were estimated using geochemical software. The removal efficiency of metal ions As(V) and Zn(II), and turbidity by the hybrid ion-exchange fabric/ceramic membrane system, were evaluated in a membrane module system including backwashing and regeneration processes.

2. Materials and Methods

2.1. Chemicals

Sodium arsenate dibasic heptahydrate (Na$_2$HAsO$_4$·7H$_2$O, Wako, Japan, 99%), zinc sulfate heptahydrate (ZnSO$_4$·7H$_2$O, Duksan Chemicals, Korea, 99%), and kaolin (Daejung Chemicals, Korea) were used to prepare the synthetic wastewater. The solution pH was adjusted using NaOH (Duksan Chemicals, Korea, 93%) and HCl (Duksan Chemical, Korea, 35–37%). Reagent grade NaCl (Duksan Chemicals, Korea, 99%) was used to prepare the regeneration solution. Distilled water (EXL5 U Analysis, Vivagen, Korea) was used for the preparation and dilution of all solutions.

2.2. Preparation of the Ion-Exchange Fabric/Ceramic Membrane Hybrid System

The specifications of the ceramic membrane are described in detail elsewhere [2,3]. It was a flat membrane coated with alumina and had a nominal pore size of 0.1 µm, an effective surface area of 94.7 cm$^2$, a height of 7 cm, a width of 6 cm, and a thickness of 0.4 cm. The commercial ion-exchange fibers (Kanecaron™ KC31, SA1, and SA2) were supplied by Kaneka Co., the characteristics of which were presented in our previous studies [13,14,20]. Among them, SA1 ion-exchange fibers were used to synthesize the ion-exchange fabric by combining 50% ion-exchange fiber with polyethylene and polypropylene. The prepared ion-exchange fabric (10 g) was mounted on the ceramic membrane in the ion-exchange fabric/ceramic membrane hybrid system (Figure 1).

2.3. Removal Experiments for Heavy Metals and Turbidity

The removal efficiency of the system was evaluated on prepared samples containing heavy metals and turbidity. First, the ceramic membrane was used to confirm the removal of As(V), Zn(II), and turbidity according to solution pH. Heavy metal contaminants As(V) and Zn(II) were prepared at initial concentrations of 50 mg/L, and 2 g/L kaolin was used to create turbidity [21]. The pH values in the experimental solutions were adjusted to 2, 4, 6, and 8 using HCl and NaOH. The removal experiments were carried out with an internal submerged dead-end flow regime membrane system at a flow rate of 10 mL/min using a peristaltic pump (BT100-2J, Longer, China), and the change in pollutant concentration of the solution passed through the ceramic membrane was analyzed.

The second set of experiments was conducted to evaluate As(V) removal by the ion-exchange fabric. To test the effects of solution pH on As(V) removal, the pH of the solutions was adjusted from 2 to 12 using HCl and NaOH. The test was carried out in a 50 mL solution containing a fabric dose of
2.0 g/L at an initial As(V) concentration of 10 mg/L. The solution was shaken for 6 h using a shaking incubator (HS330, MTOPS, Korea) at 150 rpm and 25 °C, and the samples were collected after the reaction to measure the residual As(V) concentration. The effects of reaction time were evaluated under the same experimental conditions with different reaction times of 5, 10, 15, 30 60, 120, 240, and 360 min. By varying the concentration of As(V) to 10, 50, 100, 200, and 500 mg/L, the effects of the initial contaminant concentration were examined, and 500 mg/L As(V) solution was used for the comparative experiment with other ion-exchange fibers. Regeneration experiments were carried out using 0.1 M NaCl, 0.1 M NaOH, and 0.1 M HCl regeneration solutions for 3 h after the removal test with 10 mg/L As(V) solution for 6 h.

Finally, the ion-exchange fabric/ceramic membrane hybrid system was used to remove As(V), Zn(II), and turbidity according to solution pH. Heavy metal contaminants As(V) and Zn(II) were prepared at initial concentrations of 50 mg/L, and 10 g/L kaolin was used to create turbidity. The pH values of the experimental solutions were adjusted to 4, 6, 8, and 10 using HCl and NaOH. The removal experiments were carried out at a flow rate of 60 mL/min using a peristaltic pump, and the flow measurements and sampling were conducted every 10 min. Backwashing was performed for 3 min every 30 min using a peristaltic pump (77 mL/min), and the experiment was conducted for a total of four cycles. The transmembrane pressure (TMP) measured by a pressure sensor (PX409-015GUSBH; Omega Engineering Inc., Stamford, CT, USA) was below 1 bar during the whole experimental process.

![Figure 1. Schematic diagram of the (a) experimental setup and (b) ion-exchange fabric/ceramic membrane module. Digital images of (c) ceramic membrane, (d) ion-exchange fabric, and (e) ion-exchange fabric/ceramic membrane module.](image)

2.4. Analysis Methods

The initial and residual concentrations of heavy metals were measured using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (Optima 5300DV, Perkin Elmer, USA), and the turbidity was determined using a turbidity meter (HL93707, Hanna Instruments, Portugal). The solution pH was measured with a pH probe (D-51, Horiba, Japan), and the distribution of the ionic species as a function of solution pH was estimated using geochemical software (Visual Minteq 3.1).
3. Results and Discussion

3.1. Removal of Heavy Metals As(V) and Zn(II) and Turbidity According to Solution pH Using the Ceramic Membrane

The removal rates of As(V) and Zn(II) by the ceramic membrane were investigated under various pH conditions (Figure 2). When only As(V) was present in the solution, its removal at solution pH values of 2, 4, and 6 was negligible. Only 7% of As(V) was removed by the ceramic membrane in solution pH 8. Meanwhile, the As(V) removal rate increased to 50% at solution pH 8 in a solution containing As(V) and Zn(II) (As + Zn). This is due to the precipitation of As(V) with Zn(II) and/or adsorption of As(V) on the zinc hydroxide carbonate precipitate [22,23]. In a solution containing metal ions and turbidity (As + Zn + Kaolin), the removal rate of As(V) increased to 31% at solution pH 6 and reached 54% at solution pH 8. Here, the geochemical modeling with Visual Minteq 3.1 suggests that adsorption was the predominant reaction of As(V) removal at pH 6 whereas precipitation was the main mechanism at pH 8 (Figure 3a). The saturation index (Table 1) calculated using Visual Minteq 3.1 suggests that adsorption of As(V) on the zinc hydroxide carbonate precipitate [22,23]. In a solution containing As(V) and Zn(II) (As + Zn). This is due to the precipitation of As(V) with Zn(II) and/or adsorption of As(V) on the zinc hydroxide carbonate precipitate [22,23]. In a solution containing metal ions and turbidity (As + Zn + Kaolin), the removal rate of As(V) increased to 31% at solution pH 6 and reached 54% at solution pH 8. Here, the geochemical modeling with Visual Minteq 3.1 suggests that adsorption was the predominant reaction of As(V) removal at pH 6 whereas precipitation was the main mechanism at pH 8 (Figure 3a). The saturation index (Table 1) calculated using Visual Minteq 3.1 suggests that adsorption of As(V) on the zinc hydroxide carbonate precipitate [22,23]. 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The pH dependence of As(V) removal by the IEF is attributed to the number of protonated sites on the fabric surface and the anionic form of As(V) present in the solution, which further increased to 31% and 98% from the As + Zn + Kaolin solution, respectively. The removal fractions of Zn(II) from the As + Zn + Kaolin solution were 14% phase-change, 8% precipitation, and 9% adsorption, at solution pH 6 and 91% phase-change and 7% precipitation, but without adsorption, at solution pH 8 (Figure 3b). The saturation index value confirmed that Zn(II) was phase-changed mainly to Zn(OH)₂ (am, beta, delta, epsilon, gamma) at pH 8 (Table 1). The turbidity caused by kaolin was completely removed by the ceramic membrane at all solution pH values (data not shown).

### 3.2. Evaluation of the As(V) Removal Capacity of the Ion-Exchange Fabric

The removal capacity of As(V) by the ion-exchange fabric (IEF) was evaluated. The influence of the solution pH on the As(V) removal capacity was tested, and the removal of As(V) by the IEF was affected by the solution pH (Figure 4a). The removal capacity of As(V) was less than 1 mg/g at solution pH 2 and increased sharply and reached a plateau at solution pH 4. Next, the As(V) removal capacity decreased gradually with increasing solution pH from 4 to 12 and dropped to 0.44 mg/g at solution pH 12. The pH dependence of As(V) removal by the IEF is attributed to the number of protonated sites available for anion exchange. At low solution pH, the amine groups on the fabric surface protonate to form NH₄⁺, and the surface is subsequently more positively charged [15,16]. However, due to the speciation of As(V), un-dissociated H₂AsO₄⁻ was the dominant form at solution pH 2 and the removal capacity by the IEF became very low [13]. The optimum adsorption capacity at solution pH 4 was due to the large number of protonated sites on the fabric surface and the anionic form of As(V) (H₂AsO₄⁻). As the pH increased, As(V) removal decreased due to a decrease in protonated sites. At solution pH 12, almost none of the amine groups were protonated, thus the removal capacity of As(V) by the IEF became negligible. The effect of contact time on the As(V) removal capacity was evaluated (Figure 4b). The As(V) adsorption capacity of the IEF rapidly increased and reached equilibrium within 120 min, with the rapid adsorption characteristic of As(V) being due to the easily accessible sites on the fabric surface [20]. A further increase in the contact time only had a minor effect on the As(V) adsorption capacity.

### Table 1. Saturation index of As and Zn calculated via Visual MINTEQ 3.1 according to solution pH.

| pH | As₂O₅(s) | Blanchite | Goslarite | Mirabilite | Thenardite | Zincite | Zincoxite | Zn metal | Zn(OH)₂ (am) | Zn(OH)₂ (beta) | Zn(OH)₂ (delta) | Zn(OH)₂ (epsilon) | Zn(OH)₂ (gamma) | Zn₅(OH)₆SO₄(s) | Zn₅(AsO₄)₂·2.5H₂O(s) | Zn₃(SO₄)₂(s) | Zn₃(OH)₆SO₄(s) | ZnSO₄·1H₂O(s) |
|----|----------|-----------|----------|-----------|------------|--------|-----------|---------|-------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 8  | -27.57   | -4.85     | -4.60    | -8.57     | -10.01     | 1.43   | -10.54    | -36.53  | 0.18        | 0.90           | 0.81           | 1.12           | 0.92           | -1.46          | 3.21           | -19.48         | 2.96           | -5.98         |
| 6  | -21.40   | -4.77     | -4.53    | -8.57     | -10.00     | -2.50  | -10.47    | -36.05  | -3.74       | -3.02          | -3.11          | -2.80          | -3.00          | -5.31          | -2.39          | -23.26         | -8.74          | -5.90         |
| 4  | -17.31   | -4.77     | -4.53    | -8.57     | -10.00     | -6.50  | -10.47    | -38.87  | -7.74       | -7.02          | -7.11          | -6.80          | -7.00          | -9.30          | -10.30         | -27.26         | -20.74         | -5.90         |
| 2  | -14.22   | -5.08     | -4.83    | -8.87     | -10.30     | -10.53 | -10.77    | -6.20    | -11.78      | -11.06         | -11.15         | -10.84         | -11.04         | -13.64         | -19.32         | -31.90         | -33.15         | -6.20         |

† n.a. = not available.
The effect of initial As(V) concentration on the removal capacity was also examined (Figure 4c). The amount of As(V) adsorbed on the IEF increased rapidly to 12.22 mg/g with an initial As(V) concentration of 200 mg/L, and the As(V) uptake further increased to 13.29 mg/g with an initial As(V) concentration of 500 mg/L. This increment is due to the higher mass-transfer driving force from the solution to the ion-exchange sites of the fabric at the higher initial concentration [20]. The ion-exchange capacity of the IEF was compared with commercial ion-exchange fibers supplied by Kaneka Co. (Table 2); the characteristics of these ion-exchange fibers were presented in our previous studies [13,14]. The IEF was synthesized by combining SA1 ion-exchange fibers on a polyethylene/polypropylene base; its adsorption capacity was around one-third of those of the commercial ion-exchange fibers.

The adsorption capacity of an IEF can generally be regenerated using NaCl, NaOH, and HCl, with the regeneration rate depending on the solution conditions and ion-exchanger properties [15]. As shown in Figure 4d, the regeneration rate with 0.1 M NaCl solution averaged around 95% and decreased slightly as the number of regenerations was increased. The regeneration rate with 0.1 M HCl solution was similar to NaCl (94%) during the first regeneration cycle but decreased significantly compared to NaCl, with an increase in the number of regeneration cycles. On the other hand, the NaOH solution was not able to regenerate the As(V) adsorption capacity of the IEF at all.
Table 2. Comparison between the As(V) adsorption capacities of the commercial ion-exchange fibers and the novel ion-exchange fabric (IEF).

| Adsorbent | Conditions | \( q_c^* \) (mg/g) |
|-----------|------------|---------------------|
| KC31      | Initial concentration = 500 mg/L; pH = 8.6; contact time = 360 min | 47.16 |
| SA1       | Initial concentration = 500 mg/L; pH = 8.6; contact time = 360 min | 47.19 |
| SA2       | Initial concentration = 500 mg/L; pH = 8.6; contact time = 360 min | 38.05 |
| IEF       | Initial concentration = 500 mg/L; pH = 8.63; contact time = 360 min | 13.29 |

*\( q_c^* \), equilibrium adsorption capacity.

3.3. Removal of Heavy Metals As(V) and Zn(II) and Turbidity According to Solution pH Using the Hybrid Ion-Exchange Fabric/Ceramic Membrane System

The removal efficiency of the hybrid ion-exchange fabric/ceramic membrane system was evaluated with contaminated solutions of heavy metals and turbidity. First, the variation in flow rate and the Zn(II) removal rate from a Zn + Kaolin solution according to solution pH is shown in Figure 5. Unlike the ceramic filter, the hybrid ion-exchange fabric/ceramic membrane system was able to remove some Zn(II) even at solution pH values of 4 and 6. This is because Zn(II) ions can be chemically bonded with the amine groups on the surface of the ion-exchange fabric under the given pH conditions [26]. However, Zn(II) was not stably removed at solution pH values of 4 and 6, while it was almost completely removed at solution pH values of 8 and 10 during the hybrid process. The removal of Zn(II) at solution pH values of 8 and 10 was caused by the ceramic membrane; the flow rate was stable at pH 8 but changed severely at pH 10. It is well known that the solution pH affects both foulant and the membrane surface, thereby altering the membrane performance significantly [27,28]. The decreased flow rate could be recovered through the backwashing process under all conditions.

Figure 5. Effect of solution pH on the flow rate and Zn(II) removal rate during the hybrid ion-exchange fabric/ceramic membrane process in Zn + Kaolin solution: (a) pH 4, (b) pH 6, (c) pH 8, and (d) pH 10.
The variation of flow rate and As(V) removal rate according to solution pH in As + Kaolin solution was also examined (Figure 6). The removal rate of As(V) by the hybrid ion-exchange fabric/ceramic membrane system was higher than that of the ceramic membrane alone. The hybrid process showed the highest removal rate at solution pH 4, and the removal rate decreased with increasing solution pH, which is consistent with the As(V) adsorption data described in the previous section. In particular, the removal rate of As(V) dropped rapidly at solution pH values of 8 and 10 during the hybrid process, and the flow rate also decreased more rapidly than with the Zn + Kaolin solution. This is because the As(V) precipitate formed at the given pH condition covered the surface pores of the membrane. The flow rate and As(V) removal capacity were recovered successfully through the backwashing process with 0.1 M NaCl solution.

Finally, the removal efficiencies of heavy metals and turbidity by the hybrid ion-exchange fabric/ceramic membrane system from the As + Zn + Kaolin solution were evaluated (Figure 7). Zn(II) was completely and reliably removed by the hybrid process at solution pH values of 8 and 10, while the As(V) removal rate was drastically reduced. This was because more fractions of Zn(II) had been removed through phase change, as previously mentioned in Figure 2 and Table 1. Meanwhile, As(V) and Zn(II) were steadily removed to over 80% at solution pH 6, which was the highest As(V) removal rate among all of the solution pH conditions. The flow rate reduction at solution pH 4 was the lowest, but the As(V) and Zn(II) removal rates were significantly lower than under the other solution pH conditions. The decreased flow rate and As(V) removal capacity could be recovered through the backwashing process during continuous treatment of the As + Zn + Kaolin solution with the hybrid ion-exchange fabric/ceramic membrane system.
The removal of metal ions and turbidity from synthetic wastewater were investigated using a hybrid ion-exchange fabric/ceramic membrane system. The removal efficiency of As(V) and Zn(II) by the ceramic membrane was increased as the solution pH increased to 8, while the turbidity was completely removed regardless of the solution pH. The predominant reaction mechanisms of As(V) and Zn(II) were precipitation and phase-change, respectively. The removal efficiency of the ion-exchange fabric was affected by the solution pH, and the maximum removal capacity of As(V) occurred at solution pH 4. Adsorption of As(V) on the ion-exchange fabric quickly reached equilibrium in 120 min, with the adsorption capacity being around one-third of other commercial ion-exchange fibers. Over 80% of As(V) and Zn(II) was steadily removed from the As + Zn + Kaolin solution by the hybrid ion-exchange fabric/ceramic membrane system at solution pH 6. The decreased flow rate and As(V) removal capacity were recovered through the backwashing process during continuous treatment with the hybrid ion-exchange fabric/ceramic membrane system. This compact hybrid system can be used for the treatment of various industrial wastewater sources containing ionic contaminants and turbidity.

Figure 7. Effect of solution pH on the flow rate and Zn and As removal rates during the hybrid ion-exchange fabric/ceramic membrane processing of As + Zn + Kaolin solution: (a) pH 4, (b) pH 6, (c) pH 8, and (d) pH 10.

4. Conclusions

The removal of metal ions and turbidity from synthetic wastewater were investigated using a hybrid ion-exchange fabric/ceramic membrane system. The removal efficiency of As(V) and Zn(II) by the ceramic membrane was increased as the solution pH increased to 8, while the turbidity was completely removed regardless of the solution pH. The predominant reaction mechanisms of As(V) and Zn(II) were precipitation and phase-change, respectively. The removal efficiency of the ion-exchange fabric was affected by the solution pH, and the maximum removal capacity of As(V) occurred at solution pH 4. Adsorption of As(V) on the ion-exchange fabric quickly reached equilibrium in 120 min, with the adsorption capacity being around one-third of other commercial ion-exchange fibers. Over 80% of As(V) and Zn(II) was steadily removed from the As + Zn + Kaolin solution by the hybrid ion-exchange fabric/ceramic membrane system at solution pH 6. The decreased flow rate and As(V) removal capacity were recovered through the backwashing process during continuous treatment with the hybrid ion-exchange fabric/ceramic membrane system. This compact hybrid system can be used for the treatment of various industrial wastewater sources containing ionic contaminants and turbidity.

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