Removal of NO$_3^-$ from groundwater by PP-g-AA-Am non-woven fabric using fixed-bed column reactors

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ABSTRACT

This study investigated the effect of PP-g-AA-AM non-woven fabric on the removal of nitrate nitrogen from groundwater. The breakthrough time was 1.5–2.6, 2.5–5.5, and 6.2–12.2 h for a superficial velocity of 2.0, 1.0, and 0.5 cm/s, respectively, for the nitrate nitrogen concentration in groundwater to satisfy the safe standard for drinking of 10 mg/L (as per the Ministry of Environment in Korea’s 2011 Management of Drinking Water Act); the slower the superficial velocity, the longer is the breakthrough time. The ion exchange amount was a maximum of 28.37 mg/g for a superficial velocity of 2.0 cm/s, and the ion exchange amount decreased with slower or faster superficial velocities. The ratio of adsorbent used shows a linear relationship with the column diameter to length ratio and an inverse one with the superficial velocity. It is a maximum of 79% for a superficial velocity of 0.5 cm/s and a column diameter to length ratio of 1:10. Multiple regression analysis with the superficial velocity, nitrate nitrogen concentration in groundwater, and column diameter to length ratio showed that the initial nitrate nitrogen concentration has the strongest influence on the ion exchange amount. A 10% NaCl regenerant solution of 20 times the reactor volume is required to accomplish >99% of ion exchange bed regeneration in a groundwater treatment facility when applied to a packed column filled with PP-g-AA-Am.

Key words | anion exchange, fixed-bed column, groundwater, nitrate nitrogen, PP-g-AA-Am non-woven fabric

INTRODUCTION

In Korea, water consumption is increasing considerably with improvements in the standard of living. However, water resources are limited, with most of the water supply in the country being dependent on surface water. In recent years, therefore, groundwater has increasingly been exploited to reduce the imbalance between the supply and demand for water that is being caused by water overconsumption. However, groundwater, while being an important resource, is fragile in that it is vulnerable to pollution.

Groundwater pollution is caused by organic chemicals such as agricultural chemicals and organic solvents, heavy metals, viruses, pathogenic bacteria, human and animal excreta that includes parasites, and sewage. Among these, nitrate nitrogen is a major pollutant in Korea. While nitrate nitrogen is produced by natural sources in that it is contained in rainfall, it is mainly produced by human and industrial sources. These include domestic and industrial wastewater, organic and inorganic fertilizers used in agriculture, plant residues, and livestock industry wastes. Nitrate nitrogen is often detected in groundwater in high concentrations, along with volatile organic chloride compounds such as trichloroethylene (TCE) and tetrachloroethylene. The 2010 groundwater quality report showed that 143 samples (3.7%) out of 3,882 obtained across the country contained pollutant concentrations that exceeded the safe standard for drinking. Many of these samples were obtained in the vicinity of urban residential areas, industrial complexes, and waste landfills.

Nitrate ions contained in drinking water are reduced to nitrite ions in the human digestive tract. These ions can
cause methemoglobinemia, which can be fatal to humans because it prevents the effective delivery of oxygen in the human body. The safe standard for nitrate nitrogen in drinking/well water is up to 10 mg/L (MEK 2011), because nitrate ions can in turn form N-nitroso compounds, which are known carcinogens (Pontius 1995).

Owing to these issues, many studies have focused on the removal of nitrate nitrogen from groundwater. Towards this end, many approaches such as chemical reduction, reverse osmosis (National Research Council 2004), electrodialysis, biological denitrification, ion exchange (Ruixia et al. 2002; Boumediene & Achour 2004; Samatya et al. 2006), and reduction with zero-valent metals have been investigated (Lin & Kiang 2003; Al-Bastaki 2004; Chen 2004; Esplugas et al. 2004; Öztürk & Bektas 2004; Hu et al. 2005; Xu 2005; Yeon et al. 2005; Geraldes & Afonso 2007; Hasar et al. 2008; Kabaya et al. 2008). However, most of these methods suffer from certain disadvantages: chemical reduction involves the addition of chemicals; reverse osmosis and electrodialysis are expensive; biological denitrification involves the addition of large amounts of disinfectant; and ion exchange, although known to be the most efficient method, is expensive and involves a regeneration process that requires a considerable amount of sodium chloride and releases effluents containing excessive nitrate ions and salt.

In our previous papers (Park & Na 2006), we have reported the preparation method for PP-g-AA-Am non-woven fabric using the photo induced graft polymerization of acrylic acid (AA) onto polypropylene (PP) non-woven fabric and subsequently converting the carboxyl (–COOH) group in the grafted AA to an amine (Am) group through a reaction with DETA. First, AA was grafted onto PP fabric by a conventional photo induced grafting technique. The grafting solution was prepared using 70/30 (v/v)% water/methanol, and it contained 15 (v/v)% AA, 0.2 (w/v)% BP, 0.2 M H2SO4 and 5 × 10⁻³ M FeSO4·7H2O. Thirty milliliters of grafting solution and PP non-woven fabric were placed in a glass tube and then exposed to UV light for 1 h at 60 °C. A 400-W high-pressure mercury lamp (Miya Electric Co., Korea) was used as the light source. After the grafting reaction, the samples were washed with methanol for 10 h in a Soxhlet apparatus to remove the homopolymer and dried at 60 °C to constant weight. The degree of grafting was calculated from the weight gain according to a procedure described elsewhere. By graft polymerization, AA-grafted PP (PP-g-AA) fabrics with a degree of grafting of 150 ± 5% were prepared and used as the substrate for chemical modification.

**EXPERIMENTAL**

**Materials and reagents**

PP non-woven fabric of 180 g/m² was washed with a neutral detergent solution for use as the substrate polymer for grafting. AA (Daejung Chemical Co., Korea) was used as the monomer; benzophenone (BP, Yakuri Pure Chemical Co., Japan), as the photoinitiator; H2SO4 as the graft accelerator; FeSO4·7H2O, as the homopolymer inhibitor; methanol, as the homopolymer removal solvent; DETA (Daejung Chemical Co., Korea), as the amination reagent; and AlCl3, as the reaction catalyst for transforming the functional carboxyl group of the grafted AA on the PP non-woven fabric into a functional amine group.

Extra pure KNO3 and NaCl respectively, were used to prepare the anion solution and to regenerate the adsorbent in the column.

**Preparation of PP-g-AA-Am fabric**

PP-g-AA-Am fabrics were prepared by grafting AA onto PP non-woven fabrics and subsequently converting the carboxyl (–COOH) group in the grafted AA to an amine (Am) group through a reaction with DETA according to the procedure described in our previous paper.

First, AA was grafted onto PP fabric by a conventional photo induced grafting technique. The grafting solution was prepared using 70/30 (v/v)% water/methanol, and it contained 15 (v/v)% AA, 0.2 (w/v)% BP, 0.2 M H2SO4 and 5 × 10⁻³ M FeSO4·7H2O. Thirty milliliters of grafting solution and PP non-woven fabric were placed in a glass tube and then exposed to UV light for 1 h at 60 °C. A 400-W high-pressure mercury lamp (Miya Electric Co., Korea) was used as the light source. After the grafting reaction, the samples were washed with methanol for 10 h in a Soxhlet apparatus to remove the homopolymer and dried at 60 °C to constant weight. The degree of grafting was calculated from the weight gain according to a procedure described elsewhere. By graft polymerization, AA-grafted PP (PP-g-AA) fabrics with a degree of grafting of 150 ± 5% were prepared and used as the substrate for chemical modification.
Subsequently, PP-g-AA fabrics were immersed in DETA solution containing 4 (w/v)% of AlCl₃ catalyst to convert the hydroxyl groups of the grafted AA into amine groups. The amination reaction continued for 2–6 h at 150 °C with periodic stirring. After the reaction, the aminated PP-g-AA (PP-g-AA-Am) fabrics were repeatedly washed with 1 N HCl solution and deionized water to remove the unreacted solution, following which they were dried at 60 °C to constant weight. The degree of amination was calculated from the weight gain and the molar ratio between AA and DETA according to a procedure described elsewhere. Through the amination reaction, PP-g-AA-Am fabrics with a degree of amination of 55–65% were prepared and used for sorption experiments.

Continuous column test

The groundwater for the ion exchange test was obtained from a household groundwater hole. An ion chromatograph (ICS-3000, Dionex, USA) was used to analyze for Na, K, Mg, Cl, NO₃, SO₄, F and PO₄. The pH of the groundwater ranged between 6.5 and 6.7, and values for Na⁺ (13.5 mg/L), K⁺ (2.5 mg/L), Ca²⁺ (35 mg/L), Mg²⁺ (9 mg/L), HCO₃⁻ (62 mg/L; titration), and CO₃²⁻ (0 mg/L; titration) were analyzed. It was found to contain 27 mg/L of Cl⁻, 15.4 mg/L of NO₃⁻, and 19 mg/L of SO₄²⁻; F⁻ and PO₄³⁻ were below the detection limit. Potassium nitrate was used to adjust the nitrate nitrogen concentration in groundwater.

Seventy milliliter columns were made of cylindrical acryl. The inflow and outflow were blocked using absorbent cotton, and the column was packed with 43 g of PP-g-AA-Am non-woven fabric which had been ground to a size of 1–2 mm. The packing density of the column was 0.9 g/cm³, adsorbent volume was 47.5 cm³, and pore volume was 22.5 cm³. The groundwater and sodium chloride (NaCl) regenerant solution were pumped upstream using a metering pump and collected every 5 L to analyze the NO₃ concentration. Table 1 lists experimental conditions such as the column diameter to length ratio, superficial velocity, and nitrate nitrogen concentration.

All experiment results were analyzed by multiple regression analysis using SPSS 19.0 software to examine factors that affect the ion exchange amount of the adsorbent.

Regeneration of adsorbent

The column packed with PP-g-AA-Am was regenerated by cleaning using 1, 2, and 3 mol/L of NaCl solution with a superficial velocity of 0.5–1.0 cm/s. The column was then cleaned using 3–5 L of distilled water after the regeneration before it could be used again for experiments. The nitrate nitrogen concentration was measured using a UV spectrometer as well as by the standard method for examination of water.

RESULTS AND DISCUSSIONS

A fixed column test was carried out under various experimental conditions to investigate the nitrate nitrogen removal efficiency of the PP-g-AA-Am non-woven fabric (adsorbent). PP-g-AA-Am having a degree of amination of 55–65% was ground before being used. Figure 1 shows the chemical structure of the PP-g-AA-Am non-woven fabric. Its physicochemical and ion exchange characteristics have been studied previously (Park & Na 2006).

Change in breakthrough time

In the column test, the adsorbent amount depends on the type and concentration of material in the water. In addition, the column size could determine the adsorbent amount. Therefore, the column diameter to length ratio (D:L ratio)
is related to the ion exchange efficiency, which helps in determining the optimal column size.

Figure 2 shows the results of the column test for column D:L ratios of 1:4, 1:7, and 1:10. The respective end points were found to be 130, 170, and 210 min at 2.0 cm/s of superficial velocity (Figure 2(c)). The breakthrough time was found to increase with the column length of the adsorbent.

The ion exchange bed should be changed or regenerated when the groundwater treated through the column contains over 10 mg/L of nitrate nitrogen, which would exceed the standard for drinking water, because the adsorbent is considered to have lost its ability to remove nitrate nitrogen at such concentrations. The breakthrough time when the nitrate nitrogen concentration is below 10 mg/L (drinking water standard) is shorter than the saturated breakthrough time ($C/C_0 = 0.5$), as shown in Figure 2. When the nitrate nitrogen concentration is over 10 mg/L, the breakthrough times for the respective ratios mentioned above were found to be 85, 115, and 145 min for a superficial velocity of 2.0 cm/s.

**Change in ion exchange amount**

First, the ion exchange amount was calculated along with the change in column size and superficial velocity, and then each ion exchange amount per unit weight under different conditions was compared, to determine the optimal column size for the column ion exchange process. The ion exchange amount per unit weight (mg/g) is obtained by dividing the ion exchange amount (mg) by the weight of filled adsorbent (g). Figure 3 shows the ion exchange amount with the column size, superficial velocity, and

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Figure 1 | Synthetic route and chemical structure of PP-g-AA-Am non-woven fabric.

Figure 2 | Saturated breakthrough time for various column diameter to length ratios (the dashed line the point at which NO$_3^-$ = 10 mg/L, which varies with initial concentration).

Figure 3 | Ion exchange amount for various column diameter to length ratios.
breakthrough time for nitrate nitrogen concentrations below 10 mg/L. When the column D:L ratio is 1:10 and the superficial velocity is 0.5 cm/s, the maximum ion exchange amount is 26 mg/g. For various column D:L ratios, with a nitrate nitrogen concentration below 10 mg/L, it was observed that the amount of nitrate nitrogen adsorbed shows a linear relationship with the column length but an inverse one with the superficial velocity.

For column D:L ratios of 1:4, 1:7, and 1:10, the ion exchange amount was 24, 25, and 26 mg/g, respectively, for a superficial velocity of 0.5 cm/s. Furthermore, for superficial velocities of 0.5, 1.0, and 2.0 cm/s, the ion exchange amount was 26, 23, and 22 mg/g at D:L = 1:10, respectively. Groundwater passes through the column slowly, as a result of which the contact time with the adsorbent can be increased. In other words, the total ion exchange amount increases for the same amount of nitrate nitrogen because the ion exchange progresses more readily under low superficial velocity. Therefore, the effects of superficial velocity and D:L ratio are comparable rather than significantly different. The contact time controls the ion exchange amount.

**Capacity for groundwater treatment**

The bed volume as compared with the packing volume of the ion exchange bed (BV) is shown in Figure 4. The BV is observed at different superficial velocities ranging from 0.5 to 2.0 cm/s to evaluate the capacity for groundwater treatment. The flow rate is an important factor in column ion exchange because the superficial velocity decides the retention time of polluted groundwater in a column filled with adsorbent. Figure 4 shows the BV results for column D:L ratios of 1:4, 1:7, and 1:10 for a nitrate nitrogen concentration of 37 mg/L. The BV is compared with the breakthrough time \( \left( \frac{C}{C_0} \right) \) because the inflow of the groundwater with time was different.

The BV results for various superficial velocities do not agree with the breakthrough times \( \left( \frac{C}{C_0} = 1 \right) \) and saturated breakthrough times \( \left( \frac{C}{C_0} = 0.5 \right) \). When the column D:L ratio is 1:4 (Figure 4(a)), BV increases with the superficial velocity at the breakthrough time, with values of 980, 1,070, and 1,230 BV for a superficial velocity of 0.5, 1.0, and 2.0 cm/s, respectively. On the other hand, BV increases with a slower superficial velocity at around the saturated breakthrough time when the nitrate nitrogen concentration is below 10 mg/L. In other words, the slower the superficial velocity, the more the groundwater is treated, thus maintaining a nitrate nitrogen concentration below 10 mg/L, with values of 650, 610, and 580 BV for a superficial velocity of 0.5, 1.0, and 2.0 cm/s, respectively. The same tendency is also observed in the case of the column D:L ratio.

Figure 4 shows a comparison of the capacity for groundwater treatment with the column D:L ratio. A longer column has a better capacity for groundwater treatment, for a nitrate nitrogen concentration of 10 mg/L, with values of 650, 710, and 730 BV for a column D:L ratio of 1:4, 1:7, and 1:10 at 0.5 cm/s of superficial velocity, respectively. In other words, a slower superficial velocity and longer column show better capacity for groundwater treatment, for a nitrate nitrogen concentration below 10 mg/L.
Ratio of adsorbent used for ion exchange

The ratio of adsorbent used for ion exchange along with the superficial velocity is computed by extrapolation using $\frac{C}{C_0} = 0.5$ to determine the improvement in the ratio with changes in the superficial velocity (Figure 5). The ratio of adsorbent used for ion exchange is 67, 74, and 79% for a superficial velocity of 2.0, 1.0, and 0.5 cm/s, respectively, for a column D:L ratio of 1:10. The same tendency is observed for the other column D:L ratios of 1:4 and 1:7. For the same superficial velocity, 1.0 cm/s, the ratio of adsorbent used for ion exchange increased with the column length, with values of 63, 67, and 74% for column D:L ratios of 1:4, 1:7, and 1:10, respectively.

Relationship of ion exchange with nitrate nitrogen concentration in groundwater

To investigate the relationship of ion exchange with the initial concentration of nitrate nitrogen in groundwater, the superficial velocity was fixed at 1.0 cm/s, and the ratio of ion exchange with BV was investigated for initial nitrate nitrogen concentrations of 15, 24, and 37 mg/L, respectively (Figure 6).

For a higher initial nitrate nitrogen concentration, breakthrough was obtained for a narrower and shorter endpoint. For a column D:L ratio of 1:10, values of 1,240, 910, and 690 BV were obtained for initial concentrations of 15, 24, and 37 mg/L nitrate nitrogen, respectively.

Multiple regression analysis was performed to examine how the effective superficial velocity, initial nitrate nitrogen concentration, and column size affect the ion exchange amount.

The regression equation for estimating the ion exchange amount in terms of these three variables is as given below ($P < 0.001$):

$$Y = 19.60 - 1.56 \times A + 0.457 \times B$$

$$Y = 11.64 - 1.27 \times A + 0.46 \times B + 0.294 \times C$$

$Y$: amount of ion exchange, $A$: superficial velocity, $B$: column diameter to length ratio, $C$: initial nitrate nitrogen concentration in groundwater.

The effect of these variables on the ion exchange amount is 12.7% when the column D:L ratio and superficial velocity are provided and 54.4% when the initial nitrate nitrogen concentration is provided. Thus, 41.7% of the
increase results from the initial nitrate nitrogen concentration, which has the strongest influence.

**Effect of regeneration**

**Variation of mole concentration**

Generally, the adsorbents filling the ion exchange reactor are regenerated using dilute acid or dilute alkali. The regeneration efficiency is as important a factor as the ion exchange efficiency for efficient ion exchange because it is related to the economic feasibility. In this study, NaCl was used for regeneration, and its concentration was adjusted to 1–3 N. The slower the superficial velocity was, the less regenerant solution was required, and the highest removal ratio was more than 30% at 0.5 cm/s superficial velocity as shown in **Figure 7**. Concentrations of 1, 2, and 3 N of NaCl at 0.5 cm/s of superficial velocity are equivalent to concentrations of 5.8, 11.6, and 17.4% respectively.

The adsorbents were regenerated using NaCl solution after treating a nitrate nitrogen concentration of 24 mg/L until the breakthrough time, and then the desorption efficiency and desorbed nitrate nitrogen were calculated as shown in **Figure 8**. When a 1 N NaCl solution was used as the regenerant solution, the highest nitrate nitrogen concentration in the regenerant solution is ∼3,100 mg/L, and therefore a NaCl solution of 30 times the reactor volume should be used to reduce the nitrate nitrogen concentration below 10 mg/L. For a 2 N NaCl solution, the highest concentration is 5,700 mg/L, and therefore, more than 20 times the reactor volume is required. For a 3 N NaCl solution, the highest concentration is 6,700 mg/L, and therefore, a volume similar to that in the case of a 2 N NaCl solution is required.

These results suggest that the minimum volume of a 2 N NaCl regenerant solution is 20 times the reactor volume for
a groundwater treatment facility using a packing column filled with PP-g-AA-AM. In addition, the waste NaCl regenerant solution contains more than 10% NaCl and a high nitrate nitrogen concentration of ∼1,400 mg/L. When a 1 N NaCl regenerant solution is used, the required volume is 30 times the reactor volume and the waste NaCl solution contains more than 5% NaCl and a high nitrate nitrogen concentration of 1,000 mg/L.

Number of regenerations

The ion exchange and regeneration tests were repeated to investigate the recycle ratio of PP-g-AA-Am as an adsorbent for the removal of nitrate nitrogen from groundwater. For the ion exchange test, a column with a D:L ratio of 1:4 and groundwater with a nitrate nitrogen concentration of 37 mg/L were selected; the test was performed for an outflow of \( C/C_0 = 1 \). For the regeneration test, a 2 N NaCl regenerant solution was used with a superficial velocity of 0.5 cm/s.

The adsorptivity per unit packed weight of PP-g-AA-Am remained constant when regeneration was repeated 10 times (Figure 9). This result implied that PP-g-AA-Am can be used at least 10 times without loss of adsorptivity by cleaning using 2 N NaCl regenerant solution.

CONCLUSIONS

Groundwater is an important water resource, but it is vulnerable to pollution. In Korea, nitrate nitrogen is a major groundwater pollutant. Owing to the adverse health effects of nitrate nitrogen, its removal is essential if the groundwater is to be used for drinking. This study investigated an ion exchange process using PP-g-AA-Am non-woven fabric for groundwater treatment and suggested the most efficient conditions for ion exchange and regeneration. This study was performed under the condition that the outflow satisfied the safe standard of nitrate nitrogen concentration in groundwater, which is 10 mg/L. The key observations of our study are listed below.

1. The breakthrough time shows a linear relationship with the column D:L ratio and an inverse one with the superficial velocity.
2. The ion exchange amount and capacity for groundwater treatment increase with the column D:L ratio.
3. The longer the column, the higher is the ratio of adsorbent used for ion exchange, with the maximum being 79% for a superficial velocity of 0.5 cm/s and column D:L ratio of 1:10.
4. The maximum ion exchange amount was 26 mg/g for a superficial velocity of 0.5 cm/s and column D:L ratio of 1:10. For a constant superficial velocity of 0.5 cm/s, the ion exchange amount was 24, 25, and 26 mg/g for a column D:L ratio of 1:4, 1:7, and 1:10, respectively.
5. For a superficial velocity of 0.5–2.0 cm/s, the capacity for ion exchange treatment of groundwater to reduce the nitrate nitrogen concentration from 37 mg/L to below 10 mg/L is 580–740 times the reactor volume and 1,600–1,950 times the packed adsorbent weight.
6. The ion exchange amount is most strongly influenced by the initial nitrate nitrogen concentration, as found through a multiple regression analysis with the superficial velocity, initial nitrate nitrogen concentration, and column D:L ratio.
7. An ion exchange reactor packed with PP-g-AA-Am requires a 2 N NaCl regenerant solution that is 20 times the reactor volume. Moreover, waste NaCl regenerant solution contains ∼1,500 mg/L of nitrate nitrogen.

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REFERENCES


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