Article

Ammonium Removal by Mixed-Bed Ion Exchange

Gangchoon LEE, Taekyung YOON

Department of Environmental Engineering, Dongeui University, Gaya-dong 24, Busanjin-gu, Busan 614-714, Korea

Byeongil NOH

Department of Chemical Engineering, Dongseo University, Busan 617-716, Korea

Dong-Hyo KANG

Environmental Installations Corporation, Busan 607-102, Korea

Hak Sung LEE

School of Chemical Engineering, University of Ulsan, Ulsan 680-749, Korea

Nak Chang SUNG

Department of Environmental Engineering, Donga University, Busan 604-714, Korea

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Abstract

Ion exchange performance to remove ammonium in drinking water was studied experimentally with the effects of the difference between single-bed and mixed-bed, the cation-to-anion resin ratio, the column configuration, and influent ammonium concentration on the performance of anion exchange for the ammonium removal. The experiments were performed in continuous packed bed ion exchange column with commercially available exchange resins under the various conditions. The performance was evaluated with the breakthrough curves obtained. The results showed that better ammonium removal performance can be achieved under the following system conditions; in mixed-bed, in the lower cation-to-anion resin ratio, in the anion bed-cation bed series configuration or in high influent concentration. The results of this study can be used to the development or improvement of simulation tool for an ion exchange process design.

1 Introduction

Ammonium in water itself is not toxic to men, but toxic to some fishes as a function of pH, fish species and size, and ammonium concentration. Ammonium can cause oxygen depletion in water as it is oxidized to nitrite and then to nitrate which is toxic especially to pregnant women and infants. Ammonium is also an algal nutrient source for growth-limiting factor to the causes of eutrophication. This causes a fatal damage to the sea food industries.[1] The Korean standard of 0.5 mg NH_4^+ -N/L or less in drinking water was established for the human health.

Methods of removing ammonium from water and wastewater can be; either biological processes like microbial nitrification-denitrification, or chemical-physical processes such as ammonia stripping, ion exchange,

and breakpoint chlorination.

Ion exchange can be provided as an economical and convenient process for the treatment of ammonium in small or medium sized water treatment plants containing relatively low concentration level of ammonium.[2] As a previous research, Yoon et al.[3] experimentally studied the effect of operating parameters on the anion exchange performance to remove ammonium using batch and continuous systems under various experimental conditions. They obtained the results that the ammonium removal increases with small column diameter or large column height, low initial feed concentration, low volumetric flow rate or high operating temperature. In addition, Yoon et al.[4] carried out the research for cation exchange performance to remove nitrate with the same experimental method with reference,[3] and described the effect of operating parameters on exchange performance.

This paper deals with the effects of ion exchange bed type(single and mixed beds), cation/anion ratio, bed configuration, and influent ammonium concentration on the performance of anion exchange for the ammonium removal. The results of this study can be used to the development or improvement of simulation tool for an ion exchange process design with previous researches.[3,4]

2 Experimental

Dowex Monosphere 650C cation exchange resin of H^+ form and Dowex Monosphere 550A anion exchange resin of OH^- form were used in single and mixed bed experiments. The experiments were conducted with continuous operation, and the glass column was used in a single or a mixed bed set-up of packed type.

The experimental system consisted of a packed-bed column, a feeding pump, a flowmeter, a water bath, a feed storage, and an ion chromatography for analyzing effluent concentrations, and is shown in Fig. 1. The continuous operation was performed to investigate the effects of the cation-to-anion resin ratio in the column, the difference and configuration between single- and mixed-bed, and influent ammonium concentration on the breakthrough curves of ammonium.

1. Feed storage 2. Pump 3. Flow meter
4. Column 5. Resin 6. Silicone Stopper
7. Glass wool 8. Water bath 9. Ion chromatography

Table 1. Experimental conditions

Parameters	Conditions
Feed Concentration	NO_3^- 9.92 mg/dm ³ , NH_4^+ 2.88 mg/dm ³
Feed Flow Rate	10.8 dm ³ /h
Column Diameter	12 mm
Bed Depth	20 – 70 mm
Dry Resin Weight	0.5 – 4.0 g
Temperature	15°C

Fig. 1. Schematic diagram of the continuous operation system.

A neutral salt solution of NH_4NO_3 was used as a feed solution. Table I shows the experimental conditions used in bed operation.

3 Results and Discussion

The results of water sample analysis were described by breakthrough curves expressed as the ratio of the effluent concentration(C) to the feed concentration(C_o) vs. run time or solution volume passed through the experimental column. The results from each experiment discussed the comparisons of single-bed and mixed-bed ion exchange, the effects of cation-to-anion resin ratio, column configuration, and influent ammonium concentration.

The results of the single-bed and the mixed-bed column experiments are given in Fig. 2. The initial leakages might result from the insufficient contact time between the solution and the resin due to the high flow rate and the relatively short bed depth. These conditions were selected for the reasonable duration of the experimental runs in order to get a breakthrough curve. It is observed in this figure that mixed-bed gives the steeper breakthrough curve at around 30 dm^3 , and the initial leakage of ammonium in single-bed was higher than

Fig. 2. Comparison of ammonium breakthrough curves with mixed- and single-bed

Fig. 3. Ammonium breakthrough curves of MBIE as a function of cation/anion resin ratio

that in mixed-bed. The performance of mixed-bed ion exchange for various cation-to-anion ratios was compared in Fig. 3. The same amount of cation exchange resin with larger amounts of anion exchange resin produced a steeper slope of breakthrough curve than with smaller amounts of anion exchange resin. In this operating condition, an aqueous phase has alkaline pH.

Harries showed that cation exchange is faster in an alkaline aqueous pH than in an acidic pH since the mass-transfer coefficient(MTC) of cation is higher at the high pH [5]. Thus the ammonium exchange rate becomes faster in mixed bed than in single bed, where the exchange is performed under alkaline to less acidic pH range. The higher MTCs in mixed beds can be explained by neutralization in bulk phase and liquid film.[6] In mixed bed the hydrogen-hydroxide neutralization reaction stoichiometrically forms water molecules. In the mixed bed with excess anion resins, high aqueous concentration of hydroxide shifts the neutralization reaction plane into the film inside surrounding the cation resin, thus promotes the cation exchange rate. Therefore the curve for mixed bed in Fig.2 and the curve for cation-to-anion resin ratio of 1:2 in Fig. 3 show steeper slopes of breakthrough curves than others.

This can be explained when the series configurations of single beds, such as cation bed-anion bed or anion bed-cation bed, are used instead of mixed bed. Figure 4 shows the effect of column configuration. In this

figure we have a better breakthrough curve when the inlet solution pass through anion bed first and cation bed later. This configuration makes the solution very alkaline and MTC of ammonium high. Accordingly, the higher MTC of ammonium gives lower initial ammonium leakage level and better ammonium removal. This configuration is even better than the mixed-bed.

Figure 5 shows the effect of influent concentration on the ammonium breakthrough curve. As expected, the curves in Fig. 5 indicate the steeper slope and the faster breakthrough when the concentration increases. The initial leakage also increases with the influent concentration. The ratio of the treated solution volume, which is the left-hand side area of the breakthrough curves, agrees with the ratio of the influent concentration. Therefore, it can be said that the capacity of the resin is likely not to be changed by the variation of the initial influent concentration.

Fig. 4. Cation breakthrough curves with inlet flow cation to anion, anion to cation single bed and mixed bed

Fig. 5. Effect of influent concentration on ammonium breakthrough curves with MBIE

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