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# Combination of Na-modified zeolite and anion exchange resin for advanced treatment of a high ammonia–nitrogen content municipal effluent

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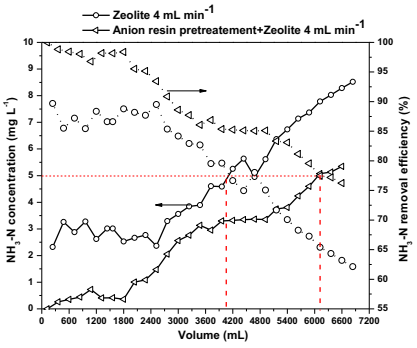
## GRAPHICAL ABSTRACT

The field experiments to treat bio-treated secondary effluent proved that the reduction of dissolved organic matter by the magnetic anion exchange resin improved the removal efficiency of ammonia–nitrogen by the zeolite.

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## ABSTRACT

In this study, the exchange equilibrium and kinetic experiments of ammonia–nitrogen on the Na-form zeolite were conducted. The results indicated that the presence of humic acid have a negative effect on the equilibrium exchange capacity but have limited influence on the equilibrium time except shorten the sole intra-particle diffusion control time. The exchange equilibrium data could be well fitted by Freundlich model in the absence of humic acid but Langmuir model in the presence of humic acid. While the exchange kinetic data could be well described by pseudo-second-order kinetic model in both situations. An anion exchange resin exhibited high removal efficiency to humic acid and dissolved organic matter through kinetic results and fluorescence excitation-emission matrix (EEM) spectroscopy results. The use of the anion exchange resin prior to the Na-form zeolite improved the ammonia–nitrogen removal efficiency from 78% to 95% and increased the treatment volume of the Na-form zeolite from 51 BV (bed volume) to 76 BV. Both the resin and the Na-form zeolite could be successfully regenerated by the combination of alkaline and sodium chloride. Complete elution of ammonia–nitrogen was achieved when the mass percentage of sodium chloride and alkaline was 10% and 0.6% respectively.



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## 1. Introduction

To countermeasure the increasing water crisis, the reclaimed municipal wastewater may be considered as a major supplementation water source for rivers and lakes. While ammonia–nitrogen ($NH_3$–N) and organic matter are two important pollutant factors respectively in advanced treatment. In some cases, $NH_3$–N concentration in municipal effluent may be higher than 20 mg N $L^{-1}$ [1], which may induce the eutrophication problems especially in some enclosed waters. $NH_3$–N plays a very important role in the formation and speciation of Disinfection By-Products (DBPs) during chlorination [2]. $NH_3$–N was found to result in the emergence of N-nitrosodimethylamine, which are much more genotoxic than chloroacetic acids [3]. Wang et al. [1] noted that genotoxicity is increased significantly in wastewater with a high ammonia–nitrogen concentration (>10–20 mg N $L^{-1}$) after chlorine disinfection. On the other hand, remaining organic matter after bio-treatment may impart taste, odor and color to water and also produce DBPs during chlorination. To realize reuse of wastewater safely, studies on removal of ammonia–nitrogen and organic matter from municipal effluent should be done deeply. According to the previous reports, organic matters (humic acid, citric acid and a number of proteins) also have influence on ammonium exchange of zeolite [4,5], which may be used to remove ammonium from waters [6,7] for its cheaper and natural characteristics.

The objective of this study is to confirm the effect of dissolved organic matter (DOM) on ammonium removal efficiency by the zeolite, and try to improve $NH_3$–N removal efficiency by DOM reduction. In very recent years, Magnetic Anion Exchange Resin (such as MIEX®) has been accepted as an effective adsorbent to remove organic matter from water for its polyacrylic matrix, quaternary amine functional group and macroporous structure [8,9]. In this study, the batch mode experiments were carried out to determine the kinetic and equilibrium characteristics of the zeolites in the presence of humic acid. A series of combined experiments were then conducted to determine the optimal condition in the real municipal effluent treatment. With the findings from this study, we can also have a better understanding of the removal mechanisms for both contaminants.

## 2. Methods

### 2.1. Materials preparation

The natural zeolite used in this study was taken from Jinyun, Zhejiang Province, China. The ore is mainly clinoptilolite accompanied with mordenite and quartz. The samples were ground and sieved 20 mesh size and then washed with distilled water to remove any non-adhesive impurities and small particles, and then dried at 105 °C for 24 h to remove moisture. In some reports, modification of zeolites by sodium chloride can transform low-grade natural materials to high capacity cation exchangers [10,11]. For obtaining the Na-form modified zeolite, 20 g of the natural zeolite was immerged into 500 mL of 15% sodium chloride solution prepared by de-ionized water under 40 ± 1 °C and stirring 48 h in a thermostatic shaker. Residual NaCl solution on zeolite surface was washed with 2 L distilled water, and then dried at 105 °C for 24 h.

A magnetic anion exchange resin similar to MIEX®, called NDMP resin, was developed by Nanjing University. Because of its quaternary amine functional groups (strong basic groups), hydrophilic matrix, small size and macroporous structure [12], NDMP resin has successfully applied in advanced treatment of drinking waters, municipal effluents and dye wastewater. Furthermore, exchange kinetics of NDMP resin is fast for its smaller size (150–180 μm) than that of conventional resins (300–1200 μm) and its magnetism avoids a possible loss. Because of the easy separation, a completely mixed contactor could be used for water treatment instead of a fixed-bed column. In this study, the resin was used in chloride form and was measured by volume.

Municipal secondary effluent from wastewater treatment plant (WWTP) in Nanjing was used in this study. Ammonia–nitrogen model solution was prepared by analytical grade $NH_4Cl$ dissolving in deionized water.

### 2.2. Effect of humic acid

Humic acid obtained from Aldrich (Milwaukee, WI) was used in both kinetic and equilibrium experiments to simulate the effect of DOM on the performance of the zeolites. In equilibrium experiments, 0.1 g zeolite particle was added into 100 mL of 5 to 100 mg N $L^{-1}$ ammonium model solutions with or without 40 mg $L^{-1}$ humic acid respectively. Each flask was placed into a shaker at 298 K and 130 rpm for 24 h so that the removal can reach equilibration. Kinetics experiments were performed as follow: 1.5 g zeolite was added into 500 mL of 10 mg N $L^{-1}$ ammonium solutions with or without 40 mg $L^{-1}$ humic acid in flasks and stirred for 300 min at 298 K and 130 rpm. Samples were taken at intervals to assess the uptake characteristics of the materials.

### 2.3. Adsorption of NDMP resin to humic acid

5 mL NDMP resin was added into 500 mL solution containing 40 mg $L^{-1}$ humic acid and stirred for 1500 min at 298 K and 130 rpm. Samples were taken at intervals to assess the uptake characteristics of the materials.

### 2.4. Field application

NDMP resin adsorption were conducted as followed: 5 mL NDMP resin was added into a completely mixed contactor containing 500 mL municipal secondary effluent from WWTP. During the continuous operation, 10% of used NDMP resin was replaced with regenerated resin. The residual used resin was continuously in contact with untreated water while only a small fraction of fresh/regenerated resin added. In this way, the resin achieved service runs equivalent to 1000–1500 bed volumes (BV). The flow rate of the effluent was about 8 mL $min^{-1}$. which was correspond to the optimum conditions for DOM removal (based on lab-scale tests). Zeolite exchange were conducted by using a glass column of internal diameter of 50 mm and height of 450 mm, which was packed with 80 mL of wet zeolite, and a 6672 reciprocating pump (Beijing Analytical Instrument Plant) to ensure a constant flow rate. The regenerant solution of the zeolite containing a predetermined combination of sodium chloride and alkaline flowed upward through the column at a flow rate of 2 mL $min^{-1}$. The ammonia–nitrogen concentration in the eluate was analyzed.

### 2.5. Chemical analysis

In these experiments, the ammonia–nitrogen concentration in the solution was determined by using Nessler method according to standard methods [13]. Absorbance values were read using a Shimadzu UV-1800 spectrophotometer.

Fluorescence EEM spectroscopy was performed on each sample using a F-7000 FL Spectrophotometer (Perkin Elmer, New Jersey, USA) at room temperature (298 K). Excitation and emission were simultaneously scanned at wavelengths ranging from 200 to 440 nm at 5 nm intervals and from 280 to 500 nm at 1 nm intervals, respectively. The slit widths were set at 5 nm for both