



Dissolved organic matter removal by magnetic anion exchange resin and released ion elimination by electrolysis



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HIGHLIGHTS

- 78% DOC in municipal effluent was removed by magnetic anion exchange resin (NDMP).
- NDMP removed a large portion of humic acid-like and fulvic acid-like substances.
- Chloride released from NDMP was decreased by electrolysis with the removal of 94%.
- Free chlorine generated by electrolysis had a considerable disinfection effect.

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ABSTRACT

For the advanced treatment of municipal effluents, removal of dissolved organic matter (DOM) by a magnetic anion exchange resin and the released chloride ion were both investigated. A total of 78% of dissolved organic carbon was removed at an optimized dosage of 1.0 g resin in 300 mL effluent with a contact time of 60 min. DOM characterization by excitation–emission matrix spectroscopy revealed that humic acid-like substances, fulvic acid-like substances, and a significant portion of soluble microbial products can be efficiently removed by the resin. Ion exchange of humic acid- and fulvic acid-like substances onto resin resulted in an increase of chloride, which can be efficiently decreased by electrolysis. A disinfection effect caused by electrolysis was found as a result of the free chlorine generated from electrolysis. Results suggested that the combination of anion exchange and electrolysis is a feasible advanced treatment of municipal sewage for DOM removal and disinfection.

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1. Introduction

Municipal sewage causes serious environmental problems because of its large amount and high content of contaminants for discharge. Although biological methods are typically used in municipal sewage treatment for its high efficiency and low cost, there are still some pollutants in the biological effluents including soluble microbial products (SMPs) [1]. The presence of these organic pollutants threatens the safety of human and ecology for their potential of disinfection by-products (DBPs) formation and regrowth of bacteria or the direct toxicity. Therefore, many physiochemical methods such as membrane filtration, adsorption, and oxidation were developed for advanced treatment of biological effluent.

Adsorption by activated carbon is considered to be a promising technology because of its easy operation and acceptable cost [1–3]. However, the ineffective removal of hydrophilic/small molecular

matter by activated carbon and its regeneration problems have limited its application [4,5]. Adsorption by anion exchange resin is becoming an increasingly used technology for DOM removal because of its efficiency and regeneration [6–12]. Nevertheless, conventional fixed-bed process by anion exchange resin has been limited by the small load of influent and high operating pressure. Alternatively, mixed contactor process by using magnetic anion exchange resin can be used for water treatment. The resin beads with a small size can be easily dispersed in water under stirring and fast sedimentation as a result of their magnetism [13,14]. Up to now, mixed contactor has been increasingly employed in water treatment for DOM removal by using MIEX resin with magnetism and small size [14–19].

DOMs with high-molecular-weight and high-hydrophobicity, composing of humic acid- and fulvic acid-like substances was reported to be removed by MIEX resin [20–25]. However, the study of Boyer et al. (2008) on ten DOM isolates from different sources indicates that the charge density of natural organic matter (NOM) is the most important factor in the interaction between

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DOM and MIEX [22]. Similarly, electronegativity was the most important factor for adsorption of different humic acid fractions onto magnetic anion exchange resin in our previous study [18,26]. These findings are consistent with the theoretical interaction of anion exchange, which inevitably result in releasing of counter ions during the ion exchange.

Anion exchange resins in chlorine form were mostly used for DOM removal for its better performance than the OH-type resin [15,27]. Therefore, the anion exchange for DOM removal leads to the chloride increase, which has negative effects on water quality, sewage reuse and hydroenvironment [28]. However, chloride ion release has not caused significant attention, and few studies have been conducted on the increase and treatment of released chloride ion in water treatment. Furthermore, the released chloride for waste water treatment is probably different with that for drinking water treatment because of their difference on DOM removal by anion exchange resin. Therefore, it's vital to evaluated DOM removal and the chloride release during the resin treatment.

DOM removal for municipal sewage by a magnetic anion exchange resin is investigated in this work by using 3D emission–excitation matrix (3D-EEM). The released chloride during DOM removal is detected, and electrolysis is further performed under different operation conditions to remove the released chloride ion. The combination of resin adsorption and electrolysis for advanced treatment of municipal sewage is then evaluated.

2. Materials and methods

2.1. Material

The biological effluent was collected from Jiangxinzhou Sewage Treatment Plant (Nanjing, China), which is a typical municipal sewage plant in China using A/O activated sludge process with the processing capacity of 640,000 m³/d. The water was filtered through 0.45 μm nitrocellulose membrane and stored at 4 °C before analysis. The dissolved organic carbon (DOC) and the pH of raw water were 4.8 mg/L and 8.3, respectively.

A magnetic anion exchange resin with acrylic matrix, NDMP, has been prepared by our group in previous studies [18,19]. The average-sized beads of this resin range from 100 μm to 150 μm, as listed in our previous study [19]. NDMP resin was treated with alcohol in a Soxhlet extractor for 8 h, subsequently rinsed with deionized water, then dried at 50 °C for 12 h in vacuum before use.

2.2. Adsorption

To investigate the effect of resin dosage, different amounts (0.1, 0.2, 0.5, 1.0, 2.0 mg) of resin were shaken with 300 mL raw water in conical flasks 20 °C with 170 rpm for 1 h. The temperature of raw water was elevated to 20 °C before the experiment. And the pH of raw water (8.3) was not adjusted. The effluents after adsorption were all separated with the help of a magnet and collected for measurement and subsequent electrolysis.

2.3. Electrolysis

The effluent after adsorption was further treated by electrolysis, and the process was illustrated in Fig. 1. Electrolytic process was performed in a cylindrical polymethyl methacrylate single cell with a distance of 6 cm between electrodes at 20 °C under magnetic stirring at 500 rpm. RuO₂–IrO₂-coated titanium plate with an area of 18.62 cm² (Baoji Qixin Titanium Co., Ltd., China) was employed as the anode, and a graphite plate with an area of 18.62 cm² (Haimen Wuzhou Graphite Co., Ltd., China) served as the cathode. Electric currents were controlled by a stabilized

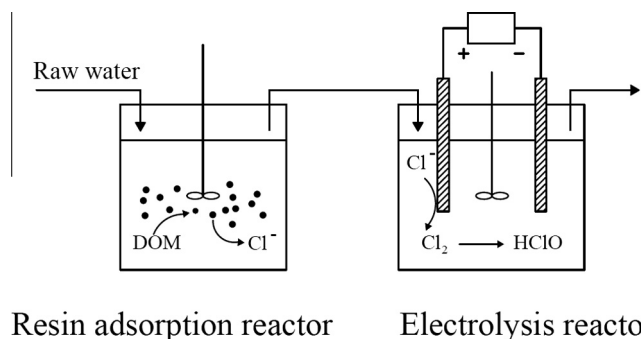


Fig. 1. Schematic diagram of resin adsorption and electrolysis technologies.

current supply (PS-3005D, Zhaoxin Electronic Instrument Equipment Co., Ltd., China).

2.4. Analysis

DOC was measured with a TOC analyzer (Aurora 1030C, OI Analytical Co., Ltd., United States) with autosampler (Model 1088, OI Analytical Co., Ltd., America). UV spectrophotometer (UV-1800, SHIMADZU Co., Ltd., Japan) was used to determine UV absorbance at 254 nm. 3D-EEM was measured with a fluorescence spectrophotometer (F-7000, Hitachi Co., Ltd., Japan) with Xe lamp light source. Chloride ion concentration was measured using an ion-selective electrode (MP551 ISE, Shanghai San-Xin Instrumentation Co., Ltd., China). The concentration of free residual chlorine was measured with a rapid residual chlorine analyzer (S-LC501, Sinsche Technology Co., Ltd., China). All water samples were filtered through 0.45 μm nitrocellulose membrane before the measurement.

Most probable number (MPN) was used to evaluate the disinfection effect [29]. In brief, water samples were inoculated onto lactose peptone broth and cultured for 24 h ± 2 h in an incubator at 36 °C ± 1 °C. Samples that produced acid and gas were positive. Then, these samples should be isolated for Gram staining testing on methylene blue agar for 24 h culture and confirmed testing for another 24 h culture. MPN index is calculated by checking the results in the MPN table in Standard Methods for the Examination of Water and Wastewater.

3. Results and discussion

3.1. DOM removal

Fig. 2 plots the DOC content after treatment by NDMP resin with different dosages. Result shows that DOC decreases with a sharp increase of NDMP dosage from 0 g to 1.0 g for 300 mL water treatment, while it slightly rose from 77.8% to 79.2% with the dosage ranged from 1.0 g to 2.0 g. The remaining DOC indicates the presence of neutral substances or positive charged organics which are recalcitrant for ion exchange. In addition to DOC content, UV absorbance at 254 nm is an important parameter that reflects the concentration of aromatic carbon. The declining trend of UV absorbance as resin dosage increases is similar to the trend of DOC (Fig. 2b). UV absorbance sharply decreased with a removal of 73% when the dosage is increased from 0 g to 1.0 g and slowly decreased with a removal of 78% at 2.0 g dosage. These results indicate the efficient DOC and UV removal by NDMP for the advanced treatment of municipal sewage, which is similar to the performance of MIEX in other studies [6–10]. The downtrends of DOC and UV are similar, exhibiting slight fluctuations of SUVA before and after resin treatment. A number of studies have indicated that

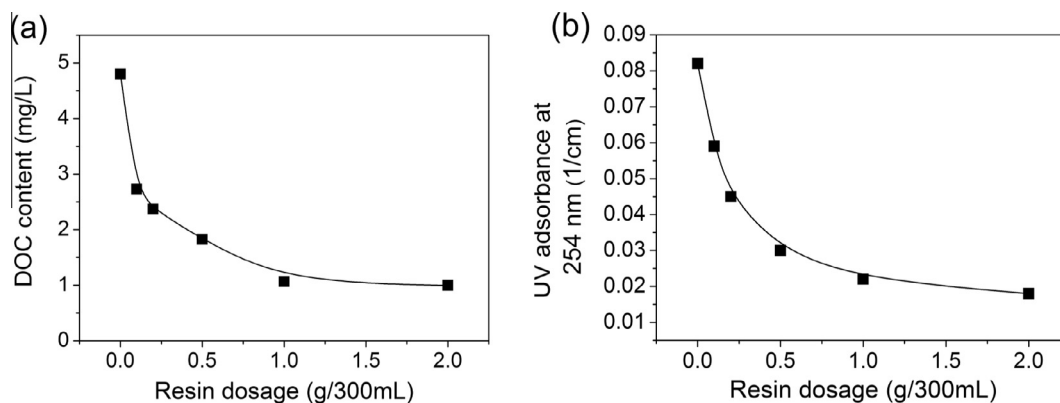


Fig. 2. Effect of resin dosage on DOC content (a) and UV₂₅₄ (b) absorbance with contact time of 60 min at 20 °C.

aromatic organic compounds are preferentially removed by MIEX resin, and this removal results in the reduction of SUVA [8,13]. However, this preferential removal was not found in MIEX treatment of water with low SUVA value. In theory, anion exchange resin preferentially removes anionic DOM with high negative charge because of the electrostatic interaction. Moreover, the adsorption of DOM onto resin is generally affected by other properties such as molecular size of DOM because of size exclusion [16,24,30].

To further explore DOM removal by NDMP, EEM was used to analyze the change of DOM after NDMP treatment. EEM spectra are typically divided into five classes according to different excitation and emission wave lengths [17,31]. In brief, at short-wavelength regions ($Ex < 250$ nm, $Em < 380$ nm), fluorescence peaks were identified as protein-like fluorescent peaks resulting from aromatic amino acids such as tryptophan and tyrosine (Class I & II). Tryptophan- and tyrosine-like substances also cause the corresponding fluorescent peaks at longer wavelengths of excitation ($Ex > 250$ nm, $Em < 380$ nm), which belong to SMPs (Class IV) [31–33]. Fulvic acid-like fluorescence comes from two areas of long emission ($Em > 380$ nm): UV fulvic-like substances ($Ex < 250$ nm, Class III) and visible fulvic-like substances ($Ex = 310–360$ nm), which partially overlap with humic acid-like fluorescence ($Ex > 250$ nm, $Em > 380$ nm, Class V) [34].

The EEM spectrum of raw effluent is depicted in Fig. 3a. Fluorescence was mainly derived from Classes II and III, indicating that the major constituents of raw water are protein-like and fulvic acid-like substances. Classes IV and V were also seen in EEM responses, indicating the presence of SMPs and humic acid-like substances. With an increase in resin dosage from 0.1 g to 1.0 g, fluorescence intensity was obviously decreased for all regions (Fig. 3b–g). To semi-quantify the concentration of constituents, the regions were integrated on the basis of fluorescence intensity. The calculation equation is expressed as follows [31]:

$$\Phi_i = \int_{ex} \int_{em} I(\lambda_{ex}\lambda_{em})d\lambda_{ex}d\lambda_{em} \approx \sum_{ex} \sum_{em} I(\lambda_{ex}\lambda_{em})\Delta\lambda_{ex}\Delta\lambda_{em} \quad (1)$$

At 0.1 g dosage, removals of all constituents were all at approximately 30%. However, the removal of each constituent differed when the dosage was increased to 1.0 g. Removal for Classes II, III, IV, and V suggests that protein-like substances, SMPs, and humic acid- and fulvic acid-like substances were removed by 40%, 55%, 65%, and 74%, respectively.

3.2. Chloride release

The concentration of chloride after ion exchange was detected, and the results are shown in Fig. 4. Chloride ion increased from

52.9 mg/L to 210 mg/L with an increase in NDMP dosage from 0 g to 2.0 g. The amount of released chloride was linearly related to DOM removal with both correlation coefficients higher than 0.9 for DOC and UV₂₅₄ indicating that the interaction between the resin and DOM mainly attributes to the electrostatic effect. However, the exchange of coexisting inorganic ions can also interact with ion exchange resin and release chloride, thereby the linearity could be influenced.

The relationship between EEM fluorescence intensity removals of each class and concentration of the released chloride are presented in Fig. 5b. Removal of humic acid-like, fulvic acid-like substances and SMPs increased more linearly with chloride ion release than that of protein-like substances. This results suggests ion exchange play more important role in humic acid-like, fulvic acid-like substances, which can be explained by larger amount of negative groups such as carboxyl groups [16,22]. Nevertheless, ion exchange is also the main interaction in the removal of protein-like substances because of the low initial concentration of these substances in raw effluent.

3.3. Chloride ion removal

Fig. 6a illustrates chloride ion concentration during the electrolytic process of NDMP-treated water samples under different current densities within 240 min. In the first 20 min, chloride ion concentration was rapidly reduced, such that the removal of chloride ion increased from 40% to 49%. Then, removals of chloride ion of almost all experiment samples exceeded 70% after 90 min. During the period from 90 min to 240 min, reduction rates of chloride ion concentration gradually slowed down. Final removals for the three current densities all exceeded 86%. However, 3 mA/cm² was selected as current density for future applications on chloride removal because of the considerable removal efficiency and lower cost at this value.

Fig. 6b shows chloride removal by electrolysis of resin-treated water for different dosages. Higher chloride removal efficiency can be obtained from water treated with a larger dosage because the released chloride increased the initial concentration and conductivity. Within 90 min, the removal of chloride ion of three experiment samples exceeded 66%, and then reached 80.5%, 85.5%, and 93.5% in 240 min.

Free residual chlorine containing HClO and ClO⁻ is related to the disinfection of water, it can be theoretically generated from electrolysis of chloride [35–37]. The concentration of free residual chlorine was measured in this work, and the free residual chlorine concentration rapidly increased as electrolysis proceeded in the first 50 min (Fig. 7). Then, it gradually slowed down after 50 min. After 240 min, the highest free residual chlorine concentration

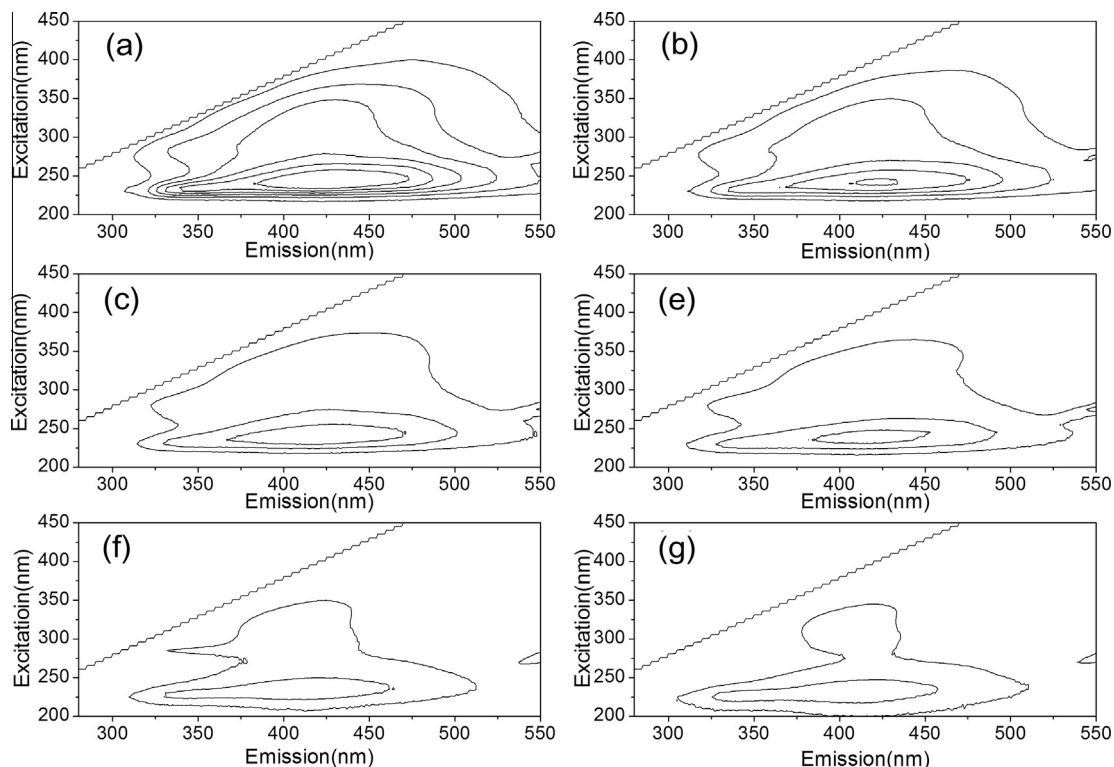


Fig. 3. EEM contour plots for raw water (a) and NDMP-treated water of various dosages increasing from 0.1 g to 2.0 g (b–f).

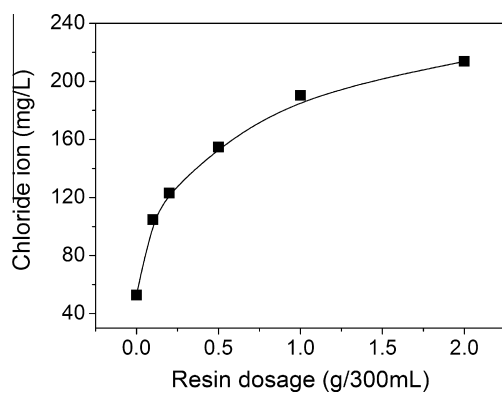


Fig. 4. Impact of resin dosage on chloride ion concentration after adsorption with contact time of 60 min at 20 °C.

(108.5 mg/L) was obtained at the dosage of 2.0 g, whereas the lowest free residual chlorine concentration was only 16.1 mg/L at the dosage of 0.1 g. This increase of free residual chlorine is consistent with the decrease of chlorine ion, which confirms the generation of Cl_2 from electrolysis of chloride ion.

To further investigate the disinfecting effect, microbial index experiment and total coliform MPN experiment were conducted in this study. There were 140 total coliforms/100 mL existed in raw water, which were much higher than those of standards of reclaimed water quality of many states in the United States (<2.2 MPN/100 mL, Guidelines for Water Reuse, US EPA, 2004). The results of the electrolyzed effluent treated by various resin dosages under a current density of 3 mA/cm² are listed in Table 1. Longer electrolytic time or larger dosage of used resin can both lead to a better disinfection effect due to the larger amount of free chlorine generation. At a resin dosage of 2.0 g in 300 mL effluent and an electrolytic time of 20 min under 3 mA/cm², total coliforms

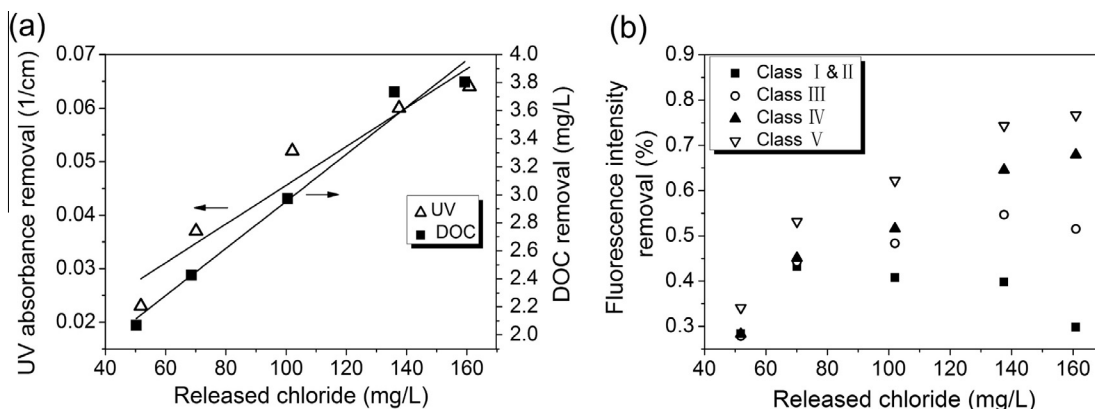


Fig. 5. Correlation between the amounts of released chloride and UV, DOC removal (a), EEM fluorescence intensity removal (b).

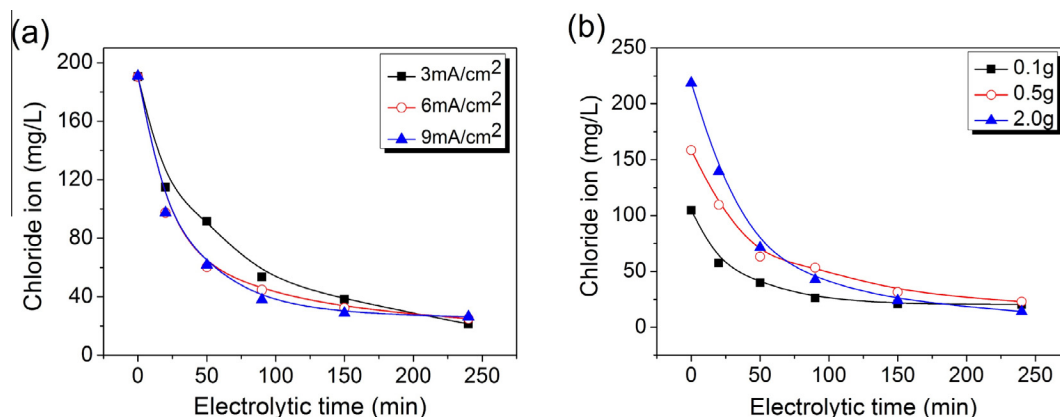


Fig. 6. Removal of the released chloride ion under different current densities at resin dosage of 1.0 g in 300 mL NDMP-treated water (a) and at different dosages under the current density of 3 mA/cm² (b).

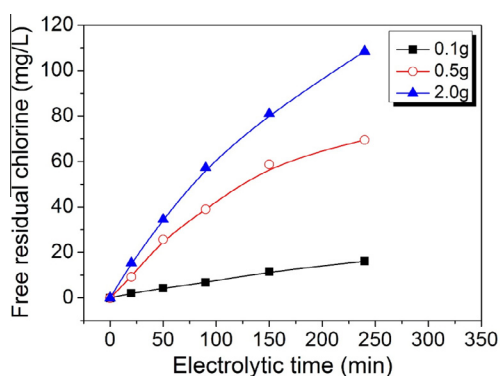


Fig. 7. Free residual chlorine concentration after electrolysis of NDMP-treated water with different resin dosages of 0.1, 0.5 and 2.0 g under the current density of 3 mA/cm².

Table 1

Total coliform MPN and sterilizing rates of various resin dosages under a current density of 3 mA/cm².

Electrolytic time (min)	Resin dosage (g/300 mL)	Total coliforms (MPN/100 mL)	Sterilizing rate (%)
0	-	140	-
5	0.1	>16	<88.6
	2.0	9.2	93.4
20	0.1	>16	<88.6
	2.0	<2.2	>98.4

meets the requirement of reclaimed water standards (<2.2 MPN/100 mL) of the United States and quality of Class IV (<10 MPN/100 mL) of quality standard for groundwater in China (GB/T 14848-93). These results indicate that electrolysis has efficient disinfection performance during the removal of released chloride from anion exchange.

4. Conclusions

NDMP had great removal efficiency on DOM in municipal wastewater with both DOC and UV₂₅₄ removal nearly 80%. Humic acid-like and fulvic acid-like fractions were substantially removed by NDMP, and a significant portion of soluble metabolism products were also reduced. Ion exchange was mainly attributed to DOM removal with chloride release, which contributes to a dramatic increase in chloride in the effluent together with the ion exchange

with inorganic ions. Electrolysis is a feasible process for treating the released chloride, with a maximal removal of 93.5%. Free chlorine generated from electrolysis can serve as an efficient disinfectant. Results suggest that the combination of ion exchange and electrolysis is a promising method for the advanced treatment of municipal effluent.

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