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

Jun Wang, Haibo Li, Aimin Li, Chendong Shuang *, Qing Zhou

State Key Laboratory of Pollution Control and Resources Reuse, School of the Environment, Nanjing University, Nanjing 210023, PR China

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.

1. Introduction

Municipal sewage causes serious environmental problems because of its large amount and high content of contaminates 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 threats 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

* Corresponding author. Tel./fax: +86 25 89680377.
E-mail address: shuangchendong@nju.edu.cn (C. Shuang).

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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 m^3/d. The water was filtrated 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. RuO_2–IrO_2-coated titanium plate with an area of 18.62 cm^2 (Baoji Qixin Titanium Co., Ltd., China) was employed as the anode, and a graphite plate with an area of 18.62 cm^2 (Haimen Wuzhou Graphite Co., Ltd., China) served as the cathode. Electric currents were controlled by a stabilized current supply (PS-3005D, Zhaoxin Electronic Instrument Equipment Co., Ltd., China).

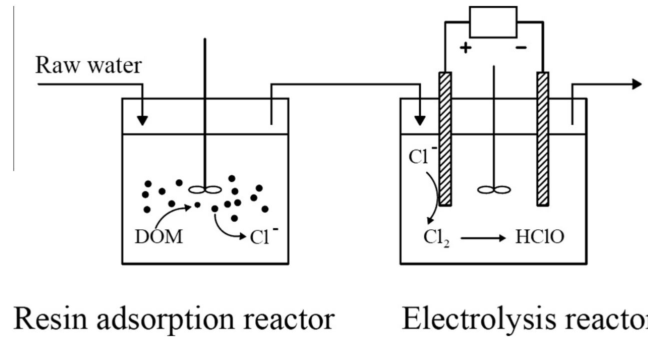

Fig. 1. Schematic diagram of resin adsorption and electrolysis technologies.

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