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Evaluation of the potentials of humic acid removal in water by gas phase surface discharge plasma

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ABSTRACT

Degradation of humic acid (HA), a predominant type of natural organic matter in ground water and surface waters, was conducted using a gas phase surface discharge plasma system. HA standard and two surface waters (Wetland, and Weihe River) were selected as the targets. The experimental results showed that about 90.9% of standard HA was smoothly removed within 40 min's discharge plasma treatment at discharge voltage 23.0 kV, and the removal process fitted the first-order kinetic model. Roles of some active species in HA removal were studied by evaluating the effects of solution pH and •OH radical scavenger; and the results presented that O_3 and •OH radical played significant roles in HA removal. Scanning electron microscope (SEM) and FTIR analysis showed that HA surface topography and molecular structure were changed during discharge plasma process. The mineralization of HA was analyzed by UV–Vis spectrum, dissolved organic carbon (DOC), specific UV absorbance (SUVA), UV absorption ratios, and excitation-emission matrix (EEM) fluorescence. The formation of disinfection by-products during HA sample chlorination was also identified, and $CHCl_3$ was detected as the main disinfection by-product, but discharge plasma treatment could suppress its formation to a certain extent. In addition, approximately 82.3% and 67.9% of UV_{254} were removed for the Weihe River water and the Wetland water after 40 min of discharge plasma treatment.

1. Introduction

Humic substances, including humic acid (HA), are widely present in soils, sediments and natural waters, which are derived from the decomposition of animal and plant residues; they are yellow-to-black colored natural organic matter and have a wide range of molecular weights (Liu et al., 2008). The major functional groups in the humic substances are phenolic, carboxyl, carbonyl and hydroxyl groups connected with aliphatic or aromatic carbons (Qin et al., 2015). As a major fraction of natural organic matter in natural waters, the humic substances can cause several environmental or health problems. On the one hand, the humic substances can result in undesirable yellow or brown color and serve as substrate for microorganism growth (Pinhedo et al., 2005); on the other hand, they have very strong chelate ability with many heavy metals and organic pollutants, which make these toxins more difficult to be removed (An et al., 2015). Even worse, they are the main precursors of disinfection by-products such as trihalomethanes, formed in the chlorination process in drinking water disinfection (Wei et al., 2011). It is therefore imperative to eliminate the humic substances from natural waters.

Some methods such as coagulation (Wang et al., 2012), activated carbon adsorption (Rauthula and Srivastava, 2011), Fenton treatment (Wei et al., 2011), nano-TiO_2 photocatalysis (Liu et al., 2008), membrane filtration (Peeva et al., 2011), biological treatment (Moura et al., 2007), and ozonation (Wei et al., 2011) have been employed to remove humic substances. There existed some shortcomings for these methods. For example, the metal ions concentration in treated water during coagulation may exceed the recommended guidelines for drinking water, and the flocculation effect is dependent on solution pH and coagulant dosage. The cost of activated carbon is high and the removal efficiency of humic

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substances is limited because of their large molecular weights; the adsorption is just the phase transfer of pollutants, and the pollutants still exist in the adsorbent, and thus post-treatment for the adsorbent is necessary. Great performance for the humic substances removal can be obtained by Fenton treatment and photocatalysis; however, the addition of some chemical reagents or nano-materials into waters may bring secondary pollution in drinking water system. Membrane fouling is the main problem for membrane filtration, and membrane size exclusion, solute–solute and solute–membrane interactions and operational conditions all influence membrane rejection. The commonly used method of biological treatment for natural water is biofiltration; however, biofiltration late in the treatment may cause hazards due to the release of bacteria suspended in the water phase. Ozone is a strong oxidant and can oxidize humic substances by an electrophilic addition to double bonds, but this reaction is very selective. Bromate is more easily generated due to relatively high ozone concentration provided by traditional ozone generator, which can react with Br^- in natural waters. In addition, the oxidizing capacity of direct ozone is poor, and it is usually combined with ultraviolet, H_2O_2 and metal oxides to produce ·OH radicals, which would bring extra operating cost and risk. Recently, the combination of different methods for humic substances removal has also been used, such as ozone coupled with biofiltration (Seredynska-Sobecka et al., 2006), and coagulation coupled with membrane (Wang et al., 2012); although humic substances removal can be enhanced in the combination processes, the problems of each single technique still exist. Therefore, it is significant to develop some new approaches for the humic substances removal from natural water.

Recently, non-thermal discharge plasma has caused considerable interest in environmental pollution control due to its high removal efficiency and environmental compatibility. Different discharge plasma types have been developed for wastewater treatment, such as pulsed corona discharge (Wang et al., 2007a, 2007b), dielectric barrier discharge (Qu et al., 2009), contact glow discharge plasma (Wang et al., 2015), and gliding arc discharge (Liu et al., 2013). Various pollutants in wastewater have been attempted to remove by non-thermal discharge plasma, such as dyes (Mok et al., 2008; Liu et al., 2013), phenols (Wang et al., 2007a, 2007b), pesticide (Mededovic and Locke, 2007), antibiotic (He et al., 2014), bromoform (Wang et al., 2015), bacteria inactivation (Lin et al., 2015), and As^{3+} and Cr^{6+} (Jiang et al., 2015). In our previous research, a gas phase surface discharge plasma reactor was designed to treat dye wastewater, where chemically active species generated during discharge plasma process could be injected into the dye wastewater rapidly, and thus great performance was obtained for dyes decoloration (Li et al., 2011a, 2011b). In this type of discharge plasma system, main active species such as O_3, H_2O_2, ·OH, and ·O are generated, accompanied by strong ultraviolet. These strong oxidative active species and physical effect are expected to synergistically act on humic substances and realize high-efficient removal; due to quite low concentration and short lifetimes of these active species, relatively less risk can be brought during drinking water treatment. Comparing with other techniques, non-thermal discharge plasma may be considered as a relatively safe and efficient alternative for HA removal from drinking water. For example, Al^{3+} residual would bring risk for drinking water when HA was removed by coagulation (Wang et al., 2012); the disinfection by-products with high concentration were easily generated during HA oxidation by Fenton or ozone (Wei et al., 2011); low HA removal efficiency and long time consumption was observed during HA treatment by TiO_2 photocatalyst (Rashid et al., 2015). Indeed, some electric energy is consumed by the non-thermal discharge plasma; it can be used for emergency drinking water supply, and emergency treatment for sudden pollution of urban water supply. However, little has been reported on discharge plasma treatment of humic substances, and the formation potentials of disinfection by-products is not unknown after the humic substances in natural water are treated by non-thermal discharge plasma.

Therefore, the aim of this study was to evaluate the potentials of humic substances removal by gas phase surface discharge plasma. Standard HA and two surface waters were chosen as the treatment targets. HA removal efficiency was investigated under different conditions such as discharge voltages and pH values. The roles of chemically active species in HA removal process were evaluated. The decomposition of HA was characterized by scanning electron microscope (SEM), dissolved organic carbon (DOC), UV–Vis absorbance, specific UV absorbance (SUVA), fourier transform infrared spectroscopy (FTIR) and excitation-emission matrix (EEM) fluorescence analysis. In addition, the formation of disinfection by-products was also identified. This study is expected as preliminary investigation to develop a new approach for the control of precursors of disinfection by-products.

2. Materials and methods

2.1. Materials

HA was purchased from Aladdin Industrial Corporation, China, which is extracted from peat coal and contains 58.3% of C, 4.2% of H, and 36.1% of O. The average molecular weight of the HA is 2485 Da. The contents of total acidity, carboxylic and phenolic groups of the HA are 5.92, 2.62, and 3.58 mmol g^{-1}. All other reagents were analytical grade and were used as purchased without further purification.

2.2. Gas phase surface discharge plasma reactor

The schematic diagram of the gas phase surface discharge plasma reaction system was shown in Fig. 1, which was similar with our previous research (Li et al., 2011a, 2011b). Alternating Current (50 Hz) power supply was used in the present research. The reactor container was made of Plexiglas cylinder with 5 cm inner diameter and 35 cm height. A stainless steel spring (1 mm wire diameter) was used as the high voltage electrode which was attached on the inside wall of the cylindrical quartz tube medium tightly, and the

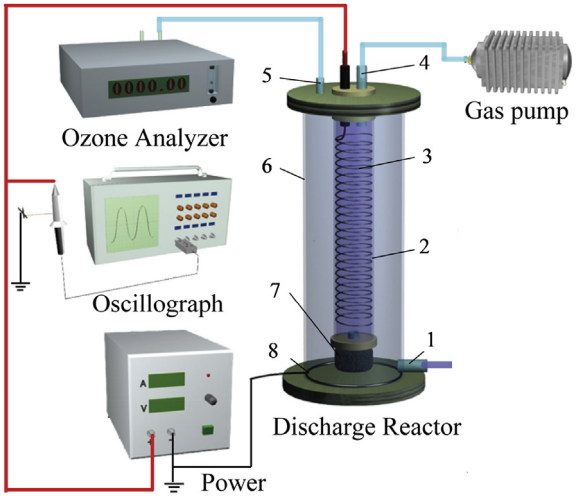

Fig. 1. Schematic diagram of discharge plasma reaction system (1 sampling port; 2 quartz tube; 3 spiral electrode; 4 gas inlet; 5 gas outlet; 6 Plexiglas cylinder; 7 aerator; 8 ground electrode).