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Surface modification of carbon fiber support by ferrous oxalate for biofilm wastewater treatment system

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ABSTRACT

In order to overcome the shortcoming of poor hydrophilicity and smooth surface of carbon fiber, and to improve water treatment effect of biofilm system using carbon fiber as support, this paper employed nitric acid and ferrous oxalate to modify carbon fiber. A series tests were conducted on untreated carbon fiber, nitric acid oxidized carbon fiber, nitric acid and ferrous oxalate modified carbon fiber, namely, scanning electron microscopy-energy dispersive spectrometer, X-ray photoelectron spectroscopy, static contact angle and water treatment effect. Results showed that, hydrophilic functional group containing oxygen and nitrogen on the surface of carbon fiber increased after modification by nitric acid and ferrous oxalate, which greatly improved the hydrophilicity of carbon fiber surface. The ferrum element in ferrous oxalate modified carbon fiber existed in the form of magnetic oxide (Fe_3O_4) via Fe–O–C to bond with carbon fiber, which noticeably enhanced the surface roughness of carbon fiber. Dry weight of biofilm per unit immobilized on ferrous oxalate modified carbon fiber support enhanced and it was 2.3 and 0.6 times bigger than that of untreated and nitric acid oxidized carbon fiber. Biofilm system with ferrous oxalate modified carbon fiber as support had better water treatment effect and stable effluent standard. The average removal efficiency of chemical oxygen demand, ammonia nitrogen and total phosphorus achieved 97%, 96% and 97%. In addition, removal efficiency of chemical oxygen demand, ammonia nitrogen and total phosphorus increased by 7.18%, 10.30%, 9.40% and 4.86%, 4.30%, 6.40%, compared to carbon fiber and nitric acid oxidized carbon fiber support biofilm system. Combination of nitric acid oxidation and ferrous oxalate deposition, which has never been developed before, is a promising carbon fiber surface modification method to improve its performance as biofilm support.

1. Introduction

Biofilm is a complex microorganism layer which embeds into extracellular polymeric substance (EPS) and it makes microbial community stick to each other and form a kind of micro environment (Chrispim and Nolasco, 2017). Recently, biofilm method has been widely employed in the remediation of wastewater and has been a promising technology due to its public acceptance and cost effectiveness (Hayat et al., 2017; Karn et al., 2017). The biofilm adhered to the surface of the support and the coexistence of aerobic and anoxic zone can effectively synchronize nitrification and denitrification (Cao, 2015), thus to achieve the aim of purifying sewage. The support as the habitat place of microorganism was the core part of biofilm water treatment system (Chu and Wang, 2011), so its properties directly influenced growth and propagation of microorganism and water treatment effect as well.

Recent years, fibrous materials were applied as support in biofilm water treatment system (Terada et al., 2009). Support's texture and type had comparable effect on biofilm development, activity, composition and water treatment effect as well (Felföldi et al., 2015). Based on previous study, carbon fiber (CF) had several merits as biofilm support compared with polyamide, polypropylene and polyethylene fibers. There was no energy barrier when microorganism adhered to CF support and CF had higher adsorption capacity for nitrifying bacteria (Matsumoto et al., 2012). CF had good biocompatibility, flexibility and resistance to microbial decomposition and chemical corrosion. CF has been applied in actual water treatment practice and it proved to be a promising biofilm support material (Zhou, 2013). However, there are still some shortcomings for CF. Smooth surface and poor hydrophilicity

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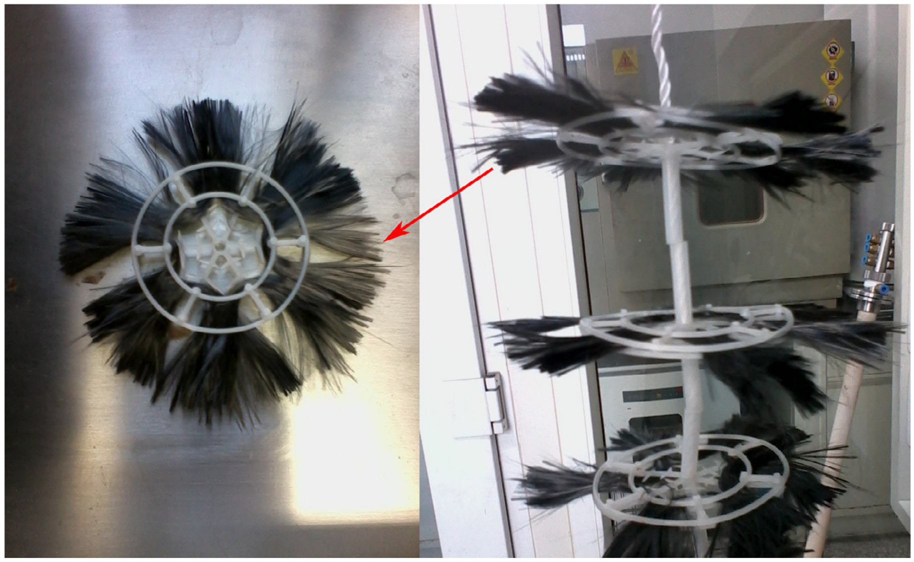

Fig. 1. Configuration of polypropylene plastic sheet wrapped with CF supports.

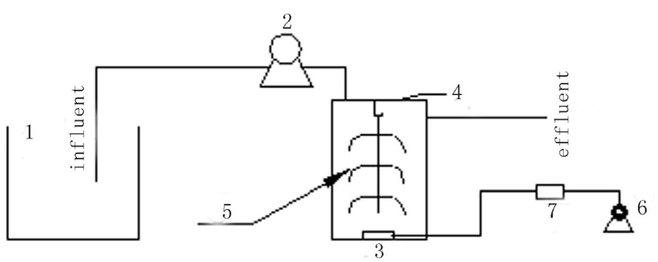

Fig. 2. The flow chart of experimental apparatus. 1-water tank, 2-peristaltic pump, 3-aeration head, 4-biofilm reactor, 5-CF biofilm support, 6-oxygen increasing pump, 7-flowmeter.

of CF influence adhesion of microorganism and lessen mass transfer efficiency. So the surface of CF should be appropriately modified to improve its properties as biofilm support. There were extensive studies in which multiple surface modification techniques such as physical activation by carbon dioxide (Yusof et al., 2012), oxidation etching method including acid etching (Woodhead et al., 2017) and electrochemical oxidation (Jiang et al., 2017), chemical vapor deposition method (Guo et al., 2016), plasma-mediated modification (Lee et al., 2017) were developed for the purpose of improving the surface properties of CF. Specially, nitric acid (HNO_3) oxidation etching method has been employed to improve surface properties of CF as biofilm support. In Amezquita-Garcia et al. (2016) research, the use of HNO_3 oxidized CF as biofilm support in biological system enhanced biotransformation efficiency of 4-nitrophenol, compared to the use of CF as received. In Bao and Dai (2013) research, CF surface was modified by HNO_3 oxidation etching to obtain better hydrophilicity by producing oxygen-based functional groups, which led to the increase of immobilization ratio of microorganisms.

Ferrum was one component of many enzymes in microorganism and it was indispensable electron carrier for the electron transfer system during redox reaction in microorganism (Wu et al., 2013). Tapia et al. (2011) demonstrated that ferrum was easily adsorbed by EPS. So there is one possibility that adhesion of ferrum on biofilm support may be helpful for the adhesion of biofilm on support. Feng et al. (2013) found that the removal efficiency of chemical oxygen demand (COD), ammonia nitrogen (NH_4^+—N) and total phosphorus (TP) of life sewage with high concentration were enhanced by adding ferrum-rich porous filler to microbial reactor. Chen. et al. (2012a, 2012b) found that surface modification of polyethylene biocarriers by chemical oxidation-surface covering with ferric ion increased surface roughness and brought hydrophilic functional groups to the biocarrier surface, and positively charged surface increased the biological affinity of the biocarrier. As a consequence, biofilm formation rate and COD removal efficiency were increased. So there is also possibility that modification of CF biofilm support by ferrum can improve support's properties. Bao et al. (2011a) used calcium-adsorption on CF surface method to relieve electrostatic repulsion between microorganism and CF support surface, and immobilization ability of microorganisms was improved. The mechanism was that calcium adsorbed on CF surface connected both the electronegative oxygen groups and the electronegative EPS. However, there was barely scientific research on the surface modification of CF by ferrum compound. In this paper, ferrum compound was employed in the surface modification of CF for the first time and the modification effect and mechanism were also primarily evaluated. Before the formal experiment, a preliminary screening experiment for CF surface modifiers was conducted, in which several kinds of ferrum compounds including organic iron ferrous oxalate (FeC_2O_4), ferric citrate ($FeC_6H_5O_7$) and inorganic iron ferrous sulfate ($FeSO_4$) were employed to modify CF. Taking the compatibility between CF and modifier and modification effect into consideration, FeC_2O_4 was selected for the modification of CF surface in this paper. Then the hydrophilicity and roughness of modified CF, biofilm attachment and water treatment effect were evaluated.

2. Materials and methods

2.1. Materials

The CF used in this study was unsized T300 PAN-based 12 K tow fibers purchased from Jilin petrochemical Chinese, the monofilament diameter is about **7** μm. HNO_3 and FeC_2O_4 (AR grade) used to modify CF were supplied by Sinopharm Chemical Reagent Co., Ltd.