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Potential effects of loading nano zero valent iron discharged on membrane fouling in an anoxic/oxic membrane bioreactor

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ABSTRACT

A laboratory-scale submerged anoxic-oxic membrane bioreactor for municipal wastewater was operated to investigate the potential effects of loading suspended nano zero valent iron (nZVI, 25 and 50 mg/L) discharged on the membrane fouling. nZVI transformed rapidly into Fe^{n+}, generated reactive oxygen species (ROS) and caused oxidative stress. This result rapidly led to the cell lysis and bacteria death, and further resulted in the decrease of biomass and extracellular polymeric substances (EPS). nZVI also thinned the membrane fouling layer. But nZVI had no obvious effects on activated sludge particle size, EPS molecule weight distribution and VOCs constitution of membrane foulant. Additionally, nZVI released Fe^{n+} and mitigated the inorganic (mainly Si element) fouling through Fe^{n+} flocculation. Consequently, membrane fouling mitigation with nZVI discharged was mainly due to oxidative stress to bacteria and Fe^{n+} flocculation of nZVI.

1. Introduction

Nanoparticles (NPs), which are particulate matter with at least one dimension lower than 100 nm, play an increasingly important role in medical device and diagnostics, construction, electronics and environmental remediation (Bagheri and Julkapli, 2016; Feng et al., 2016). Among NPs, nano zero valent iron (nZVI) is considered as the new environmental remediation technology, which is the cost-effective solution to some of the most challenging environmental clean-up problems. nZVI is currently applied for the soil and groundwater remediation based on two chemistry pathway: (1) nZVI acts as an electron donor to break down or to convert contaminant into a less toxic or mobile form; (2) nZVI works as a sorbent-, (co)precipitant- or contaminant-immobilising agent (Lefevre et al., 2016; Sacca et al., 2013). nZVI is also promising for the removal of pharmaceuticals, halogenated organic compounds, pesticides, viruses, etc. in the future (Sevcu et al., 2012).

However, the unique catalytic properties of nZVI have led to concerns regarding their potential harmful impacts on indigenous organisms in environment (Lefevre et al., 2016; Patil et al., 2016). Although nZVI treatment is a well acceptable practice in United State, few applications have been carried out in Europe, due to the potential health risks (Sacca et al., 2014). nZVI is toxic to pure-cultured bacteria in concentrations as low as a few mg/L (Otero-Gonzalez et al., 2013; Sacca et al., 2013; Sevcu et al., 2012). The attachment of NPs to the bacterial surface leads to the decrease of both cell mobility and nutrient between the cell exterior and interior compartments (Navarro et al., 2008). In addition, nZVI can cause rapid generation of free radicals. Fe^{2+}, as the outcome of redox-active nZVI reacts, can generate reactive oxygen species (ROS) with free radicals (Fenton or Fenton-like reaction) (Sevcu et al., 2012). Elevated concentrations of ROS in a cell results in the oxidative stress, which causes various dysfunctions of membrane lipids, proteins and DNA, etc., and further ends in apoptosis or death of the microorganisms (Davies, 2000). nZVI aggregates rapidly into micrometer or even larger particles in environment

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due to the nano-size adsorption (Lefevre et al., 2016), indicating that nZVI keeps hardly in the form of nano-size. Therefore, compared with long-term effects of nZVI, the potential risk of loading nZVI discharged into environment should be concerned.

This study aimed to investigate the potential effects of loading nZVI discharged on the performance and membrane fouling in an anoxic/oxic membrane bioreactor (MBR) for municipal wastewater. The performance, activated sludge characteristics and membrane fouling were measured with various methods, including gas chromatography-mass spectrometry (GC-MS), scanning electron microscopy (SEM), line-analysis of energy-dispersive X-ray (EDX), etc.

2. Methods and materials

2.1. Preparation of nZVI suspension

nZVI (>99.9%, approximate 50 nm) was purchased from Aladdin (Shanghai, China) in this study. 500 mg nZVI was sonically distributed (25 °C, 300 W, 40 kHz) in 1 L anaerobic MilliQ-water for 2 h to prepare stock nZVI suspension (500 mg/L) according to Zhou et al., (2014c). The primary size of nZVI in stock suspension was in the range of 50–100 nm (Fig. 1), which was close to the particle size provided by Aladdin.

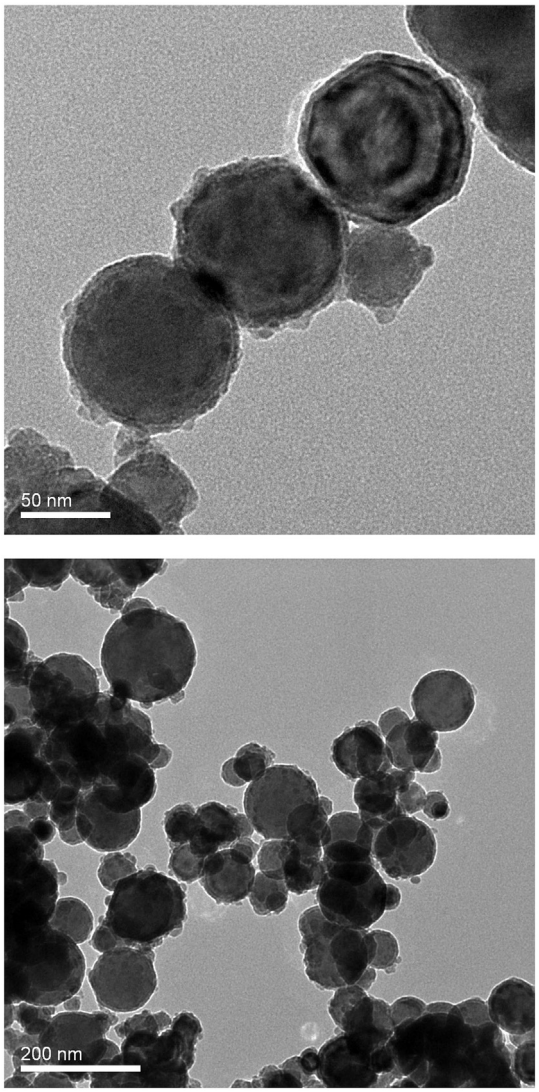

Fig. 1. The transmission electron microscopy (TEM) image of nZVI suspension.

2.2. Anoxic-oxic membrane bioreactor (A/O-MBR) setup

Three parallel laboratory-scale A/O-MBRs (Fig. S1) were operated with 0 mg/L (MBR-Blank), 25 mg/L (MBR-25 ppm) and 50 mg/L (MBR-50 ppm) nZVI discharged, respectively, for 80 days. For each A/O-MBR, a PVDF hollow fiber membrane module (total surface area = 260 cm^2; pore size = 0.4 μm; Litree Company, China) was equipped at the bottom of the oxic tank, and a constant fluid flux was set at 17 L/(m^2 h) with an intermittent suction mode (10 min/2 min on/off for each cycle). 0.4 m^3/h air was supplied continuously through a cross-flow action for effective scouring of membrane surface. The air flow rate was controlled with a gas flow-meter and trans-membrane pressure (TMP) was monitored with a pressure gauge. Hydraulic retention time (HRT) and solids retention time (SRT) were kept at 10 h and 30 days, respectively. The flow rate of recycled mixed liquor from the oxic tank to the anoxic tank was controlled at 200% of the influent flow rate (0.45 L/h).

The influent (with pretreatment, detailed in Supporting Information, SI) to the anoxic tank was the effluent from the aerated grit chamber, which was the first step of treatment in the Quyang municipal wastewater treatment plant (WWTP) (Shanghai, China). The influent pH and the reactor temperature remained within the range of 7.3–7.6 and 25–29 °C, respectively. The inoculating sludge was drawn from the return activated sludge stream in the Quyang WWTP, and washed with 0.9% NaCl solution for the original Fe removal (Fe in activated sludge was below 0.05 mg/g MLVSS (mixed liquor volatile suspended solids)). The newly inoculated A/O-MBR was initially operated for 60 days to achieve steady state for the acclimatization of activated sludge. The membrane module was then replaced with a new and similar unit and MBR was operated with an nZVI discharged (the final nZVI concentration was 0 mg/L in MBR-Blank, 25 mg/L in MBR-25 ppm and 50 mg/L in MBR-50 ppm) for 80 days. In addition, parallel A/O-MBRs with 0 mg/L, 25 mg/L and 50 mg/L nZVI discharged were also operated in the same condition for the reproducibility.

2.3. Extraction and measurement of extracellular polymeric substances (EPS)

Extraction of EPS from activated sludge was performed according to a modified thermal extraction method (Zhou et al., 2014a). 40 ml activated sludge was first centrifuged (MILTIFUGE X1R, Thermo Electron Corporation, USA) at 6000 g for 5 min and discharged the supernatant. The remaining sludge, re-suspended with 40 ml 0.9% NaCl solution, was shaken at 150 rpm for 10 min after 8 min ultrasound treatment (DS510DT, 40 kHz, 300 W, Shangchao, China). The mixed liquid was retreated with 4 min ultrasound and 30 min heating at 80 °C. The mixed liquid then was centrifuged at 12,000g for 20 min, and the supernatant was regarded as EPS. EPS has been normalized as the concentration of polysaccharide, protein, nucleic acid and humic acid (represented as TOC). They were measured by the phenol-sulfuric acid method, Branford method, diphenylamine method and TOC analyzer (TOC-V_{VPN}, Shimadzu, Japan), respectively (Xia et al., 2012).

2.4. Analysis of GC-MS

GC-MS (Focus DSQ, Thermo, USA) was carried out to identify the organic compounds of the membrane foulant. The sample was removed from the cake layer on the membrane surface and pretreated according to the description paper (Zhou et al., 2014c) (detailed in SI). Samples injection was done in the split mode (10:1)