

Short-term exposure effects of magnetic Fe₃O₄ nanoparticles on anaerobic granular sludge performance

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Abstract. Effects of magnetic Fe₃O₄ nanoparticles (Fe₃O₄ NPs) on the decontamination performance and the EPS components of sludge were studied during short-term exposure experiments. Results showed that compared with the control, the COD removal efficiency reduced from 92.8% to 84.5% with the abrupt short-term addition of excessive Fe₃O₄ NPs. The content of TB-EPS increased from 64.8 mg/gVSS to 74.5 mg/gVSS. The absorption peak of amine in LB-EPS became sharp in the FTIR spectra. In the EEM spectra, the intensity of coenzyme F₄₂₀ peak in LB-EPS was slightly enhanced.

1. Introduction

Recently, advanced oxidation processes (AOPs) have been used as a promising technology to deal with toxic and biorefractory industrial wastewater [1]. Among AOPs, Fenton reaction is accepted due to its efficient removal efficiency, easy operation and mild reaction conditions [1-2]. Especially, heterogeneous Fenton-like reaction has been widely studied by many scholars due to its advantages such as wide working pH value, lack of sludge disposal problems and efficient removal efficiency [3-4]. By heterogeneous Fenton pre-treatment, the persistent organic compounds were transformed into easily biodegradable intermediates, which would be removed by biological treatment. The combination technology of Fenton oxidation and biological process is used to treat different types of industrial wastewater. Unlike the homogeneous Fenton reactions, on account of the presence of catalysts in heterogeneous Fenton-like systems, the catalysts of flowing into the subsequent biological reactor may affect the post-treatment biological treatment unit. Based on the discussion above, the main objective of this study was to explore the effect of magnetic Fe₃O₄ nanoparticles (Fe₃O₄ NPs) on the anaerobic granular sludge system by short-term exposure experiments. Firstly, the effects of Fe₃O₄ NPs on the organic contaminant removal efficiency by anaerobic granular sludge were studied. Secondly, the components changes of loosely bound extracellular polymeric substances (LB-EPS) and tightly bound extracellular polymeric substances (TB-EPS) were analyzed by Fourier transform infrared spectra (FTIR) and excitation-emission matrix (EEM) fluorescence spectra in order to investigate the potential impacts on the characteristics of anaerobic granular sludge.

2. Materials and Methods

2.1 Seeding sludge and synthetic wastewater

In this work, seeding anaerobic granular sludge was acquired from an ABR reactor for treatment traditional Chinese medicine wastewater. The ingredients of synthetic wastewater were as follows (mg/L): glucose (3000), NH₄Cl (200), NaHCO₃ (2000), and 1 mL/L trace element solution.



2.2 Short-term exposure experiments

Short-term exposure experiments were carried out using an anaerobic device. There were two identical reaction devices during the experiments, two anaerobic bottles (a# and b#) with a volume of 250 mL, the control reactor (a#) was not added Fe_3O_4 NPs and the experimental reactor (b#) was added 200 mg/L Fe_3O_4 NPs. 40 mL anaerobic granular sludge and 160 mL of synthetic wastewater were injected into two bottles. Afterwards, two bottles were filled with nitrogen, then sealed and placed in a shaker (150 rpm) at 35 ± 1 °C for about 24 h. Collect samples at regular time intervals throughout the execution of the experiments, the COD removal rate was measured. After the short-term exposure experiments, the anaerobic granular sludge samples were collected for the LB-EPS and TB-EPS assessment.

2.3 Analytical methods

The standard method was used to monitor the influent and effluent of COD concentration. The LB-EPS and TB-EPS fractions from the anaerobic granular sludge was extracted by the modified heat extraction method [5]. The EEM spectra of EPS samples were analyzed by using Cary Eclipse fluorescence spectrometer, emission and excitation were scanned from 220 nm to 550 nm and from 220 nm to 500 nm at 5 nm slits, respectively. The primary functional groups of organics in the EPS were identified by using Nicolet 6700 FTIR spectrometer [6-7]. The polysaccharide (PS) content in EPS was analyzed using the phenol-sulfuric acid method, and the protein (PN) content in EPS was measured using the coomassie light blue spectrophotometric method [7].

3. Results and discussion

3.1 Effects of Fe_3O_4 NPs on the COD removal efficiency

During the short-term exposure experiments, the COD removal efficiency was similar between a# and b# reactor in the first 12 hours (Fig. 1). The removal efficiency of COD was 35.01% and 34.29% at 12 hour in the a# and b# reactor, respectively. However, compared with the a# reactor, the COD removal efficiency decreased from 92.8% to 84.5% with the presence of 200 mg/L Fe_3O_4 NPs at 24 hour.

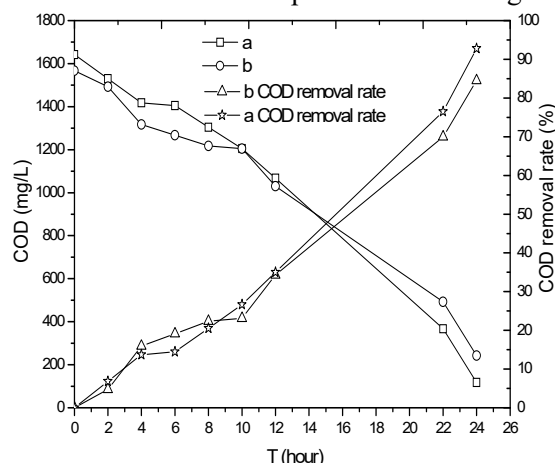


Figure 1. Effects of Fe_3O_4 NPs on the COD removal rate during short-term exposure

3.2 Effects of Fe_3O_4 NPs on the COD removal efficiency

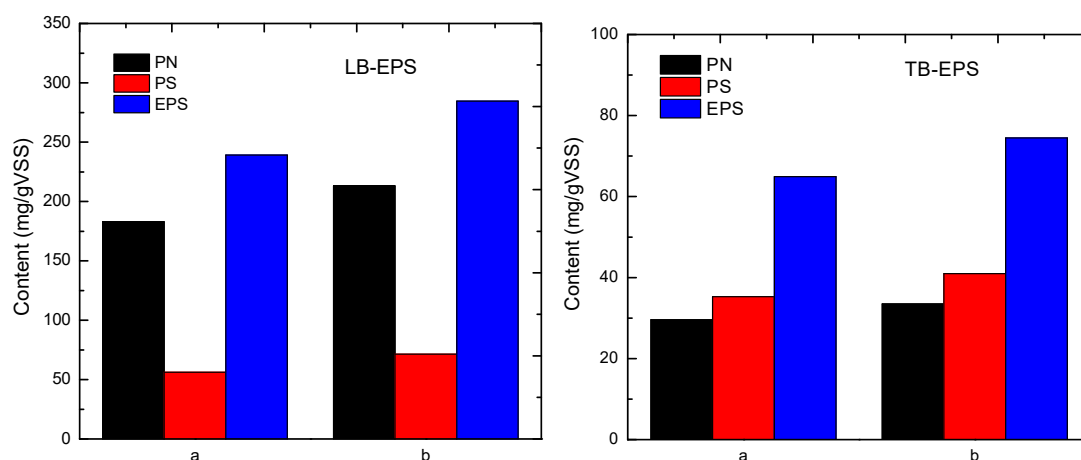
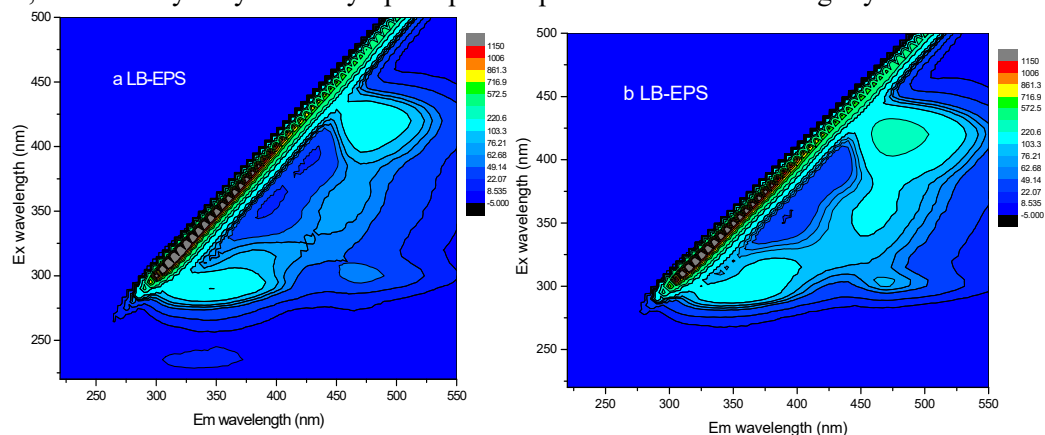


Figure 2. Variation of LB-EPS and TB-EPS contents after short-term exposure

EPS is derived from bacterial secretions, cell hydrolysis and lysis, and composed of proteins, polysaccharides, nucleic acids, lipids, and other components [8]. According to different spatial location, EPS can be divided into LB-EPS and TB-EPS. As seen from the Fig. 2, the contents of PS and PN in LB-EPS and TB-EPS were determined. After short-term exposure, the content of LB-EPS increased from 239.1 mg/gVSS to 284.5 mg/gVSS. The content of PS increased from 56.2 mg/gVSS to 71.5 mg/gVSS, and the content of PN increased from 182.9 mg/gVSS to 213.0 mg/gVSS. In addition, the content of TB-EPS increased from 64.8 mg/gVSS to 74.5 mg/gVSS. The content of PS increased from 35.3 mg/gVSS to 41.0 mg/gVSS, and the content of PN increased from 29.6 mg/gVSS to 33.5 mg/gVSS. It was indicated that the increased amounts of LB-EPS and TB-EPS were a stress response of microorganisms in anaerobic granular sludge on the environmental stimulation of Fe_3O_4 NPs after short-term exposure.

EEM spectra was further applied for the analyzing component of LB-EPS and TB-EPS (Fig. 3). Three fluorescent peaks were observed from the EEM fluorescence spectra. The first peak was located at the Ex/Em wavelengths of 260-300/300-360 nm (Peak A), and the second peak was located at the Ex/Em of 420/470 nm (peak B). Two peaks were reported as tyrosine/tryptophan protein and coenzyme F_{420} peaks, respectively. Moreover, the third peak was located at the Ex/Em of 300-320-/450-470 nm (Peak C) that was regarded as humic acid peak [9-10]. After short-term exposure, the intensity of three peaks in LB-EPS were slightly enhanced, especially coenzyme F_{420} . It was indicated that the addition of Fe_3O_4 NPs had a beneficial effect on the activity of methanogens in the reactor [11]. After short-term exposure, the intensity of tyrosine/tryptophan protein peak in TB-EPS was slightly enhanced [12].



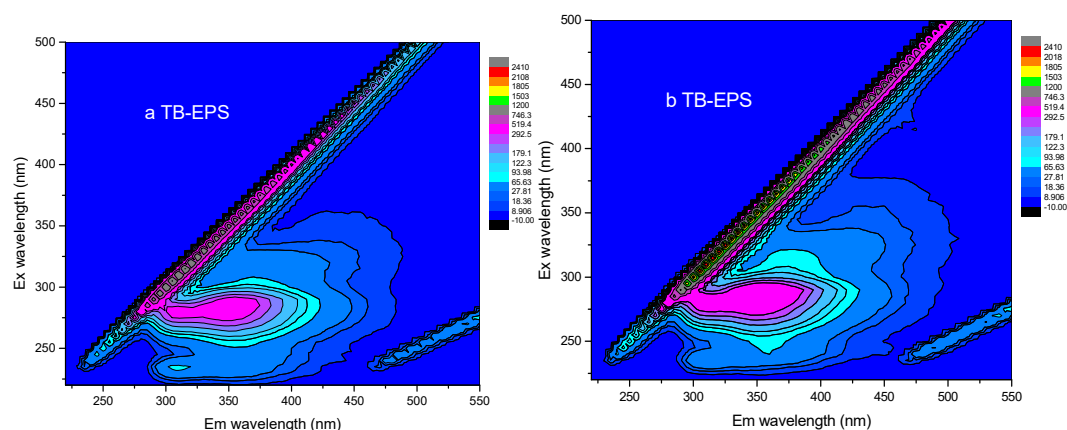


Figure 3. EEM spectra of LB-EPS and TB-EPS after short-term exposure

In order to comprehensively analyze the composition changes of LB-EPS and TB-EPS after adding Fe_3O_4 NPs, the FTIR spectra were also measured (Fig. 4). The primary absorption peaks were as follows: N-H stretching vibration ($3500\text{--}3300\text{ cm}^{-1}$), C-H stretching vibration ($3000\text{--}2920\text{ cm}^{-1}$), carboxylic group (1733 cm^{-1}), Amide I ($1640\text{--}1630\text{ cm}^{-1}$), Amide II ($1460\text{--}1440\text{ cm}^{-1}$), C=O stretching vibration ($1290\text{--}1260\text{ cm}^{-1}$), C-O-C stretching vibration ($1100\text{--}1020\text{ cm}^{-1}$) and finger print region ($900\text{--}600\text{ cm}^{-1}$) [13-14]. After short-term exposure, the absorption peak of amine in LB-EPS became sharp in the FTIR spectra. The possible reason is that the dissolution of iron ions from the Fe_3O_4 NPs reacted with the protein of LB-EPS, which resulted in the change of FTIR spectra. After short-term exposure, the absorption peaks of the TB-EPS have no obvious change in the FTIR spectra. It was indicated that Fe_3O_4 NPs as a catalyst had no significant effect on the TB-EPS components in the anaerobic granular sludge following short-term exposure.

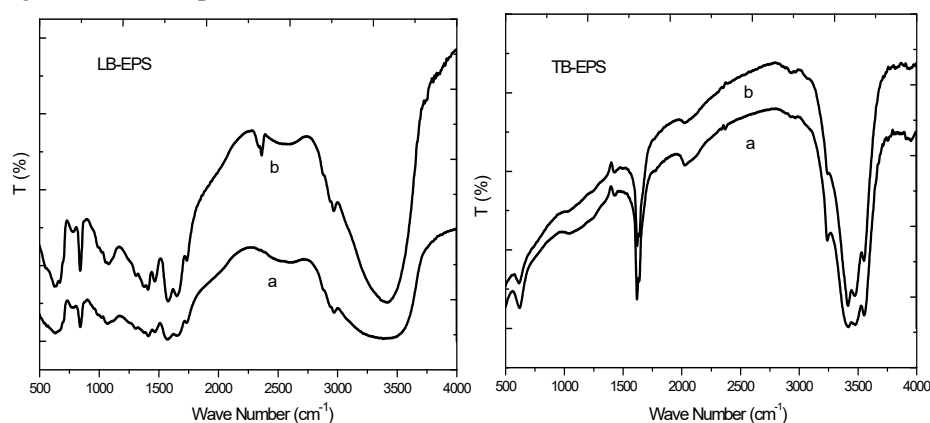


Figure 4. FTIR spectra of LB-EPS and TB-EPS after short-term exposure

4. Conclusions

In this study, the abrupt short-term addition of excessive Fe_3O_4 NPs had some influence on the COD removal efficiency. However, the contents of tryptophan protein and coenzyme F_{420} increased in the LB-EPS of anaerobic granular sludge. Therefore, using Fe_3O_4 NP heterogeneous Fenton-like technology as pre-treatment for treatment refractory wastewater is feasible.

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