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Short Communication

Effective biodegradation of nitrate, Cr(VI) and p-fluoronitrobenzene by a novel three dimensional bioelectrochemical system

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HIGHLIGHTS

- The BES showed satisfied single NO_3^-—N, Cr(VI), and p-FNB removal abilities.
- NO_3^-—N and Cr(VI) could be reduced by degrading p-FNB.
- This investigation achieved the aim of using waste to treat waste.

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ABSTRACT

p-Fluoronitrobenzene (p-FNB) was degraded in a novel three dimensional bioelectrochemical system (3D BES) and potentially utilized as carbon source for achieving both nitrate (NO_3^-—N) and Cr(VI) reduction. For single NO_3^-—N and Cr(VI) removal, 200 mg L^{-1} NO_3^-—N and 100 mg L^{-1} Cr(VI) could be almost completely converted to N_2 and Cr(III) at current 50 mA. For single p-FNB degradation, 100 mg L^{-1} p-FNB was completely degraded at current 50 mA. The critical current for defluorination was 40 mA, and the intermediate product p-fluoroaniline (p-FA) tended to decrease when current was higher than 40 mA. When NO_3^-—N, Cr(VI), and p-FNB were both coexisted in this system, the average NO_3^-—N, Cr(VI), and p-FNB removal efficiencies slightly decreased with addition of carbon source. Without carbon source, NO_3^-—N and Cr(VI) removal rates reached 34.45% and 41.38% with 91.02% p-FNB degradation, proving that NO_3^-—N and Cr(VI) could be reduced by degrading p-FNB in the BES.

1. Introduction

It is urgent to remove nitrate in natural waters because nitrate pollution becomes more and more serious with increasing industrialization, and thus causing deleterious effect on human and environment (Bi et al., 2015; Fowdar et al., 2015; Ghafari et al., 2008). Since many kinds of industrial waters such as pigmenting, textile dyeing, electroplating, agrochemicals, pharmaceuticals, and aerosol propellants (Murphy et al., 2008; Zayed and Terry, 2003) always discharge into natural waters without effective treatment, Cr(VI) and p-fluoronitrobenzene contaminations in natural waters become an imperative problem needing effective and economical approach to renovate. Although there are numerous efficient methods such as reverse osmosis, ion exchange, and aerobic biodegradation for single nitrate, Cr(VI) and p-fluoronitrobenzene removal (Karanasios et al., 2010; Lameiras et al., 2008; Xie et al., 2014), seeking for a better scheme to achieve both nitrate, Cr(VI) and p-fluoronitrobenzene degradation in one system will be a challenging problem.

In recent years, bioelectrochemical method has gained much attention because this technology has the advantages of effective pollutant removal, easy control and operation, and environmental compatibility (Nancharaiah et al., 2015). Some researchers used the bioelectrochemical method for nitrate removal (Xie et al., 2014), heavy metal degradation (Wang and Ren, 2014), organic matter and salt ions removal (Kim and Logan, 2013) and confirmed that bioelectrochemical system had a very good prospect for wastewater remediation.

In this work, a novel 3D bioelectrochemical system was developed to treat NO_3^-—N, Cr(VI), and p-FNB coexisting wastewater. This BES overcame the disadvantage of conventional system due to that sulfur autotrophic process always generated H^+, which could be used for hydrogen autotrophic phase, leading to balanced pH environment. On the other hand, sulfur part shared the pollutant load, and thus increasing the overall removal rate. An attempt was made to confirm if this system could reduce NO_3^-—N and Cr

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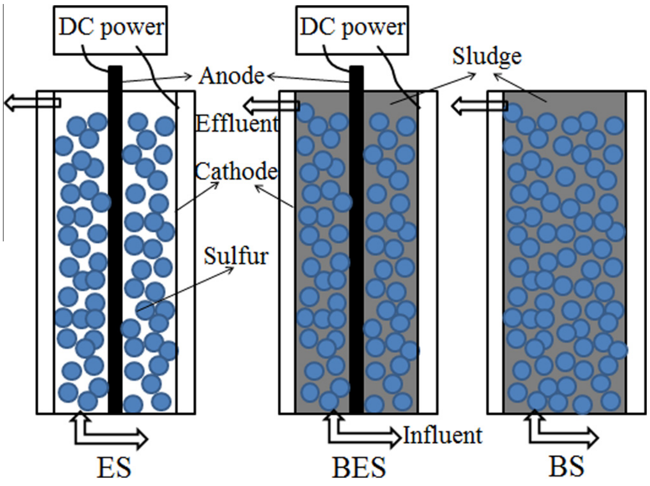

Fig. 1. Diagram of the reactor.

(VI) by degrading p-FNB. The exploration in this work would provide new thoughts for complex industrial wastewater treatment.

2. Methods

2.1. Reactor operation

A cylindrical reactor was used in this study (Fig. 1). The valid volume was 3000 mL. A piece of graphite felt was used as cathode and placed closed to the interior wall of the reactor. A carbon rod (diameter 8 mm) was used as anode and placed in the middle of the reactor. The whole reactor was filled with sulfur granules (diameter 5.0–8.0 mm). Cathode and anode were connected to a direct current power source (RPS-3005D, 0–30 V, 0–5 A). Two duplicate reactors were used as controls: a single 3D electrochemical system (ES), and a single biological system (BS).

At the initial phase, the continuous-flow reactor was inoculated with anaerobic sludge (MLSS 3300 mg L^{-1}) collected from Erlangmiao Municipal Wastewater Treatment Plant, Wuhan, China, and operated for 30 days at current 10 mA, hydraulic retention time (HRT) 16 h, pH 7.0, temperature 25 °C condition. The medium was: NO_3^-—N 30 mg L^{-1}, HCO_3^- 60 mg L^{-1}, $MgSO_4$ 10 mg L^{-1}, $MgCl_2$ 10 mg L^{-1}, $ZnCl_2$ 0.52 mg L^{-1}, $CoCl_2$ 1.90 mg L^{-1}, $MnSO_4$ 1.00 mg L^{-1}, $NiCl_2$ 0.24 mg L^{-1}, $CuCl_2$ 0.29 mg L^{-1}, $FeSO_4$ 0.25 mg L^{-1}, $CaCl_2$ 0.50 mg L^{-1}, Na_2MoO_4 0.36 mg L^{-1}.

2.2. NO_3^-—N removal

NO_3^-—N concentration was maintained at 200 mg L^{-1} under HRT 16 h, pH 7.0, temperature 25 °C condition. The current was adjusted to 10, 20, 30, 40, 50, 60 mA for each 15 days. The contents of NO_3^-, NO_2^-, SO_4^{2-}, N_2 were measured to evaluate nitrate removal efficiency of this system.

2.3. Cr(VI) removal

Cr(VI) concentration was maintained at 100 mg L^{-1} under HRT 16 h, pH 7.0, temperature 25 °C condition. The current was adjusted to 10, 20, 30, 40, 50, 60 mA for each 15 days. The contents of Cr(VI), Cr(III), SO_4^{2-} were measured to evaluate Cr(VI) removal efficiency of this system.

2.4. p-FNB removal

p-FNB concentration was maintained at 100 mg L^{-1} under HRT 16 h, pH 7.0, temperature 25 °C condition. The current was adjusted to 10, 20, 30, 40, 50, 60 mA for each 15 days. The contents of p-FNB, p-FA, F^- were measured to evaluate p-FNB removal efficiency of this system.

2.5. Biodegradation in NO_3^-—N, Cr(VI), and p-FNB coexisting system

NO_3^-—N, Cr(VI), p-FNB concentrations were adjusted to 200, 100, 100 mg L^{-1} under HRT 16 h, pH 7.0, temperature 25 °C, current 10–60 mA condition. The NO_3^-—N, Cr(VI), p-FNB removal efficiencies were assessed. Besides, the concentration of p-FNB was further increased to 150, 200, and 300 mg L^{-1} under NO_3^-—N 100 mg L^{-1}, Cr(VI) 100 mg L^{-1}, HRT 16 h, pH 7.0, temperature 25 °C, current 50 mA condition.

2.6. Analytical methods

The samples during the experiments were filtered by 0.30 μm membrane by a suction filter machine. Then the concentrations of NO_3^-—N, NO_2^-—N, Cr(VI), total Cr, were determined in accordance with the Standard Methods for the examination of water and wastewater (APHA, 2005). NO_3^-—N was measured by ultraviolet spectrophotometric method using spectrophotometer at (220–275 × 2) nm. NO_2^-—N was measured by N-(1-naphthyl) ethylenediamine dihydrochloride spectrophotometric method at 540 nm. Total Cr was determined by atomic absorption spectroscopy. Cr (VI) was measured using spectrophotometer at 540 nm after complexation with 1,5-diphenylcarbazide. Cr(III) was determined by the difference value between Cr and Cr(VI). Nitrogen gas (N_2) was measured by an Agilent HP4890D gas chromatography. p-FNB and p-FA concentrations were detected by a liquid chromatograph (Agilent 1260, Agilent Technologies, USA). F^- and SO_4^{2-}—S concentrations were measured by an ion chromatograph (881 Compact IC pro, Metrohm, Switzerland). The microbial biomass was detected by OD_{600} using spectrophotometry. The pH was measured by a pH meter (PHS-3C, Kexiao Instrument, China). The water temperature was measured by a thermometer (TM827, Zhugongda Instrument, China).

3. Results and discussion

3.1. NO_3^-—N removal

As shown in Fig. 2a, the NO_3^-—N, Cr(VI), p-FNB removal rates by ES control and BS control were very low and thus could be neglected. Fig. 2b shows that NO_3^-—N removal rate increased from 64.02% to 97.45% with current increased from 10 to 60 mA, due to the reason that higher current accelerated the electron transport in this system. The intermediate product NO_2^-—N was slightly accumulated when current varied from 10 to 40 mA. The maximum SO_4^{2-} concentration was 86.10 mg L^{-1}, which was lower than 250 mg L^{-1} (China EPA, Drinking Water Standard). Therefore, it is obvious that the main degradation products were N_2 and SO_4^{2-}. On the one hand, hydrogen autotrophic bacteria used H_2 (produced on the cathode) as electron donor (Wan et al., 2011) to achieve denitrification process. On the other hand, sulfur autotrophic bacteria could also convert NO_3^-—N to N_2 by consuming S (Wang and Qu, 2003). In addition, the sulfur autotrophic process always generated H^+, which could be used for hydrogen autotrophic phase, leading to balanced pH condition and effective removal rate.

3.2. Cr(VI) removal

Fig. 2c shows that the main metabolite for Cr(VI) removal was Cr(III). When current increased from 10 to 60 mA, Cr(VI) removal rate increased from 43.12% to 96.68%. The high Cr(VI) removal rate