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Nitrobenzene Removal in Bioelectrochemical Systems

YANG MU,* RENÉ A. ROZENDAL,
KORNEEL RABAEY, AND JÜRG KELLER

*Advanced Water Management Centre, The University of
Queensland, St. Lucia, QLD 4072, Australia*

Nitrobenzene occurs as a pollutant in wastewaters originating from numerous industrial and agricultural activities. It needs to be removed prior to discharge to sewage treatment works because of its high toxicity and persistence. In this study, we investigated the use of a bioelectrochemical system (BES) to remove nitrobenzene at a cathode coupled to microbial oxidation of acetate at an anode. Effective removal of nitrobenzene at rates up to 1.29 ± 0.04 mol m^{-3} TCC d^{-1} (total cathodic compartment, TCC) was achieved with concomitant energy recovery. Correspondingly, the formation rate for the reduction product aniline was 1.14 ± 0.03 mol m^{-3} TCC d^{-1}. Nitrobenzene removal and aniline formation rates were significantly enhanced when the BES was supplied with power, reaching 8.57 ± 0.03 and 6.68 ± 0.03 mol m^{-3} TCC d^{-1}, respectively, at an energy consumption of 17.06 ± 0.16 W m^{-3} TCC (current density at 59.5 A m^{-3} TCC). Compared to those of conventional anaerobic biological methods for nitrobenzene removal, the required dosage of organic cosubstrate was significantly reduced in this system. Although aniline was always identified as the major product of nitrobenzene reduction at the cathode of BES in this study, the Coulombic efficiencies of nitrobenzene removal and aniline formation were dependent on the current density of the BES.

Introduction

Nitrobenzene is widely used in the production of different types of products such as dyes (*1*), explosives, and pesticides (*2, 3*). Many countries have listed it as a priority pollutant because of its mutagenicity, recalcitrance, and tendency to accumulate in the environment (*4*). Therefore, it is necessary to remove nitrobenzene when it occurs as a pollutant.

During the last two decades, various advanced oxidation processes such as ozonation and O$_3$/UV processes (*5*), photocatalysis (*6*), photoassisted Fenton oxidation (*7*), supercritical oxidation (*8*), and other methods (*9*) have been applied for the degradation of nitrobenzene-rich wastewaters. However, the direct oxidation of nitrobenzene is very difficult to achieve because of the low electron cloud density in its benzene ring (*10*). Furthermore, the direct oxidation of nitrobenzene may produce byproducts such as picolinic acid, which are even more toxic than nitrobenzene itself (*11*). In addition, most of these advanced oxidation processes are energy and cost intensive (*12*).

Although some bacteria were found in the last two decades that mineralize nitrobenzene (*4*), most microorganisms are

only able to reduce nitrobenzene to aniline (*13*). However, this anaerobic reductive process is usually very slow and requires an electron donor (organic cosubstrate) to create the necessary reductive conditions (*14*). The addition of an organic cosubstrate typically far exceeds the stoichiometric requirements, leading to additional costs and unwanted methane production (*15, 16*).

Electrochemical reduction of nitrobenzene has recently aroused increasing interest (*10, 17*). Such a process has potential advantages in terms of versatility, environmental compatibility, and chemical usage. The major pathway of electrochemical reduction of nitrobenzene was proposed to include three steps with nitrosobenzene and hydroxylaminobenzene as intermediates (*10*) (Figure 1). However, chemical catalysts were used in anodes and cathodes in these studies, resulting in high energy consumption mainly due to the overpotentials at the two electrodes. In one study, for instance, electrochemical reduction of nitrobenzene was achieved at laboratory scale with an energy consumption of about 0.4–0.8 kWh mol^{-1} nitrobenzene removal (*10*).

A possible solution for reducing high overpotentials is the use of microbial catalysts. In recent years, bioelectrochemical systems (BESs) such as microbial fuel cells (MFCs) and microbial electrolysis cells (MECs) have been explored extensively for their innovative features and environmental benefits (*18, 19*). The principle relies on the fact that electrochemically active microorganisms can transfer electrons from a reduced electron donor to an electrode. The generated electrons are then transferred through an external circuit to the cathode chamber where they reduce the final electron acceptor (*18*). A number of valuable oxidation or reduction reactions demonstrating the versatility of BESs have been described (*20*). For example, BESs have been applied to remove organic and inorganic contaminants such as acetate (*21, 22*), cellulose (*23*), rhizodeposits of rice plants (*24*), and sulfide (*25*) from wastewater at the anode chamber. On the other hand, BESs can produce hydrogen (*21, 26*), reduce nitrate and nitrite (*27, 28*), reductively dehalogenate (*29*), and decolorize azo dyes (*30*) at the cathode chamber.

The present study aims to investigate whether nitrobenzene can be reduced at the abiotic cathode of a BES, while driven by microbial oxidation of organics at the anode. The focus of this study was to evaluate the efficiency and feasibility of the overall process as well as to identify the products of nitrobenzene reduction.

Materials and Methods

Chemicals. Nitrobenzene, nitrosobenzene, and aniline (analytical grade) were purchased from Sigma-Aldrich (Sydney, Australia).

Bioelectrochemical System. The BES was constructed by assembling two equal rectangular Perspex frames with internal dimensions of 0.14 m × 0.12 m × 0.2 m (*31*). The frames were bolted together between two Perspex square plates. A cation exchange membrane (Ultrex CMI-7000, Membranes International, U.S.A.) was placed between the anode and cathode. Sealing was ensured by rubber sheets
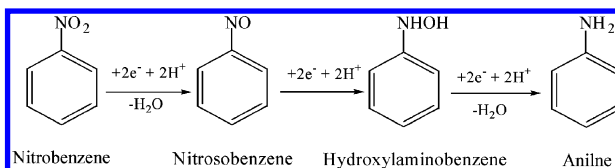
FIGURE 1. Major pathway for electrochemical reduction of nitrobenzene (*10*).

* Corresponding author phone: +61 7 3346 3218; fax: +61 7 3365 4726; e-mail: yangmu@awmc.uq.edu.au.

inserted between each frame. The total empty volume for each compartment was 336 mL (total cathodic compartment, TCC; total anodic compartment, TAC). Granular graphite with a diameter ranging from 2 to 6 mm (El Carb 100, Graphite Sales, Inc., U.S.A.) was used as the electrode in the anode and cathode compartments, reducing the compartment liquid volume to 182 mL. Prior to use, the granular graphite was washed for 24 h in 32% HCl four times, in order to eliminate any potentially catalytic foreign compounds from the graphite material (32). A graphite rod (5 mm diameter) was used in the anodic and cathodic compartments to connect the electrodes to the external circuit. By killing all microorganisms, this treatment also eliminated any potential biocatalyst that could affect cathode performance. To ensure that biological activity would not affect the results, we started the experiments immediately after adding the sterile granules to the reactor. The fact that cathode performance was established very quickly and did not change over time strongly indicates that no biocatalysis was developing during the operation of this reactor.

During startup, the anodic compartment of the BES was inoculated with a microbial consortium previously enriched in MFCs with acetate as the carbon source and continuously fed with a modified M9 medium as previously described in Rabaey et al. (33). The growth medium with 320 mg L^{-1} of sodium acetate as the electron donor was fed to the anodic reactor at a flow rate of 540 mL d^{-1}, giving rise to an organic loading rate of 0.8 kg COD m^{-3} NAC d^{-1}. The cathode feed consisted of a 50 mM phosphate buffer (pH 7) with 1.5 mM of nitrobenzene, which is a typical concentration in the industrial wastewater (34). The anode and cathode influents were sparged with nitrogen gas to remove oxygen. The nitrobenzene was added into the influent solution after gas sparging in order to avoid stripping of nitrobenzene from the solution. The system was started at an external resistance of 10 Ω and a cathodic hydraulic retention time (HRT) of 7.9 h. After six weeks of operation, the anode potential at open circuit reached −330 mV vs SHE, indicating the successful startup of the BES reactor. Throughout all of the experiments, the anolyte and catholyte were recirculated at a rate of approximately 200 mL min^{-1} to maintain well-mixed conditions and avoid concentration gradients and clogging of the granular matrix during continuous feed. The reactors and cathode influent tank as well as all of the tubing were covered using aluminum foil in order to prevent (solar) light effects on nitrobenzene degradation (35). The cathodic half-cell potentials were measured by placing an Ag/AgCl reference electrode (assumed +0.197 V vs SHE) (ref 201, BioAnalytical Systems) in the cathode compartment of each BES. All experiments were performed at 25 ± 1 °C.

In the first phase, the BES was operated in open circuit with continuous cathode feeding for two weeks. The purpose of this control experiment was to confirm that nitrobenzene removal and aniline formation were not associated with the catalytic activity of the graphite material. Then the circuit of the BES was closed and two series of experiments were conducted in order to investigate the reactor performance at various current densities. The variations in the operational parameters are listed in Table 1. In series 1, the external resistance was reduced from 100 to 5 Ω, which allowed spontaneous flow of electrons from the electrode at lower potential to the electrode at higher potential. At this stage, the BES was driven solely by the oxidation and reduction reactions in the anode and cathode. In series 2, power was supplied to the BES to increase the current from 5.5 to 25 mA using a potentiostat. To be able to guarantee availability of nitrobenzene at the cathode, we shortened the HRT with increasing current (Table 1). After these forced current experiments, one additional experiment was carried out at short circuit conditions using a potentiostat in a three-

TABLE 1. Experimental Setup for Cathode[a]

series	conditions[b]					
1[c]	external resistance (Ω)	100	50	20	10	5
2[d]	controlled current (mA)	5.5	10	15	20	25
	HRT (h)	7.9	4.4	2.9	2.2	1.8

[a] Anode operation conditions were the same as those used during BES startup. [b] The steady-state period of each experiment lasted 3−4 days, and three samples were taken during each period. [c] HRT 7.9 h, influent nitrobenzene 1.5 mM, pH 7.0. [d] Influent nitrobenzene 1.5 mM, pH 7.0.

electrode setup (0 V applied voltage; HRT 7.9 h; influent nitrobenzene 1.5 mM). Each experiment lasted 1−2 weeks to ensure that the reactor reached steady state, judging from the constant nitrobenzene removal and aniline formation rates and constant anode and cathode potentials. Only those results obtained under steady-state conditions are reported here.

Chemical Analysis. Samples taken from the anode and cathode were immediately filtered through a 0.22 μm filter. For acetate analysis, 0.9 mL of sample was added to 0.1 mL of 10% formic acid solution and analyzed with a gas chromatography method using a polar capillary column (DB-FFAP) at 140 °C and a flame ionization detector at 250 °C. Nitrobenzene, nitrosobenzene, and aniline were measured by high performance liquid chromatography (HPLC) using a C8 column (5 μm; 4.6 mm × 250 mm). The mobile phase was MeOH/H$_2$O 1:1 at 1 mL min^{-1}. The detection was performed at 254 nm. In addition, the UV−vis absorption spectra of nitrobenzene, aniline, and the samples from the cathode effluent were recorded in the wavelength range from 200 to 800 nm using a spectrophotometer (Cary 50, Varian, Inc.).

Electrochemical Monitoring and Calculation. The anode was connected to the cathode through an external resistance or a potentiostat (VMP3 multichannel potentiostat, Princeton Applied Research, U.S.A.) for current control.

The current was calculated from the external resistance using Ohm's law. The Coulombic efficiency for acetate oxidation (ε_{Ac}) was evaluated according to Logan et al. (18)

$$\varepsilon_{Ac} = \frac{I}{4 \times \Delta COD \times \frac{Q_A \times 10^3}{24 \times 3600} \times F} \qquad (1)$$

where I is the current (mA), F is Faraday's constant (96485 C mol^{-1} e), ΔCOD is the change of acetate concentration in COD (mM), 4 is the number of electrons exchanged per mole of COD, and Q_A is the influent flow rate of anode (m^3 d^{-1}). The Coulombic efficiency for nitrobenzene removal (ε_{NB}) was calculated as the ratio of the theoretical current estimation based on completely converting nitrobenzene to aniline at the cathode and the current flowing across the BES

$$\varepsilon_{NB} = \frac{6 \times (C_{in\text{-}NB} - C_{ef\text{-}NB}) \times \frac{Q_C \times 10^3}{24 \times 3600} \times F}{I} \qquad (2)$$

where 6 is the number of moles of electrons that can be accepted by 1 mol of nitrobenzene assuming complete conversion to aniline, $C_{in\text{-}NB}$ is the influent nitrobenzene concentration (mM), $C_{ef\text{-}NB}$ is the effluent nitrobenzene concentration (mM), and Q_C is the influent flow rate of the cathode (m^3 d^{-1}). The Coulombic efficiency for aniline formation (ε_{AN}) was calculated as the ratio of the theoretical current estimation based on the aniline production from ni-
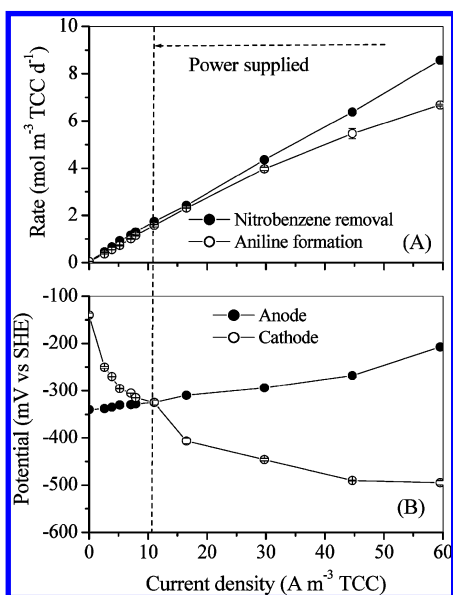
FIGURE 2. Variations of (A) nitrobenzene removal and aniline formation rates and (B) anode and cathode potentials with current density in BESs.

trobenzene at the cathode and the current flowing across the BES

$$\varepsilon_{AN} = \frac{6 \times C_{ef\text{-}AN} \times \dfrac{Q_C \times 10^3}{24 \times 3600} \times F}{I} \qquad (3)$$

where 6 is the number moles of electrons when aniline formed from nitrobenzene and $C_{ef\text{-}NB}$ is the effluent aniline concentration (mM).

As with conventional anaerobic biological methods, an electron donor (organic cosubstrate or reductant) such as acetate is required at the anode of BES to supply electrons for the nitrobenzene reduction at the cathode. In order to compare the dosage of the electron donor, the reductant usage ratio (RUR:mol COD mol^{-1} nitrobenzene removal) was calculated as

$$RUR = \frac{\Delta COD \times Q_A}{(C_{in\text{-}NB} - C_{ef\text{-}NB}) \times Q_C} \qquad (4)$$

Substituting eqs 1 and 2 into eq 4 this becomes

$$RUR = \frac{3}{2} \times \frac{1}{\varepsilon_{Ac}} \times \frac{1}{\varepsilon_{NB}} \qquad (5)$$

So, with 100% Coulombic efficiency at the anode and cathode, one would expect a RUR of 1.5 mol COD mol^{-1} nitrobenzene removal.

Results and Discussion

Reactor Performance. Figure 2A shows the reactor performance in terms of nitrobenzene removal and aniline formation at various current densities in the BES. Under an open circuit condition, i.e., current density is zero, nitrobenzene removal and aniline formation rates were negligible (i.e., 0.098 ± 0.030 and 0.054 ± 0.01 mol m^{-3} TCC d^{-1}, respectively), indicating that nonelectrochemical processes for nitrobenzene removal and aniline formation at the graphite electrode surface were minimal. During the closed circuit operation, nitrobenzene removal and aniline formation rates were significantly enhanced, demonstrating that the cathode was used as the electron donor for nitrobenzene reduction as well as for aniline formation. As current density increased
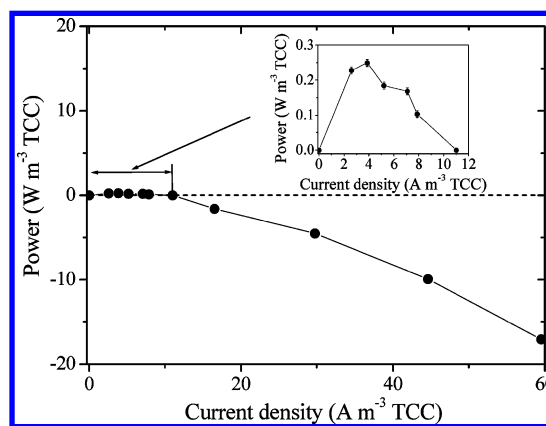

FIGURE 3. Power output and input as a function of current density during nitrobenzene reduction in BESs (positive value means power output; negative value means power input).

from 0 to 59.5 A m^{-3} TCC, nitrobenzene removal and aniline production rates increased from 0.054 ± 0.005 to 8.57 ± 0.05 mol m^{-3} TCC d^{-1} and 0.054 ± 0.027 to 6.67 ± 0.03 m^{-3} TCC d^{-1}, respectively. Figure 2A also indicates that the difference between the nitrobenzene removal rate and aniline formation rate increased with an increase in current density.

The variation of anode and cathode potentials was also monitored at various current densities during nitrobenzene removal at the cathode (Figure 2B). Higher current density resulted in higher anode potential and lower cathode potential. As the current density increased from 0 to 59.5 A m^{-3} TCC, the anode potential increased from −340 ± 5 to −207 ± 6 mV vs SHE, while the cathode potential reduced from −140 ± 5 to −495 ± 5 mV vs SHE. Throughout this experimental period, the cathodic reaction was the more limiting process for nitrobenzene removal in BES. An attempt was performed to increase the current density to 74.4 A m^{-3} TCC by galvanostatically controlling current at 25 mA. However, the anode potential increased to higher than 500 mV vs SHE, which implies that the electrochemically active bacteria at the anode lost their function. At this stage, the anodic reaction became the more limiting process for nitrobenzene removal in BES.

As shown in Figure 3, power was generated (i.e., positive values in Figure 3) simultaneously with the nitrobenzene removal in BES at current density lower than 11.0 A m^{-3} TCC. The maximum power output of 0.25 ± 0.01 W m^{-3} TCC was obtained at a current density of about 3.9 A m^{-3} TCC. However, a power input was required (i.e., negative values in Figure 3) at current densities higher than 11.0 A m^{-3} TCC, resulting in the enhancement of nitrobenzene removal activity in BESs (Figure 2A). The power consumption increased from zero to 17.08 ± 0.16 W m^{-3} TCC when the current density increased from 11.0 to 59.5 A m^{-3} TCC. The experiment performed at current density 74.4 A m^{-3} TCC can be regarded as a pure electrochemical control for nitrobenzene reduction as no bioactivity was present at the anode (due to the very high potential of >500 mV vs SHE). The energy consumption in this control, about 0.2 kWh mol^{-1} at a nitrobenzene removal rate of around 10.5 mol m^{-3} TCC d^{-1}, was somewhat lower than that of a previous pure electrochemical reduction using a carbon nanotube electrode, with energy consumption of 0.4−0.8 kWh mol^{-1} at a nitrobenzene removal rate of 18 mol m^{-3} d^{-1} (10). It is very interesting to note that the energy consumption was significantly reduced to around 0.05 kWh mol^{-1} at a nitrobenzene removal rate of 8.57 mol m^{-3} d^{-1} in BES. In addition, the applied voltages in the range of 0−287 mV used in the BES (Figure S1 of Supporting Information) were much lower compared to those typically needed for water electrolysis at 1000−2000 mV (10, 17). This could be mainly due to the
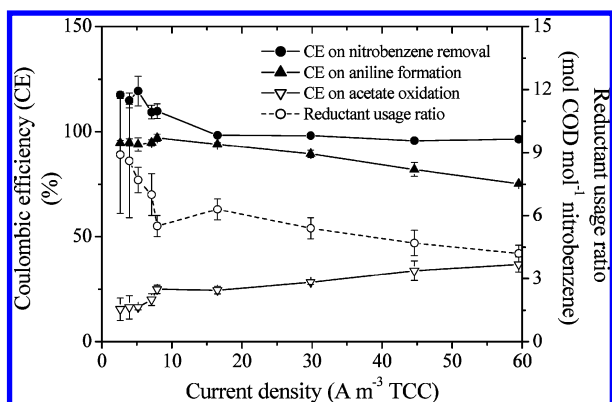
FIGURE 4. Coulombic efficiency and reductant usage ratio at various current densities.

following reasons. First, the microbial oxidation of acetate at the anode provides a (renewable) source of energy for nitrobenzene removal, which greatly reduces the energy requirement. Second, the anode reaction is catalyzed by self-selecting microbial biocatalysts, resulting in a low overpotential for the anodic acetate oxidation. Third, the cathode potentials in this BES were in the range of −140 to −495 mV vs SHE, i.e., much higher than those of electrochemical systems (typically about −600 to −1000 mV vs SHE). In this study, granular graphite was used as the cathode material with a very high specific surface area on the order 10^6 m^2 m^{-3} (*32*). Therefore, the cathode overpotential was substantially reduced because of the low current density at the cathode.

Coulombic Efficiencies. As shown in Figure 4, the Coulombic efficiencies of nitrobenzene removal and aniline formation at current densities lower than 16.5 A m^{-3} TCC were higher than 98% and 90%, respectively, indicating that the cathodic reduction was very effective. However, the Coulombic efficiencies of nitrobenzene removal and aniline formation were reduced at higher current densities as shown in Figure 4, which means that either intermediate products might be formed during nitrobenzene reduction at high current density or that electrons are diverted toward alternative reactions, e.g., hydrogen gas formation. The first possibility was supported through HPLC analysis (see further), while hydrogen gas formation would not be expected because of the insufficiently low cathode potentials used in these experiments. Figure 4 further shows that the Coulombic efficiencies for nitrobenzene removal were a bit higher than 100% at current densities lower than 7.9 A m^{-3} TCC, which indicates that a very small part of nitrobenzene was removed by nonelectrochemical processes. This is consistent with the fact that the nitrobenzene removal rate was slightly above zero under open circuit conditions. The nonelectrochemical processes might be caused by the metals of the graphite surface, although their content was substantially reduced following the acid wash process (*32*). These nonelectrochemical processes could result in the calculated Coulombic efficiencies for nitrobenzene removal greater than 100% under a closed circuit condition. However, further investigations are necessary to better understand the nonelectrochemical processes for nitrobenzene removal in BES.

The Coulombic efficiency for acetate oxidation at the anode was generally lower than 40% (Figure 4). Previous studies have indicated considerably higher Coulombic efficiencies at the anodes (*36–38*). In this study, the anodic potentials were in the range of −208 to −338 mV vs SHE at various current densities (Figure 2B), which provided the bacteria growing at the anodic electrode surface with a very limited energy gain and hence may have favored alternative processes. Acetoclastic methanogenesis and bacterial growth

may contribute to the Coulombic efficiency loss (*28*). A detailed investigation of these processes in a very similar anode system has been previously undertaken by Freguia et al. (*39*). This demonstrated that further fine-tuning of the anodic potential and loading will allow minimization of these losses and thus increase the Coulombic efficiency at the anode. In addition, the Coulombic efficiency for acetate oxidation at the anode was increased with an increase in current density, indicating that electrochemically active bacteria were more competitive than other microorganisms at higher current densities.

The reductant usage ratios (RURs) for nitrobenzene removal were calculated at various current densities (Figure 4). Theoretically, only 1.5 COD mol^{-1} acetate is needed for the conversion of one mole of nitrobenzene to aniline. However, the RURs varied from 4.2 ± 0.4 to 8.9 ± 2.2 mol COD mol^{-1} nitrobenzene removal, which is mainly due to the electron inefficiencies of the anode at low current densities and progressively included the inefficiencies of the cathode at high current densities. Therefore, the RUR values could be reduced by improving the anodic and cathodic performances of BESs.

Identification of Reductive Products. Figure S2 of the Supporting Information illustrates the UV−vis spectra of the cathode influent (nitrobenzene) and cathode effluent for a current density of 7.1 A m^{-3} TCC (R 10 Ω) and 44.6 A m^{-3} TCC (controlled current at 15 mA). Also the spectrum of a pure aniline solution is shown in this figure. The characteristic absorbance peak of nitrobenzene at 270 nm decreased and shifted to a longer wavelength, while simultaneously an absorbance peak at 229 nm was formed. This demonstrates the degradation of nitrobenzene and formation of reaction products. The new absorption spectrum has good similarity with the absorption spectra of aniline with the characteristic absorption peaks at 229 and 280 nm, suggesting that aniline may be the dominant product of nitrobenzene reduction at the cathode of BES.

The cathode effluent samples were further investigated using HPLC. Figure S3 of the Supporting Information shows the HPLC chromatogram of the cathode effluent at current densities of 7.1 and 44.6 A m^{-3} TCC, respectively. The main two peaks with retention time of 10.2 and 5.2 min were identified as nitrobenzene and aniline, respectively, further supporting the conclusion that aniline was the dominant product of nitrobenzene reduction at the cathode. However, it is very interesting to note that a peak with retention time of 11.4 min appeared at higher current densities, i.e., 16.5 A m^{-3} TCC. The retention time of this peak is consistent with that of nitrosobenzene, one intermediate of nitrobenzene reduction. A second possible intermediate of nitrobenzene reduction, hydroxylaminobenzene, was reported to be unstable in the water solution (*40*) and is therefore not expected to be present in this solution. Other side products such as azoxybenzene and azobenzene have been reported in previous studies for electrochemical reduction of nitrobenzene. In this study, these side products could be excluded as they have an additional adsorption peak in the visible range of the UV−vis spectra (*41*), which is not present in the spectra of the cathode effluent from this study (Figure S2 of the Supporting Information). Moreover, any oxidative products of nitrobenzene such as the highly toxic picolinic acid would not be expected to form at the cathode of the BES because of the reductive conditions in this chamber. Therefore, the secondary peak appearing at 11.4 min in the HPLC chromatogram is most likely caused by the presence of nitrosobenzene. On the basis of this assumption, the concentration of this compound could be determined and was found to increase from around 0.11 ± 0.01 to 0.48 ± 0.01 mM as nitrosobenzene for increasing current densities from 16.5 to 59.5 A m^{-3} TCC. This again is fully consistent with the

TABLE 2. Comparison of Nitrobenzene Degradation in BES with Anaerobic Biological Methods

	conditions					
reactor	influent concentration of nitrobenzene (mM)	substrate	T (°C)	nitrobenzene removal rate (mol m^{-3} empty bed volume d^{-1})	reductant usage ratio (mol COD mol^{-1} nitrobenzene removal)	reference
BES[a]	1.5	acetate	25	1.29 ± 0.04	5.5 ± 0.5	this study
BES[b]	1.5	acetate	25	8.57 ± 0.05	4.2 ± 0.4	this study
trickling filter	0.73	acetate	25–30	0.044	49.5	12
acidogenic reactor	0.83	sucrose	35 ± 1	1.64	9.0	16
fixed-bed reactor	1.93	mixed substrates[c]	30	1.93	20	15
anaerobic migrating blanket reactor	1.46	glucose	37 ± 1	0.24	58	44

[a] Current density 7.9 A m^{-3} TCC (external resistance 5 Ω). [b] Current density 59.5 A m^{-3} TCC (current controlled at 20 mA and power consumption 0.049 ± 0.002 kWh mol^{-1} nitrobenzene removal). [c] Ethanol:isopropanol:acetone:methanol = 1:1:1:4.

reduced Coulombic efficiency for aniline formation with increasing current density as shown in Figure 4 because some electrons would have flowed to this intermediate product.

Among these products, aniline exhibits the lowest toxicity and highest biodegradability (10). Therefore, the selective reduction of nitrobenzene to aniline using BESs is highly attractive from a toxicity and biodegradability point of view. On the basis of this point, the current densities in the BES should be maintained at a lower level in order to improve cathode performance. One possible strategy is to increase the specific surface area of cathode, such as using brush cathodes (42). However, in practice the BES system might be operated at higher current densities to achieve higher nitrobenzene conversion rates, hence reducing the reactor volume. Therefore, optimization of the conversion rates and final reaction products will be required in practice for the nitrobenzene removal in BES systems. In addition, a second treatment process such as aerobic treatment is necessary to further degrade or mineralize aniline because aniline is also a toxic chemical (43).

Comparison with Anaerobic Biological Methods. Table 2 shows a summary of nitrobenzene removal through various biological methods. Without power input, the cathodic nitrobenzene removal rate of the BES was similar to those of other anaerobic methods (12, 15, 16, 44). However, by supplying a small power input to the BES systems (e.g., through current control), the nitrobenzene removal rate could be substantially enhanced, demonstrating that the nitrobenzene removal at the BES cathode was highly efficient. For practical application purposes, a controlled current density of 59.5 A m^{-3} TCC could be applied as this would increase the nitrobenzene removal rate about 7-fold and decrease the RUR by 20%, while the power input is still low at 0.05 kWh mol^{-1} nitrobenzene removal. For a typical wastewater with 100 mg/L of nitrobenzene, the power required for complete nitrobenzene reduction in a BES would therefore be on the order of 0.04 kWh m^{-3} treated wastewater.

In the anaerobic biological nitrobenzene removal methods, an electron donor (organic cosubstrate) is required to create the necessary reductive conditions. The cosubstrate addition typically far exceeds the stoichiometric requirements as shown by the high RUR values in Table 2. This creates considerable cost and leads to possibly unwanted methane formation (12, 15, 16, 44). The RUR values for the BES are much smaller than those of the anaerobic methods, indicating that very limited organic substrate is required for the bioelectrochemical reduction of nitrobenzene, which would significantly reduce the operational cost. Further research is required to investigate how the decreased operational cost could offset the expected higher capital cost of BESs compared to anaerobic bioreactors.

Supporting Information Available
Applied voltage to BES for energy consumption at various current densities in Figure S1, evolution of UV–vis spectra for nitrobenzene reduction at the cathode of BESs in Figure S2, and HPLC chromatogram of nitrobenzene and its reductive products at the cathode of BES in Figure S3. This material is available free of charge via the Internet at http://pubs.acs.org.

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