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Bio-Electron-Fenton (BEF) process driven by sediment microbial fuel cells (SMFCs) for antibiotics desorption and degradation

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ABSTRACT

A sediment microbial fuel cell electro-Fenton (SMFC-E-Fenton) system was proposed in this study by utilizing the biological electrons produced from an SMFC to power an E-Fenton process. Antibiotics with different absorbability in both aqueous and solid phase can be removed by this system at room temperature and pressure condition, without external power or other chemical reagents. γ-FeOOH graphene polyacrylamide carbonized aerogel (γ-FeOOH GPCA) with high electrochemically active surface area (EASA), good conductivity and stable electrochemical activity were used as the cathode. After 40 h treatment, the total degradation rate of sulfamethoxazole (SMX) and norfloxacin (NOR) were 97.4 ± 2.9% and 96.1 ± 3.0%, respectively. Compared with the sludge digestion system, the residual SMX and NOR in sludge declined from 10.2 ± 1.5% to 1.1 ± 1.2% and from 31.3 ± 1.8% to 3.1 ± 1.3%, respectively. The E-Fenton process can also promote electricity production and sludge reduction efficiency of SMFC, as the maximum power density SMFC-E-Fenton system reached 472.21 ± 11.5 mW m^{-2} and 431.39 ± 15.6 mWm^{-2}, respectively. 6.2 ± 0.3% and 5.7 ± 0.8% of the initial sludge was reduced while treating SMX and NOR.

1. Introduction

Antibiotics are a kind of chemical substance widely used in pharmaceuticals, because of the ability to restrain and/or killing effect toward pathogenic microorganisms such as bacteria (Le-Minh et al., 2010). However, only part of the antibiotics can be metabolized in human and animal bodies, undegraded part thus enters the wastewater treatment plants (WWTPs) through excretion (Lan et al., 2017). Some studies pointed out that most of the antibiotics are highly resistant to traditional wastewater treatment processes (Chun Hua Feng, 2010; Trovo et al., 2009). Hydrophilic antibiotics are expected to mainly remain in the aqueous phase of the treated effluent. Whereas hydrophobic antibiotics are likely to concentrate in sludge by adsorption because of their greater affinity to solid (Bouki et al., 2013). Many researchers have demonstrated the ecological hazards of antibiotics residue in environment (Schoepp et al., 2017). Not only antibiotics themselves could cause chemical pollution, such as toxic effect on non-target organisms, they may also contribute to the prevalence of antibiotic resistant bacteria (ARB) and antibiotic resistant genes (ARGs) in effluents and surface water near WWTPs (Paul Berg et al., 2016; Zhang et al., 2013). Therefore, addition of antibiotics treatment units in WWTPs is imperatively (Rosendahl et al., 2011).

In recent years, electro-Fenton (E-Fenton) as an advanced oxidation process (AOP) has been widely studied in treating biorefractory antibiotic pollutants in wastewaters (Barhoumi et al. 2016, 2017). Furthermore, some researches pointed out that microbial fuel cells (MFCs) can be used to power E-Fenton process as bio-E-Fenton systems (Liu et al., 2015; Yong et al., 2017; Zhu and Logan, 2013). Electrons are generated via the catalyzation of electrogenic microorganisms in anaerobic anode and transferred to its aerated cathode to generate H_2O_2 and Fe^{2+}. However, most studies focused on the treatment of wastewater by bio-E-Fenton system. The excess sludge in WWTPs was usually neglected although they have a larger amount of pollutants and bioenergy than wastewater (Wang et al., 2018). Sludge microbial fuel cells (SMFCs) are a kind of single chamber MFCs. Energy extraction and excess sludge reduction can be accomplished simultaneously in SMFCs.

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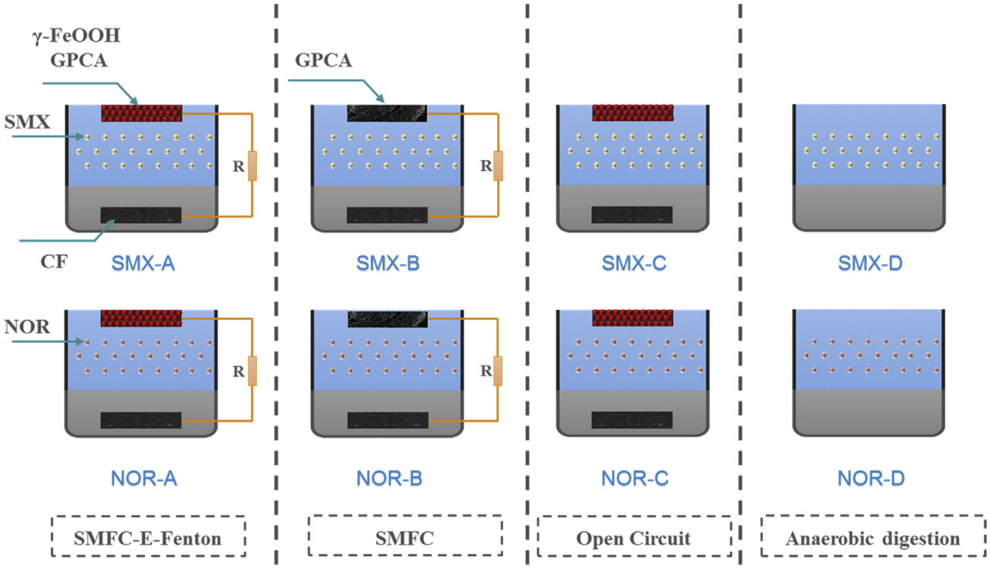

Fig. 1. Configuration of reactors.

The electrons are extracted by anodes embedded in the sediment by consuming the organics in sludge and transported to the cathode through an external load circuit to participate in the reduction of oxygen.

In this study, SMFCs were used to power E-Fenton process as an SMFC-E-Fenton system for the first time to degrade antibiotic pollutants in wastewater and sludge at the same time. In this system, partial antibiotics in sludge could be used by electrogenic microorganisms, as some researchers have proved that several kinds of antibiotics can be used as electron donor at the anode of MFC. Meanwhile, the portion of the unbiodegradable antibiotics will be desorbed along with the consumption of sludge. They can then mix with the antibiotics existed in supernatant originally, and degraded by the E-Fenton generated ·OH at cathode.

Sulfamethoxazole (SMX) and norfloxacin (NOR) with different sludge sorption constants (K_d, L kg^{-1}) were chosen as the target pollutants (Zhang et al., 2013). Their structures, chemical formulas, molecular weights ($M_{w,}$ g/mol) and K_d values were listed in Fig. S2. SMX is among the most frequently detected sulfonamides in WWTPs. Many researchers have demonstrated that SMX was only partially removed by conventional WWTPs because of its moderate sorption to sludge and limited biodegradability (Yang et al., 2012b). Meanwhile, NOR is a kind of fluoroquinolones that effect against several types of Gram-negative and Gram-positive bacteria (Hamnca et al., 2017). Although the removal efficiency of NOR has been reported relatively high (up to 90%), the predominant removal mechanism has been suggested by several authors to be adsorption to sludge. Lindberg et al. reported that more than 70% of NOR passed through the treatment plant and remained in digested sludge and/or flocs rather than biodegradation.

γ-FeOOH graphene polyacrylamide carbonized aerogel (γ-FeOOH GPCA) was used as air-cathode in electro-Fenton process. It has been investigated in our previous study and demonstrated great potential for the E-Fenton process to remove organic pollutants in water at neutral pH, owing to their advantages of high electrochemically active surface area (EASA), good conductivity and stable electrochemical activity (Wang et al., 2019).

The aim of this study is to demonstrate the feasibility of using SMFC-E-Fenton system with γ-FeOOH GPCA as air-cathode to degrade SMX and NOR at neutral pH. This study provides a high efficiency method for excess sludge reduction, electricity generation and treatment of antibiotics with different absorbability in room temperature and pressure conditions, without external energy or chemical reagents added. It should be very attractive and also challenging to develop an energy-saving E-Fenton system that can remove refractory pollutants in two phases (water and sludge) effectively.

2. Methods and materials

2.1. Chemicals and reagents

Analytical grade Sulfamethoxazole ($C_{10}H_{11}N_3O_3S$, CAS: 723-46-6) and Norfloxacin ($C_{16}H_{18}FN_3O_3$, CAS: 70458-96-7) with purity > 99% was purchased from Aladdin and used as received. p-Benzoquinone ($C_6H_4O_2$, ≥99.50%, CAS:106-51-4), p-hydroxybenzoic acid ($C_7H_6O_3$, ≥99.50%, CAS:99-96-7), oxalic acid ($C_2H_2O_4$, 99.999%, CAS:114-62-7) and methanol (CH_4O, 99.9%, CAS:67-56-1) were purchased from Aladdin. Anhydrous sodium sulfate (Na_2SO_4, ≥99.0%, CAS:7757-82-6) was used as background electrolyte. All solutions were prepared in ultra-pure water and all the other chemicals used for analysis were either of HPLC or analytical grade from Aladdin and Sigma Aldrich.

2.2. Reactors configuration and operation conditions

Reactions were carried out in 8 undivided cylindrical open reactors each containing 150 ml anaerobic sludge and 350 ml electrolyte. The anaerobic sludge inoculated was collected from the secondary sedimentation basin of Lingshui River Wastewater Treatment Plant (Dalian, China). A screen mesh with a pore diameter of 2 mm was used to filtrate the sludge and mixed liquid to remove the impurities. Then sludge was poured into each reactor equally after being mixed evenly. The average sludge concentration of anaerobic sludge was $(2.47 \pm 0.12) \times 10^{-3}$ kg L^{-1}. The total sludge quality in each reactor was $(0.37 \pm 0.06) \times 10^{-3}$ kg. Electrolytes were performed using 0.1 mM SMX or NOR solutions in 0.15 M Na_2SO_4, at natural pH and room temperature.

The configurations of 8 reactors were shown in Fig. 1. SMX-A and NOR-A are SMFC-E-Fenton systems. The anodes (carbon felt pieces with the size of 40 mm × 20 mm × 5 mm) were fixed at the bottom while the γ-FeOOH GPCA cathodes (40 mm × 20 mm × 5 mm) were floated with upper surfaces above the water at the top of reactors. The γ-FeOOH GPCA cathodes were fabricated by the *in-situ* method mentioned in our previous study, details were listed in Supplementary Information (Stankovich et al., 2007; Wang et al. 2014, 2019). The anode and cathode electrodes were connected using copper wires (the part in contact with water was replaced by titanium wires) through an external resistance (R_{ext}) of 1 kΩ. The SMX-B and NOR-B are control groups that have the same structures with SMX-A and NOR-A except the cathodes without γ-FeOOH catalyst. These two reactors were designed to analysis the degradation efficiency of SMFCs. SMX-C and NOR-C are control groups have same anodes and cathodes with SMX-A and NOR-A but conducted under an open-circuit condition to avoid any electrochemical reactions. They were used to analysis the absorption of electrodes. SMX-D and NOR-D are control groups with no electrodes but sludge and electrolyte to investigated sorption and biodegradation processes of SMX and NOR in contact with sludge.

2.3. Analytical methods

Solution pH was measured with a pH-meter (Sartorius). Total solids (TS) of mixed liquid in reactors were measured based on standard methods (GB/T 11914-1989).

Liquid chromatography tandem mass spectrometry (LC/MS/MS) was used for the analysis of antibiotics and their intermediate products. For aqueous content analysis, a slurry sample of about 0.5 mL was taken from the removed batch and filtered through a 0.22-mm polyvinylidene difluoride (PVDF) filter/syringe (Millipore, Billerica, CA, USA) and stored at −20 °C until analysis by LC/MS/MS. For sludge analysis, the entire suspension was centrifuged to collect the solids. The solids portion was freeze-dried and sieved (< 0.5 mm) to obtain a homogeneous specimen. It was extracted by solvents four times each for 5 min. The first and second times with 10 mL and 5 mL of methanol, respectively, and the third and fourth times with 15 mL of acetone each. The ultrasonicated slurry was centrifuged at 3000 rpm for 10 min; the supernatant was removed and then evaporated using a nitrogen stream under the fume hood. The concentrated extract was diluted with Milli-Q water for solid phase extraction (SPE) before LC/MS/MS analysis. The voltage of SMFCs were monitored every minute using a data acquisition system (PISO–813, ICP–DAS). The polarization curves of the SMFCs were obtained by varying the external resistance (R_{ext}) from 5000 to 10 Ω. The maximum power density (P_{max}) was determined from the polarization curves. To evaluate the catalytic activity of the cathode toward oxygen reduction, linear sweep voltammetry (LSV) measurements were performed in 100 mM PBS at pH 7.0 using by an electrochemical workstation (Chenhua, Shanghai, China).

The concentration of H_2O_2 was determined spectrophotometrically using the iodide method at 351 nm. The concentration of Fe^{2+} was measured based on the light absorption of its complex after reaction with 1, 10-phenanthroline at 508 nm. It should be noted that H_2O_2 and Fe^{2+} concentrations were detected when antibiotics were absent in the cells.

3. Results and discussion

3.1. Sorption and biodegradation of SMX and NOR in contact with sludge

The control groups of SMX-D and NOR-D in this study are imitations of traditional digested sludge process. Measured mass changes of SMX and NOR in the aqueous phase, solid phase and sum of both phases over time were shown in Fig. 2.

It can be seen that the sorption rate and quantity of SMX were much slower and smaller than NOR. Within the first hour, aqueous concentrations of SMX dropped rapidly with the mass percent of 95.6 ± 2.1%, while the mass percent of the antibiotics in the solid phase increased to 4.1 ± 1.2%. Then the mass percent of SMX in aqueous decreased gradually to 83.3 ± 0.7% at the 24th hour, while part of SMX partitioned onto the solid phase and peaked with a mass percent of 15.7 ± 0.8%. After that, the content in aqueous tended to be stable while the SMX in solid phase began to reduce, and reached 81.4 ± 1.2% and 10.2 ± 1.5% at the 40th h, respectively. The total mass percent of SMX in the system began to show a more rapid decrease after the 24th hour and reached 91.6 ± 2.7% at the 40th hour. It may due to the enrichment and adaptation of microbial in sludge, biodegradation began to take place after a lag period (Baumgarten et al., 2011).

As to the variation of NOR, aqueous concentration of NOR dropped rapidly with the mass percent of 93.7 ± 2.5%, while the antibiotics in solid phase increased to 5.8 ± 1.5% at the end of the first hour. During the next 15 h, the concentration of NOR in aqueous phase continued to decrease while the concentration in sludge. Increased gradually and reached 33.6 ± 3.1% at the 16th hour, demonstrate that the sorption rate of NOR was higher than the sum of desorption and biodegradation rate in the meantime. After the 16th hour, both the decrease rate of NOR concentration in aqueous and the increase rate in sludge slowed down indicating a dynamic balance was built between two phases and the available sites for antibiotics absorbed in the sludge was almost saturated. The total mass percent of NOR in the system was 93.1 ± 3.5% at the 40th hour. The results above show that the biodegradation ability of anaerobic sludge towards NOR was similar with SMX, although NOR was more likely to be absorbed in sludge phase.

The mechanism of sorption and biodegradation in SMX-D and NOR-D can be modeled mathematically (Göbel et al., 2005; Yang et al., 2012b). The aqueous phase concentration variation of antibiotic (SMX or NOR) due to sorption to and desorption from sludge can be modeled as Eq (1):

$$\frac{dC_A}{dt} = -k_1 C_A C_{SA} + k_{-1} C_{SS} \tag{1}$$

The mass balance of antibiotic (SMX or NOR) exist in sludge, due to sorption, desorption, and biodegradation on the sludge is expressed by Eq (2):

$$\frac{dC_{SS}}{dt} = k_1 C_A C_{SA} - k_{-1} C_{SS} - k_2 C_{SS} \tag{2}$$

At the same time, the Eq (3) and Eq (4) below are also established:

$$C_{ST} = C_{SA} + C_{SS} \tag{3}$$

$$C_{SS} = 0 \ \ at \ \ t = 0 \tag{4}$$

where, C_A is the concentration of antibiotic in aqueous phase (mM); C_{ST} is the maximum concentration of antibiotics can be adsorbed in the sludge (determine by the amount and available site for antibiotics in the sludge, mM); C_{SS} is the concentration of antibiotics in sludge (mM); C_{SA} is the concentration of available sites that accommodate antibiotics in sludge (mM); k_1 is the second-order sorption rate constant (mM h^{-1}); k_{-1} is the first-order desorption rate constant (h^{-1}); k_2 is the first-order rate constant of biodegradation (h^{-1}).

As shown in Fig. 2, the adsorptive equilibriums can be established after several hours. It took 24 h and 16 h for SMX and NOR to reach the equilibrium. After that, the change rate of both antibiotics tended to be slow, thus we can assume a dynamic balance was built between two phases. Therefore, we suppose a constant antibiotic concentration (SMX or NOR) in the sludge, namely $\frac{dC_{SS}}{dt} = 0$, and the Eq (5) can be derived from Eq (2):

$$C_{SS} = \frac{k_1 C_A C_{ST}}{(k_{-1} + k_2) + k_1 C_A} \tag{5}$$

Eq (5) can be substituted into Eq (1) and Eq (6) refers to the concentration variation rate of antibiotic (SMX or NOR) in aqueous can be obtained:

$$\frac{dC_A}{dt} = \frac{-k_1 k_2 C_A C_{ST}}{(k_{-1} + k_2) + k_1 C_A} \tag{6}$$

We can get three limiting cases from Eq (6) above:

a. When sorption of antibiotic from aqueous to solid phase is the dominant process, that is $k_1 C_A >> k_{-1} + k_2$, resulting in a pseudo-zeroth-order rate equation:

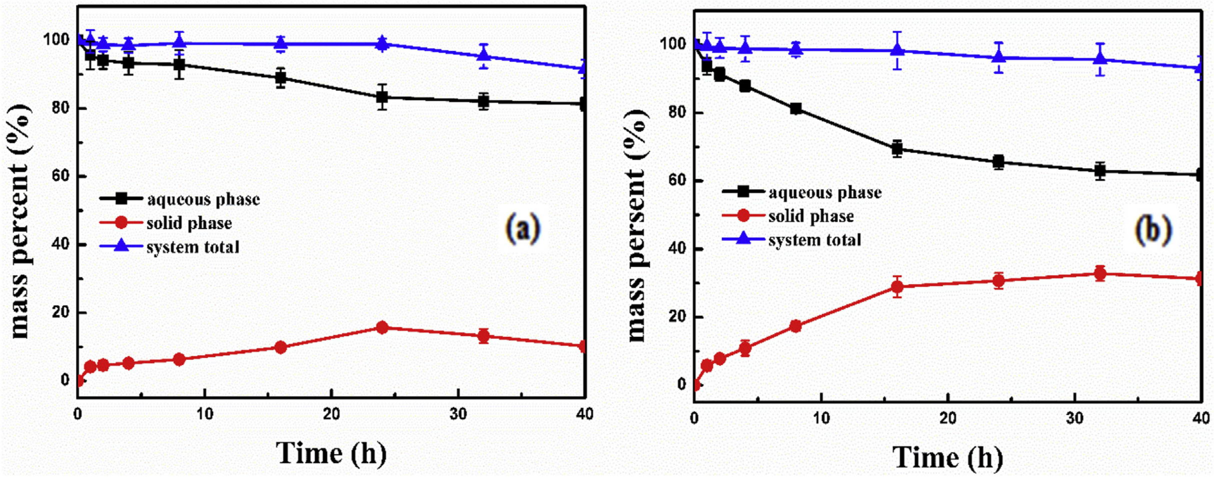

Fig. 2. Measured mass changes of SMX (a) and NOR (b) of sorption or biodegradation. Mass percent shows the remaining antibiotic concentration in the aqueous/solid phase and the system relative to the added amount.

$$\frac{dC_A}{dt} = -k_2C_{ST} = k_{S0} \tag{7}$$

b. When biodegradation and/or desorption of antibiotic in sludge catch up with the sorption efficiency, that is $k_1C_A= k_{-1}+k_2$, also resulting in a pseudo-zeroth-order rate equation:

$$\frac{dC_A}{dt} = -\frac{1}{2}k_2C_{ST} = \frac{1}{2}k_{S0} \tag{8}$$

c. When biodegradation and/or desorption of antibiotic in sludge is the main process, that is $k_1C_A < < k_{-1}+k_2$, resulting in a pseudo-first-order rate equation:

$$\frac{dC_A}{dt} = \frac{-k_1k_2C_AC_{ST}}{(k_{-1} + k_2)} = -k_{S1}C_A \tag{9}$$

Where k_{S0} (mM h^{-1}) and k_{S1} (h^{-1}) are pseudo-zeroth-order and pseudo-first-order rate constants, respectively. The aqueous concentration values of SMX and NOR over 40 h by contact with sludge was fitted to both the pseudo-zeroth and pseudo-first order equations. The concentration variation rate of SMX conformed to the to the pseudo-zeroth-order ($R^2 = 0.9669$) better than pseudo-first-order kinetic ($R^2 = 0.9328$) from the 1st h to 24th h. After that, pseudo-zeroth-order was also more suitable with the R^2 of 0.9783 (the R^2 of pseudo-first-order was 0.9274), however, the slope of this period reduced to almost half of what it was before 24th h. These results indicate that the biodegradation and/or desorption rate began to catch up with the rate of sorption after 24 h reaction. As to NOR, although both of the period from 1st h to 16th h and the period from 16th h to 40th h still conformed to the pseudo-zeroth-order with $R^2 = 0.9765$ and $R^2 = 0.9313$, respectively, the slopes of both periods were similar. These results showed that the sorption rate was always much higher than the desorption and biodegradation rate. It worth noting that neither SMX or NOR was in accord with the pseudo-first-order, indicating the desorption and biodegradation was not the main process in the during the whole reaction process. We can speculate from the results that although the total degradation efficiency of SMX and NOR were low and similar to each other in aerobic sludge treatment process, the limiting factors were different. For SMX, the low K_d value makes it difficult to fully contact with sludge to be degraded, whereas the easily absorbed NOR cannot be well used by microorganisms because of its strong structure. This is because of the different molecular structures of SMX and NOR (Fig. S2). The S-N bond on the SMX was easy to be cleaved by microbial and oxidant (Dirany et al., 2010; Michael C. Dodd, 2004). However, the piperazine ring in NOR make it comparatively stable, substitution of fluoride with hydroxyl and hydroxylation usually need to be taken place first, then the oxidative ring opening reaction could occur(Özcan et al., 2016; Yang et al., 2012a).

3.2. Degradation efficiency of SMX and NOR in SMFC-E-Fenton system

Fig. 3 shows the degradation efficiency and distribution of SMX in SMX-A, SMX-B, SMX-C and SMX-D system at neutral pH against time. In Fig. 3a, the variation tendency of SMX in SMX-C was similar to SMX-D system in both aqueous and solid phases. Therefore, the sorption of SMX on the cathode and anode material was insignificant compared with sludge sorption, degradation or other reaction.

SMX-B system was a typical SMFC system with GPCA as air-cathode. It can be seen that 17.5 ± 2.2% of initial SMX was degraded by this SMFC system, which was larger than that of SMX-D system (8.4 ± 2.7%). At the same time, 5.4 ± 0.5% initial sludge was reduced by SMX-B system, while only 0.8 ± 0.3% sludge was reduced in SMX-D (Table S1). In addition, the mass present of SMX in solid phase was lower than SMX-D system, whereas the content in aqueous was not increased. Wang et al. reported that SMX can be degraded in MFC system by electrogenic microorganism as an electron donor. Zhang et al. also acquired a removal of SMX by using MFC coupled constructed wetlands. In this study, the portion of SMX absorbed in sludge of SMX-B system was degraded by microbes near anode of SMFC, resulting in some adsorption vacancies in sludge. These vacancies were continuously replenished by SMX in aqueous, resulting in the reduction of SMX in both aqueous and solid phase.

As shown in Fig. 3b, approximately 100% of the initial SMX was degraded by SMX-A system within 40 h, demonstrated the high degradation efficiency of SMFC-E-Fenton towards SMX. Meanwhile, the sludge reduction efficiency of SMX-A system reached 6.2 ± 0.3%. It worth noting that not only the SMX in aqueous phase, but also the SMX in solid phase of SMX-A system was lower than other systems with the function of E-Fenton reaction. On one hand, the E-Fenton reaction at cathode could accelerate the consumption of H^+ because of the generation of OH^-, thus will enhance the proton transfer and the degradation efficiency of SMX by electrogenic microorganism at anode. What's more, the desorption of SMX was enhanced by faster sludge digestion, resulting in a lower SMX content in the solid phase of SMX-A. Because of the Fenton reaction, the SMX released from sludge were degraded by ·OH in short order together with the SMX exist previously.

As showed in Fig. 4, total degradation efficiency of NOR-B was 9.5 ± 3.3%, which was only 2.6% larger than NOR-D system (6.9 ± 3.5%). However, the sludge reduction efficiency of NOR-B (3.8 ± 0.3%) was much higher than NOR-D system (0.5 ± 0.3%).

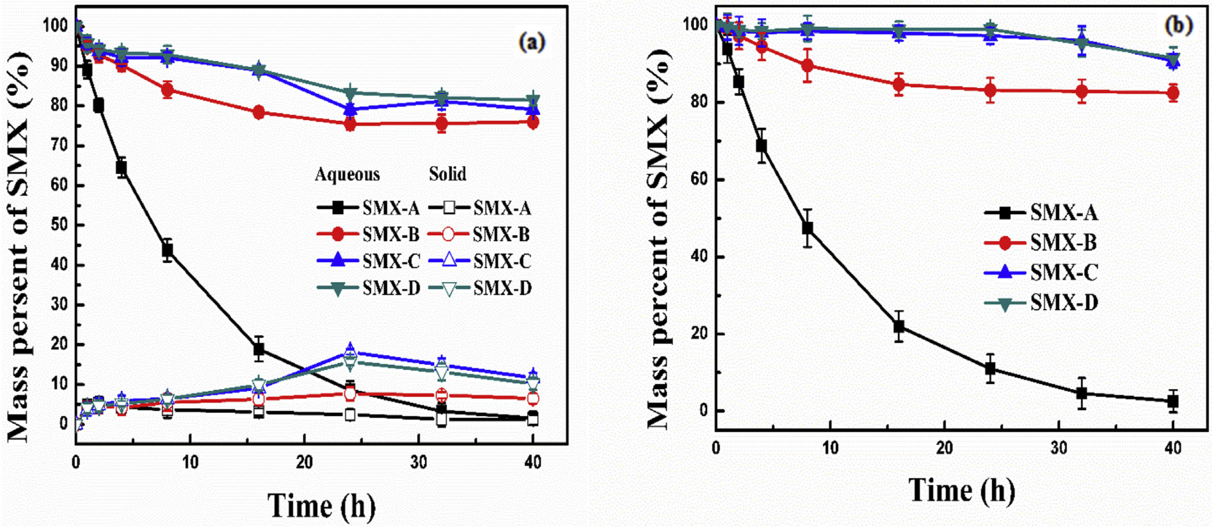

Fig. 3. Mass percent of SMX in aqueous phase, solid phase (a) and the sum of both phases (b) in SMX-A, SMX-B, SMX-C and SMX-D system. Mass percent shows the remaining antibiotic concentration in the aqueous/solid phase and both relative to the added amount.

This means that it is more difficult for SMFC system to degrade NOR than SMX, because of the more stable molecular structures of NOR discussed above (Fig. S2). The electrogenic microorganism in NOR-B system mainly uses organic in sludge as electron donor. The mass percent of NOR in solid phase of NOR-B was much lower than that of NOR-D system, demonstrated that part of NOR absorbed in sludge was released into aqueous phase along with the consumption of sludge by SMFC anode. As the NOR were not easy to be biodegraded in sludge, vacancies could hardly occur, NOR in aqueous cannot be adsorbed into sludge, thus resulting in the increase of NOR concentration in aqueous phase.

Nevertheless, approximately 100% of the initial NOR was degraded by the NOR-A system within 40 h. NOR was desorbed from sludge along with the anode reaction of SMFC, and the rapid decreasing of NOR in aqueous could also enhance the desorption of NOR. The NOR released from solid degraded by ·OH in aqueous phase together with NOR existed in water. These results demonstrated the strong degradation ability of SMFC-E-Fenton system toward the antibiotics regardless of their absorbability.

3.3. The electrochemical performance of SMFC-E-Fenton system

The effect of Fenton reaction and antibiotics on the power output of SMFCs were investigated. Fig. 5a shows the power density curves of SMX-A, SMX-B, NOR-A and NOR-B. The maximum power density of SMFC-E-Fenton systems (SMX-A and NOR-A) were higher than the SMFC systems (SMX-B and NOR-B), indicating the Fenton reaction was beneficial to the power generation of SMFCs, as the rapid consumption of electrons and H^+ anode at cathode would facilitate the proton and electron transfer of SMFC (Zhuang et al., 2010). The maximum power densities of SMX-A and SMX-B system were 472.21 ± 11.5 $\mathrm{mW\,m^{-2}}$ and 368.52 ± 8.9 $\mathrm{mW\,m^{-2}}$, respectively, which were higher than that of NOR, calculated as 431.39 ± 15.6 $\mathrm{mW\,m^{-2}}$ and 344.75 ± 10.5 $\mathrm{mW\,m^{-2}}$, respectively. These results demonstrated that SMX were more likely to be degraded by electrogenic microorganism reactions than NOR. Evidence from the cathode and anode polarization curves (Fig. 5b) also proved that E-Fenton process could facilitate the power generation of SMFC in terms of the higher open circuit potential (OCP) of SMX-A and NOR-A.

In order to further to prove that the Fenton reaction occurred at the cathode, electrochemical experiments of linear sweep voltammograms (LSV) of oxygen reduction were performed using the GPCA cathode with or without γ-FeOOH catalyst as the working electrodes. The results (Fig. S3) showed that the voltammetric curve of γ-FeOOH GPCA cathode exhibits two reduction peaks, while the one without catalyst only showed one peak. The first reduction peak of γ-FeOOH GPCA

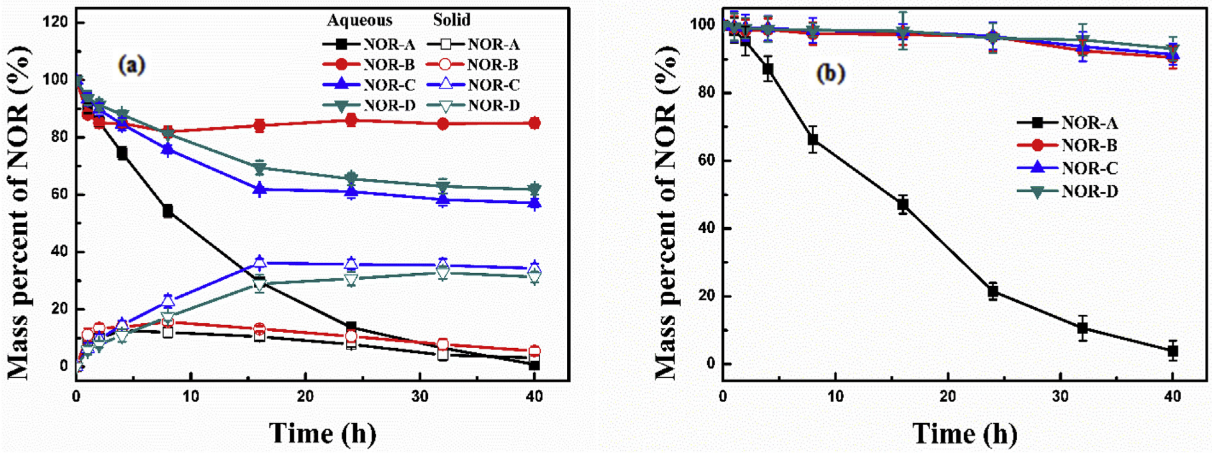

Fig. 4. Mass percent of NOR in aqueous phase, solid phase (a) and the sum of both phases (b) in NOR-A, NOR-B, NOR-C and NOR-D system. Mass percent shows the remaining antibiotic concentration in the aqueous/solid phase and both relative to the added amount.

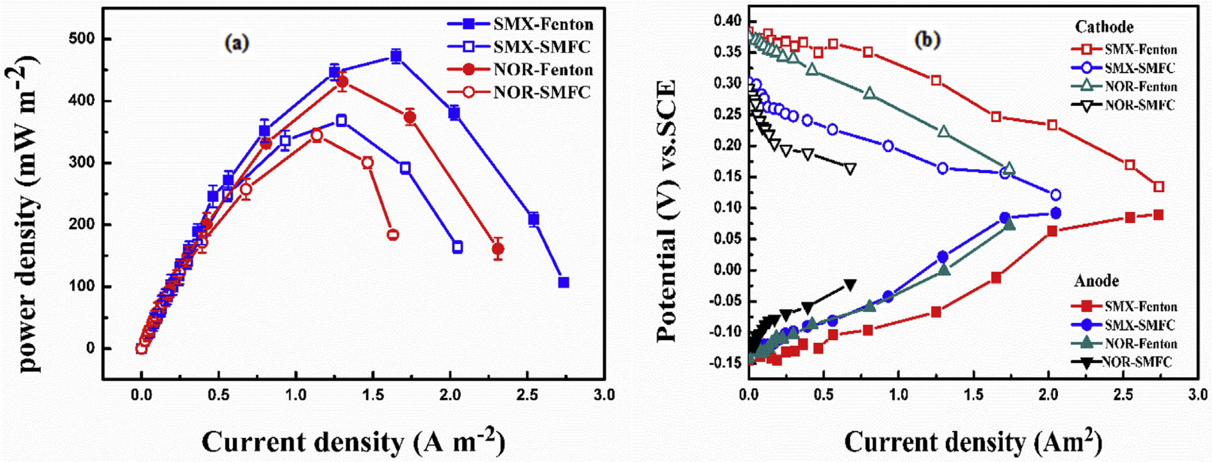

Fig. 5. Power density curves (a) and the anode and cathode polarization curves of different SMFCs (b).

cathode appears at less negative potential refers to the two-electron reduction of O_2 to generate H_2O_2, and the second reduction peak appears at more negative potential, as well as the reduction peak appears on the curve of GPCA without catalyst refers to further two-electron reduction from H_2O_2 to water and the four-electron reduction from O_2 to water.

3.4. Antibiotics degradation mechanism and the mass balance in SMFC-E-Fenton systems

According to the analysis above, the mass balance, as well as the mechanism of transformation and degradation of antibiotics in SMFC-E-Fenton systems (SMX-A and NOR-A) were proposed (Fig. 6). The intermediate products of SMX and NOR during the degradation processes were identified with an HPLC-MS/MS and plausible degradation pathways were given in supplementary information. Four kinds of chemical reactions and two physical processes were involved in the process for antibiotic transfer and consumption, that were bioelectrochemical reactions, biochemical reactions, electrochemical reactions, chemical reactions, adsorption process and desorption process.

For the bioelectrochemical reactions taken place in the sludge (near anode), SMX or NOR was degraded by electrogenic microorganism existed in sludge to produce electrons. As no artificial mediators were added, electrons were more likely transported from cells to anode during a direct transfer pathway and then transfer to the cathode through external circuit to participate in the electrochemical reactions near or inside cathode. These reactions include the reduction of dissolved oxygen to H_2O_2 or H_2O and the reduction of γ-FeOOH to Fe^{2+} adsorbed on cathode, denoted as $Fe_{ads}{}^{2+}$. The first two types of electrochemical reactions were demonstrated by the detectable amounts of H_2O_2 and Fe^{2+} (Fig. S4). At the initial period, the amounts of H_2O_2 and Fe^{2+} were reasonably low, because of the adaptation stage of the microorganism in SMFC. Then a fast-increased period was observed as these two kinds of Fenton reagents progressively produced by electrochemical reactions. At last, a stable period was achieved as the generation rate and consumption rate of H_2O_2 and Fe^{2+} reached a balance. Feng et al. obtained the same tendency of Fenton's reagents while degrading Orange II using their dual-chamber MFC system (CHUN HUA FENG, 2010). The biochemical reactions, as well as the adsorption and desorption process, can be evidenced from the SMX-C, SMX-D, NOR-C

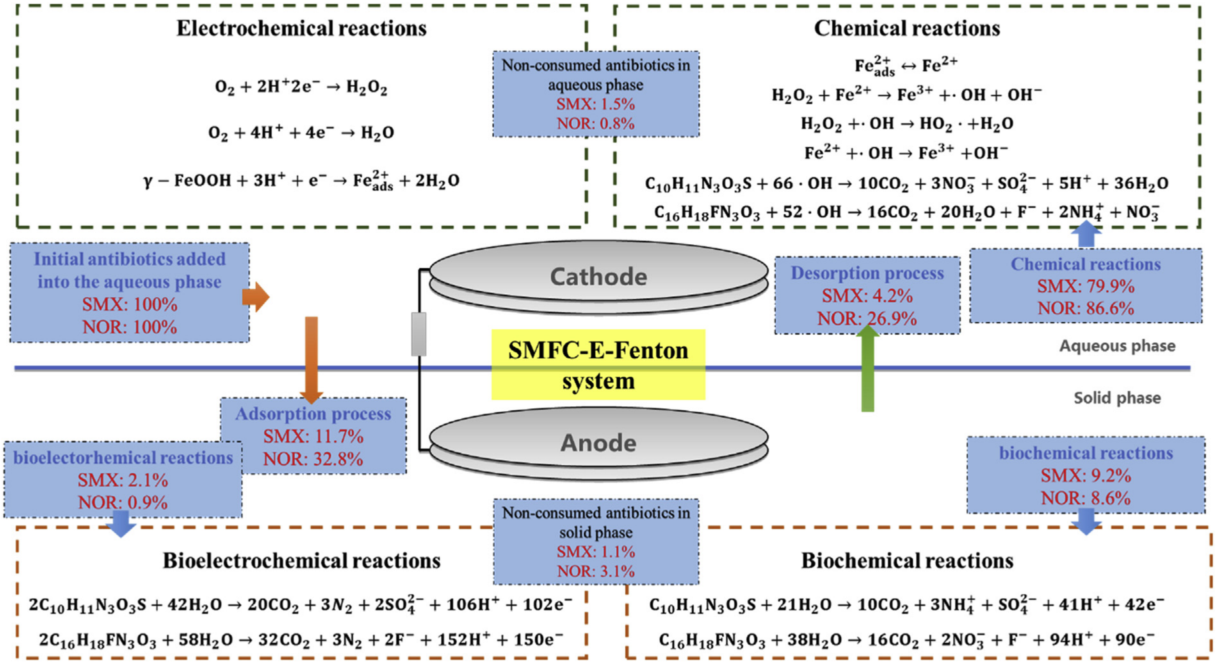

Fig. 6. The mass balance and the transformation mechanism of SMX and NOR in SMFC-E-Fenton system.

and NOR-D that the antibiotics were anaerobic digested, adsorbed and desorbed by sludge (details were discussed in section 3.1). The chemical reactions occurred near/inside cathode mainly referred to the Fenton reactions and the reactions between hydroxyl radicals and target antibiotics (SMX or NOR). In addition, ·OH may also react with excess H_2O_2 and Fe^{2+} produced which may cut down the degradation rate of antibiotics.

Based on the data above, the mass balance of SMX and NOR in SMFC-E-Fenton system was proposed, as shown in Fig. 6. The initial dosage added to the aqueous phase of SMX and NOR were both 0.1 mmol, defined as 100% mass percent. With the data of SMX-D and NOR-D, the sorption and biochemical consumption (anaerobic digestion) of antibiotics can be achieved. 11.7% and 32.8% of SMX and NOR were absorbed by sludge, respectively, which indicated that the NOR was more hydrophobic with greater absorbability. Although lager mass percent of NOR was absorbed into sludge, the consumption amounts by biochemical reactions of it were 8.6%, still lower than SMX (9.2%), which was moderately absorbed by sludge, indicating the bio-refractory character of NOR. By comparing the SMX-A (NOR-A) with SMX-B (NOR-B) system, the effect of SMFC process can be known. The degradation of SMX and NOR by anode reactions, namely bioelectrochemical reactions were very weak, as the total degradation rate of anode reaction toward SMX and NOR were 2.1% and 0.9%, respectively. However, the primary function of SMFC process here was desorbing the antibiotics. The percent of SMX and NOR desorbed to aqueous during the SMFC reaction was 4.2% and 26.9%, respectively, which means most of the antibiotics absorbed in sludge were released to water along with the consumption of organics by SMFC anode reaction. Thanks to the desorption of antibiotics by SMFC process, most of the antibiotics had the chance to contact with strong oxidizing ·OH produced by GPCA cathode with γ-FeOOH catalyst. Therefore, 79.9% of SMX and 86.6% NOR were degraded by the ·OH, respectively.

In conclusion, the reactions occurred in SMFC-E-Fenton system were quite complicated, and all the reactions and processed made a contribution to the final degradation of the target antibiotics. Regardless of the absorbability, antibiotics can be efficiently removed by the SMFC-E-Fenton system.

4. Conclusion

In this study, SMFC-E-Fenton system was constructed to conduct Fenton reaction without external energy. The electrons extracted from organics were received by the anode in the sedimentary sludge and transferred to the cathode to drove Fenton reaction at room temperature and normal pressure. SMFC-E-Fenton systems can effectively degrade SMX and NOR in both aqueous and solid phase. After 40h treatment, the total degradation rates of SMX and NOR were 97.4% and 96.1%, respectively, 79.9% and 86.6% higher than that of SMFC system, and 89.0% and 89.2% higher than that of anaerobic digestion system. In addition, the Fenton reactions take place at cathode would enhance the SMFC electricity performance as the SMFC-E-Fenton systems exhibited higher power output and sludge reduction. Future studies will attempt to construct SMFC-E-Fenton in secondary sedimentation tanks of sewage treatment plants or at marine cultures. Organics in excess sludge or sediment can be used to drive E-Fenton reaction, simultaneously remove antibiotics in aqueous and solid phase, so as to reduce the ecological harm of antibiotics.

CRediT authorship contribution statement

Yuezhu Wang: Formal analysis, Writing - original draft. **Hanmin Zhang:** Conceptualization. **Yujie Feng:** Supervision. **Baikun Li:** Supervision. **Mingchuan Yu:** Formal analysis. **Xiaotong Xu:** Formal analysis. **Lu Cai:** Formal analysis.

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Appendix A. Supplementary data

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