Applying a new pomelo peel derived biochar in microbial fell cell for enhancing sulfonamide antibiotics removal in swine wastewater

Dongle Cheng[a], Huu Hao Ngo[a,b*], Wenshan Guo[a], Soon Woong Chang[c], Dinh Duc Nguyen[c,d], Jianxin Li[e], Quang Viet Ly[e], Thi An Hang Nguyen[f], Van Son Tran[g]

[a]*Centre for Technology in Water and Wastewater, School of Civil and Environmental Engineering, University of Technology Sydney, Sydney, NWS 2007, Australia*
[b]*NTT Institute of Hi-Technology, Nguyen Tat Thanh University, Ho Chi Minh City, Viet Nam*
[c]*Department of Environmental Energy Engineering, Kyonggi University, 442-760, Republic of Korea*
[d]*Institution of Research and Development, Duy Tan University, Da Nang, Vietnam*
[e]*State Key Laboratory of Separation Membrane and Membrane Processes, National Center for International Joint Research on Membrane Science and Technology, School of Materials Science and Engineering, Tiangong University, Tianjin 300387, PR China*
[f]*Vietnam Japan University (VNU-VJU), Vietnam National University, Hanoi, Luu Huu Phuoc St., Nam Tu Liem Dist., Hanoi 101000, Vietnam*
[g]*Faculty of Environmental Sciences, VNU University of Science, Vietnam National University, Hanoi, Vietnam*

* Corresponding author: *E–mail address:ngohuuhao121@gmail.com*

Abstract

A sequential anode-cathode double-chamber microbial fuel cell (MFC) is a promising system for simultaneously removing contaminants, recovering nutrients and producing energy from swine wastewater. To improve sulfonamide antibiotics (SMs)'s removal in the continuous operating of MFC, one new pomelo peel-derived biochar was applied in the anode chamber in this study. Results demonstrated that SMs can be absorbed onto the heterogeneous surfaces of biochar through pore-filling and π-π EDA interaction. Adding biochar to a certain concentration (500 mg/L) could enhance the efficiency in removing sulfamethoxazole, sulfadiazine and sulfamethazine to 82.44 - 88.15%, 53.40 - 77.53% and 61.12 - 80.68%, respectively. Moreover, electricity production, COD and nutrients removal were improved by increasing the concentration of biochar. Hence, it is proved that adding biochar in MFC could effectively improve the performance of MFC in treating swine wastewater containing SMs.

Keywords: Sulfonamide antibiotics, swine wastewater, microbial fuel cell, biochar, adsorption

1. Introduction

As one of the common classes of veterinary medicine, sulfonamide antibiotics (SMs) are widely utilized in the swine industry to prevent diseases and promote the growth of pigs (Pan et al., 2011). However, high levels of SMs were excreted by pigs in unchanged form and/or their metabolites through their faeces and urine (Pan et al., 2011). It is no doubt that swine wastewater now constitutes an important source of antibiotics in the environment. In addition, high levels of antibiotics have been detected in the aquatic and terrestrial environments near the swine farms. Occurrence and accumulation of antibiotics in the environment can cause the generation of antibiotic-resistant bacteria and antibiotic-resistant genes, which could seriously endanger the health of people and the eco-environment (Michael et al., 2013). Thus, it is urgent to develop appropriate methods to eliminate antibiotics from swine wastewater.

A series of methods including biological treatment, chlorination, ozonation, membrane filtration and adsorption have been investigated for removing SMs from swine wastewater (Derakhshan et al., 2016). For practical applications, biological treatment is a preferred technology due to its advantages of being environmentally friendly and cost effective (Grandclément et al., 2017). In recent years, microbial fuel cell (MFC) technology has become a research favorite due to its wastewater treatment ability and simultaneous bioelectricity production. Organic pollutants in wastewater can be converted into electricity by utilizing microorganisms as biocatalysts (Logan et al., 2006). Higher removal efficiency of SMs in closed circuit MFC system than in its corresponding open circuit system has been reported recently (Hu et al., 2020). Although high removal efficiencies of SMs could be achieved in batch running mode of the MFC, their removal in the continuous flow operation of the MFC was limited. According to our pre-experiment, the sequential anode-cathode double-chamber MFC could enhance the removal efficiency of SMs by further aerobic degradation in the cathode chamber. In contrast, the average removal efficiencies for sulfamethoxazole (SMX), sulfadiazine (SDZ) and sulfamethazine (SMZ) during the running period were only 53.95 %, 15.23% and 18.34%, respectively. The predicated reason for the low removal efficiencies of SMs in the continuous flow MFC system was mainly attributed to: firstly, the inhibition of SMs to the specific SMs degrading microorganisms in both the anode and cathode chambers; and secondly, the retransformation of their degradation products to the parent substance (Tran et al., 2016). For the practical application of the MFC in swine wastewater treatment, it is critical to reduce the antibiotics' effect on the performance of the MFC and enhance the removal efficiency of SMs in the MFC system's continuous flow.

Biochar is a microporous and low-cost carbon material, which can be used as adsorbents for removing antibiotics from wastewater. Additionally, biochar could be used as biocarrier to support the growth of microorganisms in the bioreactor owing to the porous structure and specific surface area (Shanmugam et al., 2018). Hence, the addition of biochar in the MFC

system is a promising method to improve the removal of antibiotics through the combined contribution of adsorption and biodegradation. However, a study on the application of biochar in the MFC bioreactor to stimulate the removal of SMs for purifying swine wastewater has yet been done. In the present research, different dosages of biochar that derived from pomelo peel were added into the anode chamber of the MFC to investigate their potential for improving SMs removal in a continuous flow MFC system. The effect of adding biochar to the MFC in terms of electricity production, COD and nutrients removal from swine wastewater was also examined.

2. Materials and methods

2.1 Materials

Selected sulfonamide antibiotics (including sulfamethoxazole (SMX), sulfadiazine (SDZ) and sulfamethazine (SMZ)), organic solvents and other chemicals employed in this study were purchased from Sigma-Aldrich (Australia). Synthetic swine wastewater was prepared based on the composition of swine wastewater mentioned in one of previous study (Xu et al., 2019), with the main composition of glucose (3000 mg/L COD), NH_4Cl (446 mg/L), KH_2PO_4 (132 mg/L), $MgSO_4 \cdot 7H_2O$ (54 mg/L) and $CaCl_2 \cdot 2H_2O$ (4 mg/L). The MFC's anode chamber was cultivated by anaerobic sludge derived from a pilot-scale anaerobic digester in the laboratory. A new pomelo peel-derived biochar was developed and used in the current study, which has a large surface area (2457.37 m^2/g) and total pore volume (1.14 cm^3/g). Detailed methods for the biochar preparation and activation were described in one of our previous studies (Cheng et al., 2020b).

2.2 Experiment setup and operation

Firstly, batch experiments were done to investigate the adsorption behavior of SMX, SDZ and SMZ onto biochar simultaneously. The prepared biochar (100 mg/L) samples were added to flasks (50 ml) with the SMs concentration of 100 μg/L for each, and samples were

collected at 10 min, 30 min, 60 min, 120 min, 240 min, 360 min, 540 min and 720 min, respectively, until the adsorption reached equilibrium at 720 min. To investigate the adsorption isotherm, the concentrations of SMs varied from 50 μg/L to 500 μg/L. After reaching the adsorption equilibrium (56 h), the residual concentrations of SMs were measured. Flasks for all the above experiments were shaken at 120 rpm in a temperature controlled orbital shaker at 25 ℃, and all the solution pH was kept at 7.0 ± 0.5.

A sequential anode-cathode double-chamber MFC was applied in this study, and each chamber had the effective volume of 350 ml. A CEM membrane served to separate the anode and cathode chamber. A graphite felt and a carbon-fiber brush were used as electrodes in the anode and cathode chamber, respectively, and they were connected by a copper wire with external resistance of 1000 Ω. During the start-up period, the inoculated sludge was acclimated in the anode chamber with synthetic swine wastewater without antibiotics being added. A high COD removal efficiency (>90%) and a stable voltage production were achieved after 30 days operation of the MFC. SMX, SMZ and SDZ (100 μg/L for each) were then directly added into the synthetic swine wastewater simultaneously. During the whole experiment, the mixed liquor suspended solids (MLSS) concentration were around 5000 mg/L and 750 mg/L in the anode and cathode chamber, respectively, and the HRT was kept at 24 h under room temperature (around 25 °C). To study the effect of biochar dosage on the MFC's performance, different concentrations of biochar were added into the anode chamber in phase 1 (100 mg/L), phase 2 (200 mg/L) and phase 3 (500 mg/L), respectively. After each phase (7 days), the addition of SMs into the feeding swine wastewater was stopped for two days. The entire experimental process was operated under the same conditions.

2.3 Analytical methods

All water samples were filtered with a 0.2 μm filter (Merck Millipore, Burlington, USA) before testing. The concentrations of SMX, SMZ and SDZ in the collected samples were determined by using triple quadrupole liquid chromatograph mass spectrometer (LCMS-8060,

Shimadzu). Details regarding the method are described in our previous study (Cheng et al., 2020a). MLSS, COD, NH_4^+-N and PO_4^{3-}-P were analysed according to the standard method. The pH was measured using a portable multiparameter meter (6173 pH, Jenco Instruments Co. Ltd., USA). The DO concentration in the cathode chamber, which was maintained at 6 mg/L during the operational period, was monitored through a DO meter (OM-51, Horiba, Tokyo, Japan). The reactor's generated voltage was detected by a universal digital meter (VC86E, Shenzhen City Station Win Technology Co. Ltd., Shenzhen, China). All samples were analysed in duplicate and mean values were presented.

3. Results and discussion

3.1 Adsorption behavior of SMs onto biochar

The adsorption capacities of SMX, SMZ and SDZ onto biochar are displayed in Fig. 1 (a). As shown in Fig. 1 (a), the adsorption can reach equilibrium in 540 min, and a rapid adsorption could occur in 60 min. The equilibrium adsorption capacities of SMX, SMZ and SDZ onto the biochar were around 831.85, 857.39 and 671.32 μg/g, respectively. Zhang et al. (2020) indicated that the maximum adsorption capacities of SDZ and SMX onto a spent coffee grounds derived biochar were 121.5 μg/g and 130.1 μg/g after reaching the equilibrium at 72 h. Thus, the pomelo peel derived biochar used in this study with equilibrium time of 540 minutes was a promising adsorbents for sulfonamide antibiotics. By comparing the adsorption kinetic parameters, the pseudo-second order mode emerged as being more appropriate for describing the adsorption process with: firstly, a high correlation coefficients value (R^2=1); and secondly, consistency between the calculated (q_e^c) and experimental adsorption capacities (q_e^b) for SMs onto the biochar (Fig. 1 (a) and Table 1). These agreed with previous studies on the adsorption of SMs onto other types of biochar (Ahmed et al., 2017). It further indicated that the adsorption rate was determined by the square of the adsorption site vacancies on the biochar surface and the adsorption process was controlled by chemisorptive mechanisms.

Fig.1 (b) shows the adsorption isotherm of SMs onto the biochar. Comparatively, the experimental data exhibited a higher correlation with the Freundlich mode with the correlation coefficients R^2 ranging from 0.981 to 0.998, indicating that the adsorption process probably took place on the biochar's heterogeneous surfaces. 1/n is a Freundlich constant, the value of 1/n presents the intensity of adsorption. 1/n values from 0.1 to 1 indicate favorable adsorption. As shown in Table 1, the 1/*n* value (<1) suggested that the adsorption of SMs onto the biochar was a favourable process. Considering the high surface area and pore volume of the biochar used in the present study, the favorable adsorption between SMs and the biochar could be caused by the pore-filling effect. The π-π electron donor acceptor (EDA) interaction was also a potential mechanism for the biochar's adsorption of SMs, due to the graphitic surface of the biochar and the amino functional group of SMs (Peiris et al., 2017).

3.2 Removal of SMs in the MFC with a biochar dosage

The overall removal of SMs during the MFC operating period with the addition of different concentrations of biochar is depicted in Fig. 2 (a). According to the pre-experiment, the removal efficiencies of SMX, SDZ and SMZ in the MFC without the addition of biochar were 49.35-59.37 %, 13.98-16.31% and 16.75-19.45%, respectively. By adding 100 and 200 mg/L of biochar in the anode chamber, the SMX removal efficiencies rose to 55.06-68.73% and 71.58-85.53% respectively. In contrast, a higher and more stable removal efficiency of SMX (82.44-88.15%) could be achieved when a further increase in the biochar concentration to 500 mg/L occurred, which was comparable with SMX removal in other biological processes. For instance, as reviewed by Chen and Xie (2018), the removal efficiency of SMX was around -463 - 72% in various full-scale wastewater treatment plants, 90 - 100% in MBR, 0 -75% in lab-scale activated sludge systems, and 34.4% in a sulfate-reducing up-flow sludge bed reactor.

By contrast, decrease trends were observed for the removal efficiency of SDZ and SMZ by adding 100 and 200 mg/L of biochar, although their removal efficiencies did largely

improve in the present study (Fig. 2 (a)). The accumulation of SDZ and SMZ in the reactor may attribute to the toxic effect of coexistence of multiple SMs and/or their degradation intermediates on the microorganisms responsible for the degradation. Moreover, the reduction potential required in the degradation of SMZ is higher than that of SMX, which makes SMZ difficult to biodegrade (Han et al., 2020). It is noted that the accumulation of SDZ and SMZ in the reactor was alleviated by the dosage of 500 mg/L biochar, with relatively high removal efficiencies for SDZ (53.40 - 77.53%) and SMZ (61.12-80.68%). This result suggested that the removal efficiency of SMs in the MFC could be greatly improved when the addition of biochar in the anode chamber reached a certain level. The enhanced removal of SMs in the MFC with biochar added was partly due to the adsorption of SMs onto the biochar, considering the favorable adsorption process as mentioned in section 3.1. Additionally, the porous biochar used in this study could act as a microbial carrier, which could form a biofilm on the surface of biochar as time passes (Sunyoto et al., 2016). This phenomenon could enhance the activity of microorganisms and then improve the removal of SMs through biodegradation (Mumme et al., 2014). The inhibitive effect of SMs on microorganisms can be reduced due to the fast adsorption of SMs onto the biochar as observed in the above batch adsorption experiment. Consequently, it is important to investigate the relationship between the biochar and the activity of microorganisms.

During the stable operating period of the MFC with the dosage of biochar (500 mg/L), the respective contribution of the anode and cathode compartments of the MFC to the removal of SMs from swine wastewater was monitored and presented in Fig. 2 (b). As observed in Fig. 2 (b), SMs could be degraded in both the anode and cathode chambers. In the cathode chamber, the removal of SMs through air stripping and volatilization was impossible due to their polarity and very low Henry constants, suggesting that the further removal of SMs in the cathode chamber was attributed to aerobic degradation (Li & Zhang, 2010). This finding agrees with previous analyses on the biodegradability of SMs in both aerobic and anaerobic

conditions (Chen & Xie, 2018). In the present study, the average removal efficiencies of SMX, SDZ and SMZ in the anode chamber with the addition of biochar (500 mg/L) were 77.21%, 46.7% and 51.78%, respectively, which accounts for the major part of their total removal. These figures confirmed the positive effect of adding biochar for removing SMs in the MFC.

3.3 Performance of the MFC with biochar addition

The average daily voltage generation in the MFC with different concentrations of biochar has been presented in Fig. 2 (c). It was observed that the voltage production was stable during the operational period and enhanced by increasing the biochar concentration from 100 mg/L to 500 mg/L. The highest daily average voltage generated in in this study was 650 mV when the biochar concentration reached 500 mg/L in the MFC, which was comparable to previous reports about the electricity produced from swine wastewater in MFCs (Min et al., 2005). Any improvement in electricity generation in the MFC with the presence of biochar might be due to biofilm formation on the surface of biochar and the increase in conductivity of electrodes' surfaces in the MFC (Ayyappan et al., 2018; Hejazi et al., 2019).

The organic matter and nutrients removal efficiency was monitored during the MFC's operating period. As shown in Fig. 2 (d), COD could be effectively and the average removal efficiency of COD rose from 93.08% to 95.88% by dosing 100 mg/L of biochar in the reactor, which was further increased to > 98% when 200 mg/L and 500 mg/L of biochar were added. By contrast, the removal of nutrients in the MFC revealed little change when the concentrations of biochar were 100 mg/L and 200 mg/L in the reactor, which then slightly increased after the dosage of biochar increased to 500 mg/L. From Fig. 2 (d), it is observed that the average removal efficiencies of NH_4^+-N and PO_4^{3-}-P increased from 63.33% to 65.67% and 26.08% to 27.19% after the addition of 500 mg/L of biochar. This small increase in the removal of COD and nutrients could be attributed to the absorption removal of

microbial inhibitors (SMs), which further enhanced the ability of microorganisms to absorb more carbon sources and nutrients (Masebinu et al., 2019). The similarity of adding biochar to the performance of bioprocesses was also noted by dosing the apple tree-derived biochar into activated sludge processes (Kim et al., 2020). Accordingly, the removal of NH_4^+-N and PO_4^{3-}-P in the sequential anode-cathode operating mode of the MFC was mainly due to the recovery through air stripping and struvite crystallization under an alkaline environment (pH = 8.2 - 8.6) in the cathode chamber (Ye et al., 2019). It is found in this study that the addition of biochar in the MFC system has little effect on the recovery of nutrients from swine wastewater.

4. Conclusions

The addition of pomelo peel-derived biochar in the continuous flow MFC could efficiently enhance its performance for treating SMs, COD and nutrients in swine wastewater. Adsorption kinetic and isotherm results suggested that SMs were absorbed on the heterogeneous surfaces of the biochar thorough pore-filling and π-π EDA interaction mechanisms. The removal efficiency of SMs in the MFC can be improved by the dosage of biochar, probably due to the combined effect of adsorption and biodegradation. The COD and nutrients removal, as well as electricity production of the MFC were improved with a direct dose of biochar into the MFC.

Acknowledgement

This research was supported by University of Technology Sydney, Australia (UTS, RIA NGO) and the Korea Institute of Energy Technology Evaluation and Planning (KETEP) and the Ministry of Trade, Industry & Energy (MOTIE) of the Republic of Korea (Grant No. 20173010092470).

References

1. Ahmed, M.B., Zhou, J.L., Ngo, H.H., Guo, W., Johir, M.A.H., Sornalingam, K., 2017. Single and competitive sorption properties and mechanism of functionalized biochar for removing sulfonamide antibiotics from water. Chem. Eng. J. 311, 348-358.

2. Ayyappan, C.S., Bhalambaal, V., Kumar, S., 2018. Effect of biochar on bio-electrochemical dye degradation and energy production. Bioresour. Technol. 251, 165-170.

3. Chen, J., Xie, S., 2018. Overview of sulfonamide biodegradation and the relevant pathways and microorganisms. Sci. Total Environ. 640, 1465-1477.

4. Cheng, D., Ngo, H.H., Guo, W., Chang, S.W., Nguyen, D.D., Liu, Y., Shan, X., Nghiem, L.D., Nguyen, L.N., 2020a. Removal process of antibiotics during anaerobic treatment of swine wastewater. Bioresour. Technol. 300, 122707.

5. Cheng, D., Ngo, H.H., Guo, W., Chang, S.W., Nguyen, D.D., Zhang, X., Varjani, S., Liu, Y., 2020b. Feasibility study on a new pomelo peel derived biochar for tetracycline antibiotics removal in swine wastewater. Sci. Total Environ. 137662.

6. Derakhshan, Z., Mokhtari, M., Babaei, F., Malek Ahmadi, R., Ehrampoush, M.H. and Faramarzian, M., 2016. Removal methods of antibiotic compounds from aqueous environments–a review. J. Environ. Health Sustain. Dev. 1 (1), 43-62.

7. Grandclément, C., Seyssiecq, I., Piram, A., Wong-Wah-Chung, P., Vanot, G., Tiliacos, N., Roche, N., Doumenq, P., 2017. From the conventional biological wastewater treatment to hybrid processes, the evaluation of organic micropollutant removal: a review. Water Res. 111, 297-317.

8. Han, Y., Yang, L., Chen, X., Cai, Y., Zhang, X., Qian, M., Chen, X., Zhao, H., Sheng, M., Cao, G., 2020. Removal of veterinary antibiotics from swine wastewater using anaerobic and aerobic biodegradation. Sci. Total Environ. 709, p.136094.

9. Hejazi, F., Ghoreyshi, A., Rahimnejad, M., 2019. Simultaneous phenol removal and electricity generation using a hybrid granular activated carbon adsorption-biodegradation process in a batch recycled tubular microbial fuel cell. Biomass Bioenergy 129, 105336.

10. Hu, D., Min, H., Wang, H., Zhao, Y., Cui, Y., Wu, P., Ge, H., Luo, K., Zhang, L., Liu, W., 2020. Performance of an up-flow anaerobic bio-electrochemical system (UBES) for treating sulfamethoxazole (SMX) antibiotic wastewater. Bioresour. Technol. 305, 123070.

11. Kim, D.G., Choi, D., Cheon, S., Ko, S.-O., Kang, S., Oh, S., 2020. Addition of biochar into activated sludge improves removal of antibiotic ciprofloxacin. J. Water Process Eng. 33, 101019.

12. Li, B., Zhang, T., 2010. Biodegradation and adsorption of antibiotics in the activated sludge process. Environ. Sci. Technol. 44 (9), 3468-3473.

13. Logan, B.E., Hamelers, B., Rozendal, R., Schröder, U., Keller, J., Freguia, S., Aelterman, P., Verstraete, W., Rabaey, K., 2006. Microbial fuel cells: methodology and technology. Environ. Sci. Technol. 40 (17), 5181-5192.

14. Masebinu, S., Akinlabi, E., Muzenda, E., Aboyade, A., 2019. A review of biochar properties and their roles in mitigating challenges with anaerobic digestion. Renew. Sust. Energ. Rev. 103, 291-307.

15. Michael, I., Rizzo, L., McArdell, C.S., Manaia, C.M., Merlin, C., Schwartz, T., Dagot, C. and Fatta-Kassinos, D., 2013. Urban wastewater treatment plants as hotspots for the release of antibiotics in the environment: a review. Water Res. 47 (3), 957-995.

16. Min, B., Kim, J., Oh, S., Regan, J.M., Logan, B.E., 2005. Electricity generation from swine wastewater using microbial fuel cells. Water Res., 39 (20), 4961-4968.

17. Mumme, J., Srocke, F., Heeg, K., Werner, M., 2014. Use of biochars in anaerobic digestion. Bioresour. Technol. 164, 189-197.

18. Pan, X., Qiang, Z., Ben, W. and Chen, M., 2011. Simultaneous determination of three classes of antibiotics in the suspended solids of swine wastewater by ultrasonic extraction,

solid-phase extraction and liquid chromatography-mass spectrometry. J. Environ. Sci. 23 (10), 1729-1737.

19. Peiris, C., Gunatilake, S.R., Mlsna, T.E., Mohan, D., Vithanage, M., 2017. Biochar based removal of antibiotic sulfonamides and tetracyclines in aquatic environments: a critical review. Bioresour. Technol. 246, 150-159.

20. Shanmugam, S.R., Adhikari, S., Nam, H., Sajib, S.K., 2018. Effect of bio-char on methane generation from glucose and aqueous phase of algae liquefaction using mixed anaerobic cultures. Biomass Bioenergy 108, 479-486.

21. Sunyoto, N.M., Zhu, M., Zhang, Z., Zhang, D., 2016. Effect of biochar addition on hydrogen and methane production in two-phase anaerobic digestion of aqueous carbohydrates food waste. Bioresour. Technol. 219, 29-36.

22. Tran, N.H., Chen, H., Reinhard, M., Mao, F., Gin, K.Y.-H., 2016. Occurrence and removal of multiple classes of antibiotics and antimicrobial agents in biological wastewater treatment processes. Water Res. 104, 461-472.

23. Xu, Z., Song, X., Li, Y., Li, G., Luo, W., 2019. Removal of antibiotics by sequencing-batch membrane bioreactor for swine wastewater treatment. Sci. Total Environ. 684, 23-30.

24. Ye, Y., Ngo, H.H., Guo, W., Liu, Y., Chang, S.W., Nguyen, D.D., Ren, J., Liu, Y., Zhang, X., 2019. Feasibility study on a double chamber microbial fuel cell for nutrient recovery from municipal wastewater. Chem. Eng. J. 358, 236-242.

25. Zhang, X., Zhang, Y., Ngo, H.H., Guo, W., Wen, H., Zhang, D., Li, C. and Qi, L., 2020. Characterization and sulfonamide antibiotics adsorption capacity of spent coffee grounds based biochar and hydrochar. Sci. Total Environ. 716, p.137015.

Figure Captions

Fig. 1 The adsorption kinetic (a) and isotherm (b) of SMX, SMZ and SDZ onto biochar.

Fig. 2 The removal efficiency of SMs in MFC with the addition of different concentrations of biochar (a); the average removal efficiency of SMs in the anode and cathode chamber of MFC, respectively (b) (500 mg/L of biochar); the average daily voltage generation (c) and COD and nutrients removal efficiency (d) in MFC with different concentrations of biochar.

Table Captions

Table 1. Sorption coefficients of SMs onto biochar evaluated by Pseudo second-order and Freundlich models

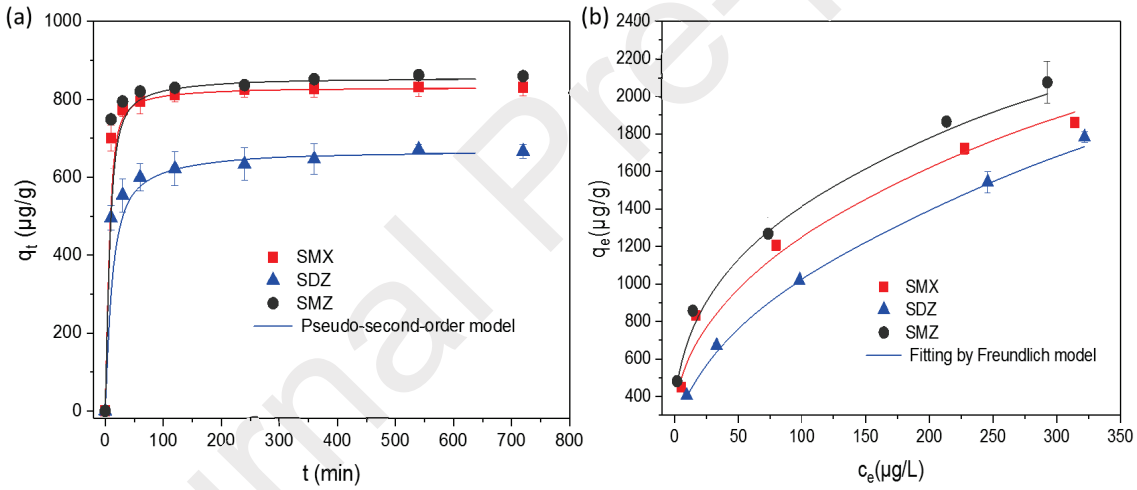

Fig. 1 The adsorption kinetic (a) and isotherm (b) of SMX, SMZ and SDZ onto biochar

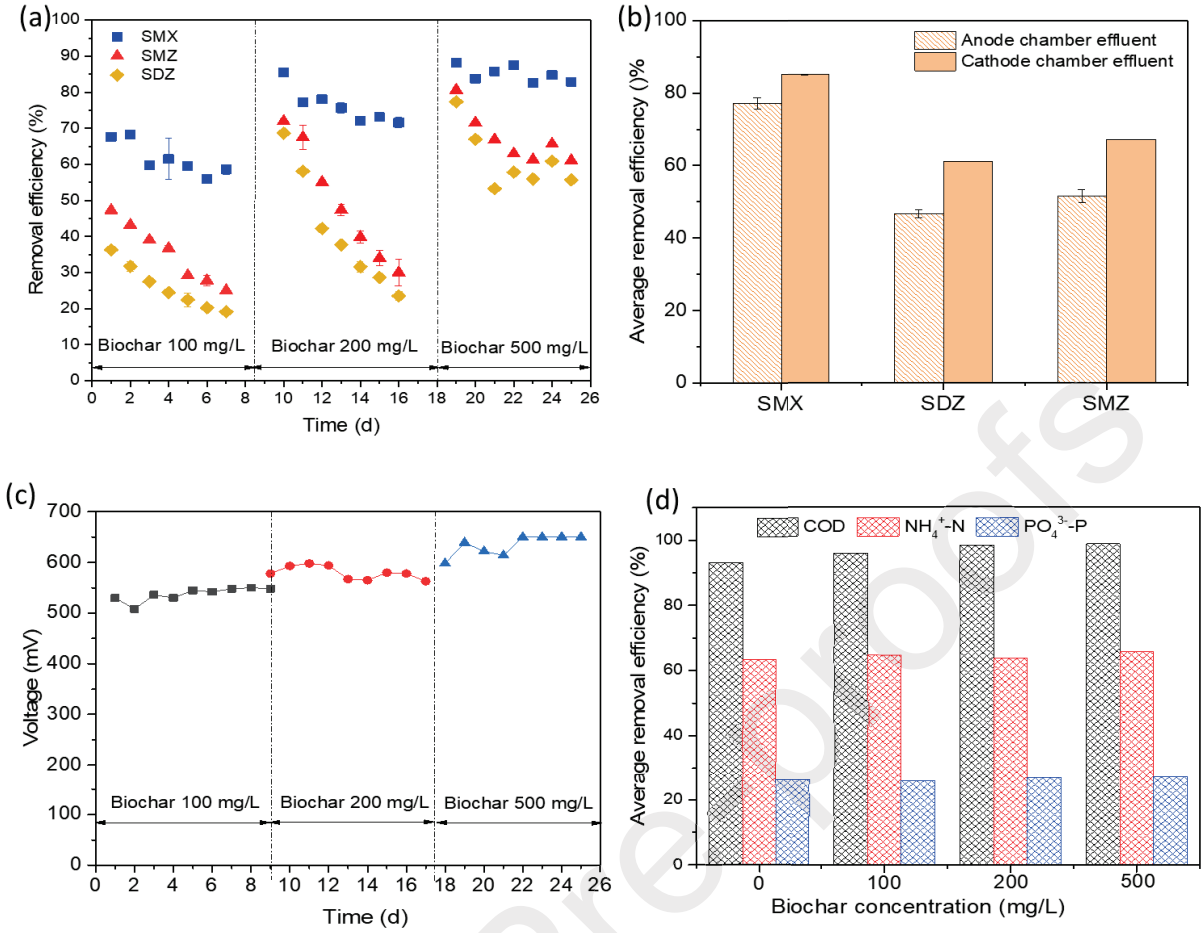

Fig. 2 The removal efficiency of SMs in MFC with the addition of different concentrations of biochar (a); the average removal efficiency of SMs in the anode and cathode chamber of MFC, respectively (b) (500 mg/L of biochar); the average daily voltage generation (c) and COD and nutrients removal efficiency (d) in MFC with different concentrations of biochar.

Table 1. Sorption coefficients of SMs onto biochar evaluated by Pseudo second-order and Freundlich models

	SMX	SDZ	SMZ
q_e[b]	831.85	671.32	857.39
Pseudo second-order model			
		$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$	
q_e[c]	833.95	673.58	864.01
K_2	4.69×10^{-4}	1.73×10^{-4}	3.09×10^{-4}
R^2	1	1	1
Freundlich model			
		$q_e = K_F c_e^{1/n}$	
K_f	288.04	157.17	396.35
1/n	0.33	0.42	0.29
R^2	0.981	0.998	0.996

q_t and q_e (μg/g) are the adsorption capacity at time t (min) and equilibrium; k_2 is the rate constants of the pseudo-second-order; c_e (μg/L) is the equilibrium concentration of SMs in solution; K_F ($\mu g^{(1-n)}L^n/g$) is Freundlich affinity coefficient indicating adsorption capacity; 1/n presents the adsorption intensity.