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Simultaneous electricity generation and tetracycline removal in continuous flow electrosorption driven by microbial fuel cells

Weilu Yang [a], Hexing Han [a], Minghua Zhou[a, *], Jie Yang [a]

[a] *Key Laboratory of Pollution Process and Environmental Criteria, Ministry of Education, Tianjin Key Laboratory of Urban Ecology Environmental Remediation and Pollution Control, College of Environmental Science and Engineering, Nankai University, Tianjin 300071, China*

A novel continuous flow electrosorption driven by microbial fuel cells (MFCs) was developed for the first time to remove tetracycline, the second most commonly used antibiotics, from a synthetic wastewater. The MFC-Sorption was proved to be cost-effective without any external power consumption. Various operating parameters including pH, electrolyte concentration, initial concentration of tetracycline, number of MFCs connected in series and flow rate were investigated, and the adsorption kinetics of tetracycline removal was studied. Three MFCs connected in series in the continuous flow MFC-Sorption system reached an adsorption capacity of 23.12 mg g^{-1}, higher than that with two MFCs (16.76 mg g^{-1}) and that with only one MFC (14.16 mg g^{-1}). The performance was compared with that in the batch mode, and it was confirmed that the continuous flow was practical for tetracycline removal. This work confirmed that continuous flow electrosorption driven by MFCs was cost-effective and environmentally friendly removal of tetracycline.

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[*] Corresponding author. Tel/Fax: +86 022 66229619. E-mail address: zhoumh@nankai.edu.cn (M. Zhou). Weilu Yang and Hexing Han contributed equally to this work.

Introduction

Antibiotics are widely used because of their vital roles on disease prevention, modern agriculture and livestock industries.[1,2] However, the excessive use of antibiotics has led to some problems such as interfering the photosynthesis of aquatic plants, disturbing the metabolism of native microbial communities.[3] What's more, antibiotic resistance in bacteria has become a great challenge for infection control all over the world since even low levels of antibiotics may cause antibiotic resistant bacteria in the aquatic environment.[4,5]

Tetracycline, the second most commonly used antibiotics in the world, is hard to be metabolized or absorbed completely in the human and animal bodies, with most of the unchanged form being released in excreta. Thus, it has been detected in many wastewater treatment plants as well as some surface water and groundwater, even in pore water and overlying water.[6,7] Due to special properties of tetracycline such as wide application, high solubility in water, high residual toxicity and low biodegradability, the abundant use of tetracycline in human and veterinary medicine has a great effect on the quality of surface water and groundwater.[8] Therefore, there is a growing international concern about the abatement of these compounds to decrease the potential impact on human health and environment.[9,10]

Though significant researches have been carried out to remove tetracycline in domestic, potable water and sludge, sound technologies are still very limited.[11] It takes more than 3 months to achieve a 89% removal efficiency for swine wastewater treatment by membrane bioreactor. [12] As one promising AOPs method for organics mineralization, photocatalysis is not regarded as a cost-effective alternative due to the need of UV light and the formation of more polar intermediates during treatment.[13] Though tetracycline could be removed by integration of ozonation and biodegradation, it's found that the toxicity increased with treatment time.[14] What's more, tetracycline electro-oxidation on boron-doped diamond (BDD) anode has also been investigated, but it is shown to be economically infeasible for practical applications.[15] Comparably, adsorption is a more practical and environmentally friendly technology,[16] and the recent studies on tetracycline removal have paid attention to the use of various adsorbents including active sludge, soils, clay minerals, carbonaceous adsorbents and bio-adsorbent.[17-19]

More recently, electrosorption has been developed as a more efficient adsorption process for metal separation, desalination and organics removal due to its particular advantages such as high capacity, no secondary waste and reversibility.[20-22] Operated with a low voltage (0.5 - 1.5 V), the charged ions or polar molecules migrate to the charged counter charge electrode, forming an electric double layer on the surface of adsorption electrode, which enhances the adsorption capacity.[23] Thus, it can be easily regenerated by removing the voltage or applying an inverse voltage on the electrodes.[24-26] To further improve the energy efficiency of the process, in our previous work, an electrosorption system driven by microbial fuel cells (MFC-Sorption) was first designed to remove phenol from wastewater in a batch mode.[27] MFC is a promising technology for wastewater treatment and electricity production at the same time,[28, 29] however, it is still far from industrial applications due to low power densities. The design of MFC-Sorption can take full advantage of the small amount of electricity generated by MFCs to achieve the electrosorption of pollutants and energy recovery at the same time. Therefore, it would be of significant environmental interest to explore the feasibility of this MFC-Sorption system for effective removal of tetracycline.

In this work, this MFC-Sorption was studied for the first time to remove tetracycline with continuous flow (Fig. 1), which would be more practical than bath flow for real-world applications. Important operating parameters such as pH, electrolyte concentration, initial tetracycline concentration, number of MFCs connected in series, flow rate and so on were systematically investigated, which would be predictive for some real wastewaters treatment application. The continuous flow performance was also compared with that in batch mode. This research showed that continuous flow MFC-Sorption system was effective and environmentally friendly for tetracycline removal in synthetic wastewater.

Results and discussion

Tetracycline removal in batch flow MFC-Sorption system

Fig. 2A shows the adsorption capacity of tetracycline by MFC-Sorption and traditional adsorption as well as their removal ratios under similar conditions in batch mode. It was observed that the trend of adsorption capacity was similar in these two systems, both increasing with time, which was consistent with the trend of phenol removal in our previous work.[27] In the MFC-Sorption system, the adsorption capacity of tetracycline was 69.3 mg g^{-1}, which increased by about 20% when compared with that in traditional adsorption (57.6 mg g^{-1}). Such an enhancement was due to the double electric layer on the anode surface.[30] The removal ratio of tetracycline in MFC-Sorption system was also higher than that in the traditional sorption (insert Fig. 2A).

It is known that pH plays a significant role on the adsorption capacity since it is related to the pk_a of tetracycline. Fig. 2B shows the effect of pH on adsorption capacity and tetracycline removal ratio. It was observed that the adsorption capacity of tetracycline decreased with pH decrease. When the solution pH was 3, the adsorption capacity was 35.1 mg g^{-1}, and decreased slightly at pH 5, 7 and 9, but at pH 11, it decreased noticeably by about 46% (19.0 mg g^{-1}). This phenomenon could be explained as follows: when the solution pH was below 3.3, the tetracycline in solution existed in the form of THC^{3+}, which was easy to be combined with the negative charge on the surface of activated carbon fibers (ACF) electrode with cation exchange to accomplish adsorption. The percentage of negative charge keeps rising with the increase of solution pH, and there was less chance for cationic group on the tetracycline to be combined with the negative charge on ACF electrode, leading to a lower removal ratio.

Fig. 2C shows the effect of electrolyte concentration on the adsorption capacity of tetracycline, which increased with the electrolyte concentration from 44.1 mg g^{-1} (0.001 mol L^{-1} Na_2SO_4) to 64.6 mg g^{-1} (0.1 mol L^{-1} Na_2SO_4). The enhancement of adsorption could be attributed to the increase of current with higher electrolyte concentrations. Moreover, the adsorption capacity and removal efficiency increased with the initial concentration of tetracycline from 50 mg L^{-1} to 200 mg L^{-1}. The adsorption capacity increased from 39.9 mg g^{-1} (50 mg L^{-1}) to 122.2 mg g^{-1} (200 mg L^{-1}), but the corresponding removal ratio decreased from 99.7% to 76.4% (Fig. 2D). These results agreed well with literature in which the deionization was found increased with the increase of initial NaCl concentration.[30] This fact also indicated that in the case of treatment of highly-concentrated tetracycline (*e.g.*, > 200 mg L^{-1}), several single MFC-Sorption systems connected in series would help to reach a better effluent water quality to meet the discharge requirement since one MFC-sorption could not achieve a satisfactory tetracycline removal efficiency.

(Fig. 2)

MFC-Sorption systems with different numbers of MFCs connected in series were investigated since it would affect the performance of electrosoption due to varied power supplies by the MFCs. As shown in Fig. 3A, the adsorption capacity increased slightly with time, and the more MFCs connected in series, the higher adsorption capacity was. For example, the adsorption capacity of tetracycline with 3 MFCs connected in series was 69.3 mg g^{-1}, slightly higher than that for the single-MFC system (62.5 mg g^{-1}), which was due to the higher current output as shown in Fig. 3B. It showed that the current for 3 MFCs connected in series dropped from 2.1 mA to 0.4 mA, higher than the current which decreased from 1.4 mA to 0.1 mA in case of a single MFC. This non-linear current relations with the numbers of MFCs connected in series indicated that cell reversal behavior happened in the present MFC-Sorption system, which was observed in many researches on MFCs connected in series.[31,32] Thus it was important to operate under similar conditions and sufficient substrate concentration to improve the power performance since it was reported that the imbalance in these MFCs would often cause cell reversal.[33] Fig. 3C presents the power density output of the MFCs connected in series, which reached the maximum at 752 mW m^{-2} (3 MFCs), 573 mW m^{-2} (2 MFCs), and 394 mW m^{-2} (1 MFC), respectively.

(Fig. 3)

Tetracycline removal in continuous flow MFC-Sorption system

Similar to batch flow experiments, several tests were designed to explore the adsorption of tetracycline in a continuous flow MFC-Sorption. Fig. 4A compares the adsorption capacity with that in the traditional adsorption system under the same flow rate of 12 mL min^{-1}. In both systems, the adsorption capacity increased with time, and after reaching the maximum at 150 min, they gradually decreased with more feed solution flowing into the reactor. It might be explained that ACF electrodes gradually reached adsorption saturation with time, and the further increasing feed solution led to the decrease of adsorption capacity of tetracycline. The maximum adsorption capacity of tetracycline in the continuous flow MFC-Sorption system was 16.76 mg g^{-1}, increased by about 31% compared with the traditional adsorption (11.56 mg g^{-1}). This result was in agreement with the case in the batch mode.

The effect of initial tetracycline concentration on electrosorption performance was explored in the continuous flow MFC-Sorption system at the concentration of 20 mg L^{-1}, 50 mg L^{-1} and 100 mg L^{-1}. Fig. 4B presents the adsorption capacity and removal ratio of tetracycline. It confirmed that the adsorption capacity was related to the initial tetracycline concentration, and the higher the initial concentration, the higher adsorption capacity achieved. The adsorption capacity were 11.27 mg g^{-1} (20 mg L^{-1}), 16.76 mg g^{-1} (50 mg L^{-1}) and 25.44 mg g^{-1} (100 mg L^{-1}), respectively, which indicated that a high initial tetracycline concentration was more favorable for tetracycline adsorption due to a higher driving force of the concentration gradient.[29,34] However, the removal efficiency decreased with the initial tetracycline concentration, decreased from 51.1% (20 mg L^{-1}) to 26.4% (100 mg L^{-1}), which were similar to the results in the batch flow system.

It has been reported that the adsorption rate has a close relationship with the mass transfer rates,[35] because a proper flow rate is important for the electrosorption of tetracycline in continuous flow MFC-Sorption system.[36] When the flow rate is too small, it limits the wastewater volume to be treated, while a very high flow rate decreases the retention time of tetracycline on electrodes, leading to a low adsorption capacity. Fig. 4C shows the adsorption capacities and removal ratios under three different flow rates (6, 12 and 24 mL min^{-1}). It was observed that the trend of the three curves was similar, increasing first with time and then dropped gradually. The adsorption capacity and removal efficiency of tetracycline both decreased with the increase of flow rate. This observation was consistent with literature.[34,35] For example, the electrosorption removal efficiency decreased from 94.2% to 65.8% with the increase of flow rate from 1.0 to 4.5 L min^{-1}.[35] It was also noticed that the removal efficiency of tetracycline in continuous flow MFC was lower than that in batch mode. This limitation might be overcome by improving the electrosorption reactor design, for example, shortening electrode spacing and increasing electrode area.[37]

(Fig. 4)

The effect of MFCs connected in series (1 MFC, 2 MFCs and 3MFCs) on the adsorption capacity and removal ratios of tetracycline were explored in continuous mode. It showed that the adsorption of tetracycline increased with time and reached the maximum after about 2 h, and then decreased with time (Fig. 5A). With more MFCs connected in series, higher adsorption capacity and removal efficiency of tetracycline were obtained. In the case of 1 MFC, the maximum adsorption capacity was 14.16 mg g^{-1}, while with 3 MFCs connected in series as the power supply for the electrosorption, the adsorption capacity was 23.12 mg g^{-1}, increasing by 63.31%. Consequently, the removal ratio increased from 31.5% to 51.5% (insert Fig. 5A). The variations of current in the MFC-Sorption system are presented in Fig. 5B. Similar to the current changes of MFCs in batch flow system, the currents also increased initially in the first 1 h and then dropped. The maximum current with 3 MFCs connected in series was about 1.3 mA, increasing by about 85.7% compared with the single one (0.7 mA).

(Fig. 5)

Comparison of MFC-Sorption in batch and continuous flow

In order to compare the adsorption properties in batch and continuous flow systems, relative parameters after 2 h removal of tetracycline were evaluated, as indicated in Figs. 3A and 4A. The adsorption capacities in batch flow system were higher than those in the continuous flow MFC-Sorption system. For example, with 3 MFCs connected in series, the adsorption capacity in batch flow was 69.3 mg g^{-1}, much higher than that in continuous flow (23.1 mg g^{-1}). Similarly, the tetracycline removal efficiency in batch flow (93.16%) was larger than that in continuous flow (51.48%) However, it should be noted that the treated volume in the continuous flow system (1440 mL) was more than 3 times that of the batch one (400 mL), indicating that continuous flow mode would be more effective for practical application.

MFC-Sorption adsorption kinetics

The pseudo-first-order kinetic and pseudo-second-order kinetic models were applied to fit the adsorption of tetracycline by MFC-Sorption in batch flow.[38] The two model equations are as follows:

Pseudo-first-order kinetics:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (1)$$

Pseudo-second-order kinetics:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\ 2}} + \frac{t}{q_e} \qquad (2)$$

where q_e and q_t (in mg g^{-1}ACF) are the amount of adsorbed tetracycline at equilibrium and time t (min), respectively. k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the pseudo-first-order and pseudo-second-order adsorption rate constant, respectively.

Figs. 6A and 6B display the tetracycline MFC-Sorption kinetics with different numbers of MFCs connected in series. The experimental results were fitted by the pseudo-first-order kinetic model (Fig. 6A) and pseudo-second-order kinetic model (Fig. 6B), respectively. Table 1 shows the relevant parameters of the kinetics in the above two systems. The results suggested that the adsorption capacity and the rate constant of tetracycline increased with the MFCs in series from 1 to 3 in both models. It was found that the pseudo-second-order kinetics model could fit the experimental results better than the pseudo-first-order kinetics equation due to the higher value of the correlation coefficients. A better criterion for the assessment of experimental results is a parameter called percent relative deviation modulus, P,[39] or normalized percent deviation,[40] as shown in equation (5):

$$P = \left(\frac{1}{N}\sum_{i=1}^{N}\frac{\left|q_{\mathrm{e(expt)}} - q_{\mathrm{e(pred)}}\right|}{q_{\mathrm{e(expt)}}}\right)\times 100\% \qquad (3)$$

where N is the number of experimental data points, $q_{\mathrm{e(expt)}}$ is the experimental q_e, and $q_{\mathrm{e(pred)}}$ is the corresponding predicted q_e according to the proposed kinetic equation. It is obvious that the lower the P value, the better is the fit, and it is generally accepted that when the P value is less than 5, the fit is considered excellent.[39] Thus it is clear that in the present work the pseudo-second-order kinetics model fitted much better when comparing these two models, which was in agreement with the results using correlation coefficients.

(Fig. 6)

Materials and methods

MFC configuration and operation

A series of MFCs without membranes were used with a total volume of 14 mL. All of the anode of MFCs were made by carbon cloth (Jilin Shenzhou Carbon Fiber Co., Ltd., China) with a surface area of 7 cm^2, and the cathode (7 cm^2) were made by the same material with a 0.2 mg cm^{-2} Pt loading. A 1000 Ω external resistance was fixed to connect with the anode and cathode. In the beginning, the MFC was inoculated with anaerobic sludge with about 20%-30% inoculum to reactor liquid volume fraction, 50 mM phosphate buffer solution (PBS) containing KCl 0.13 g L^{-1}, NH_4Cl 0.31 g L^{-1}, $Na_2HPO_4 \cdot 12H_2O$ 10.36 g L^{-1} and $NaH_2PO_4 \cdot 2H_2O$ 3.32 g L^{-1}; 5 mL L^{-1} vitamins; 12.5 mL L^{-1} trace minerals and 1 g L^{-1} glucose as carbon source. All of the MFCs were operated in a 30±0.5°C temperature-controlled biochemical incubator.

MFC-Sorption system

The continuous flow MFC-Sorption system (Fig. 1a) consisted of four parts: MFCs connected in series as the power supply, electrosorption unit, an external resistance used to measure the current of system and a peristaltic pump to control the flow rate of the feed solution. In the electrosorption unit (10×4×10 cm), both the anode and cathode (10×10 cm) were ACFs, a certain concentration of tetracycline with the supporting electrolyte of sodium sulphate were used as the synthetic wastewater. MFCs were connected in series in order to obtain a suitable voltage output for the electrosorption unit. For the batch flow MFC-Sorption system (Fig. 1b), it was very similar with that of the flow system using the same reactor materials and sizes except the absence of the peristaltic pump and the flow of the feed solution.

(Fig. 1)

Analysis

The current of this system was calculated from $I=U_1/R$, where U_1 represents the voltage of the external resistance, and power density could be calculated from $P=IU_2$, where U_2 represents the voltage applied to the adsorption process.

The concentration of tetracycline was determined from the experimentally derived standard curves and the absorbance of tetracycline was obtained by a UV-Vis spectrophotometer (VI-1501, Tianjin Gangdong Instrument Analysis Instrument Co., Ltd) at the wavelength of 357 nm. The adsorption capacity (*q*) and the removal ratio (R) of tetracycline in the electrosorption unit were calculated from the following two equations, respectively:

Adsorption capacity (mg g^{-1})
$$q = \frac{(c_0 - c_t)V}{m} \quad (4)$$

Removal ratio
$$R\% = \frac{c_0 - c_t}{c_0} \times 100\% \quad (5)$$

Where c_0, c_t (mg L^{-1}) represent the initial concentration and the given time concentration of tetracycline, respectively, V represents the available volume of the reactor (400 mL), and *m* represents the mass of the ACF electrode in the electrosorption unit (g).

Conclusions

A novel continuous flow MFC-Sorption system was developed for the first time in our study, which achieved a tetracycline removal ratio of 51.48%, and the results showed that high concentration of electrolyte, initial tetracycline concentration and low value of pH could enhance the adsorption capacity of tetracycline in the synthetic wastewater. This work indicated that the adsorption capacity of tetracycline increased with the increased numbers of MFCs connected in series, proving that the higher voltage and current could accelerate the removal efficiency of tetracycline. At pH 3, flow rate of 6 mL/min, and 3 MFCs connected in series, the removal efficiency for 20 mg/L tetracycline was the best. The adsorption process of tetracycline fitted the pseudo-second-order kinetics model better than the pseudo-first-order kinetics equation. The continuous flow MFC-Sorption system without an external power supply was proven to be an efficient and energy saving process for the removal of tetracycline in synthetic wastewater.

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Figure captions

Fig. 1. The schematic diagram of a continuous (a) and batch (b) flow MFC-Sorption apparatus.

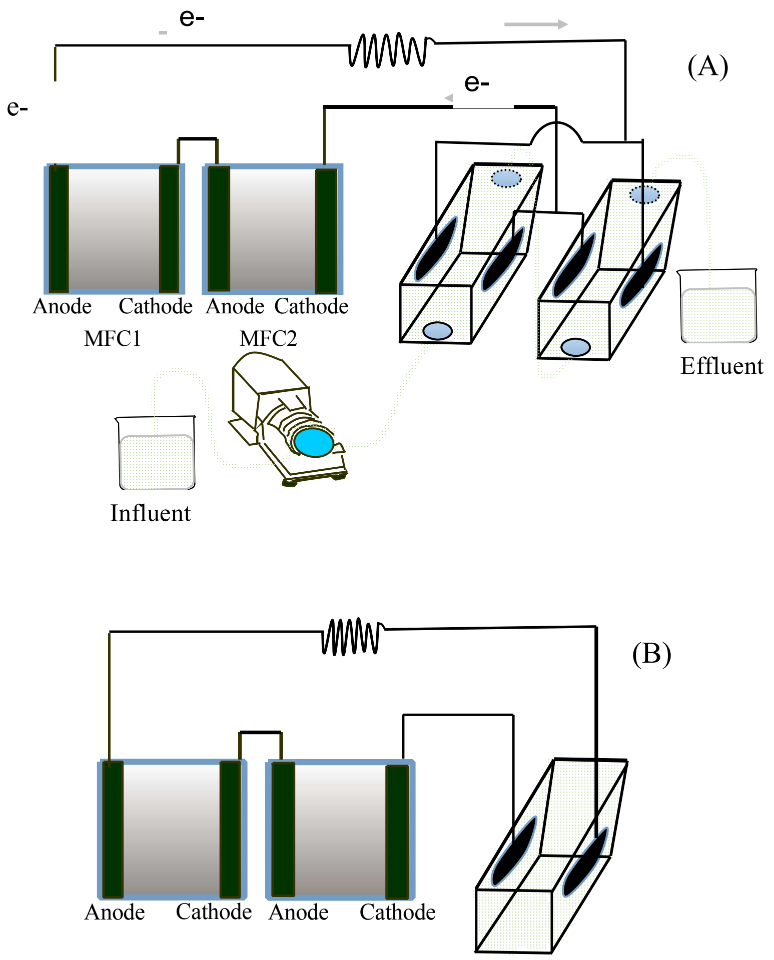
Fig. 2. Operating parameters (power supply, pH, electrolyte concentration and initial concentration of tetracycline) in batch flow MFC-Sorption system.

Fig. 3. Effect of MFCs connected in series on the adsorption of tetracycline (A), current (B) and power density (C) in batch flow MFC-Sorption system.

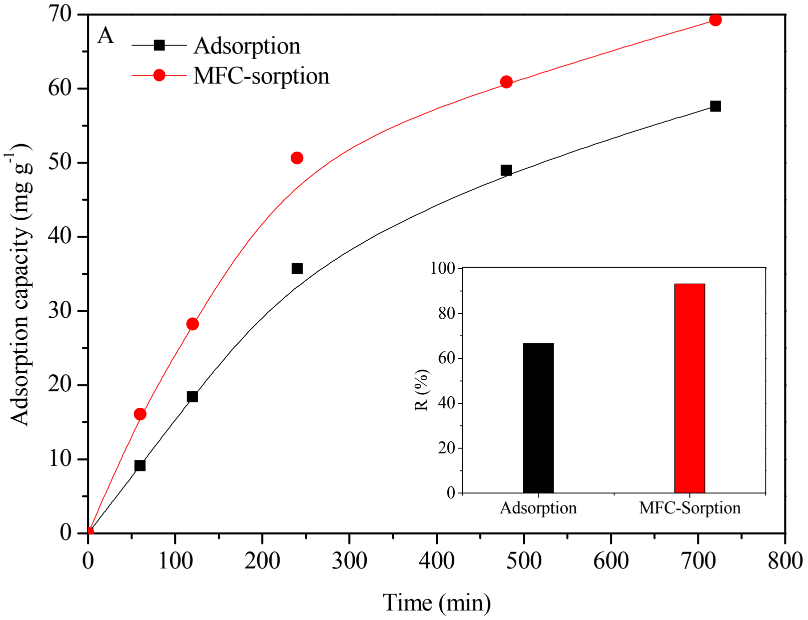
Fig. 4. Operating parameters (power supply, initial concentration of tetracycline and flow rate) in continuous flow MFC-Sorption system.

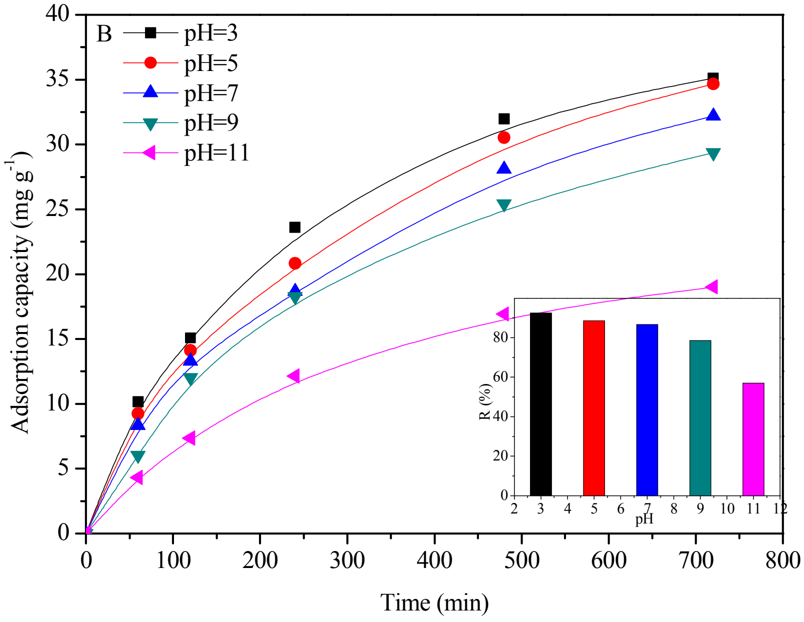
Fig. 5. Effect of MFCs connected in series on the adsorption of tetracycline (A), current (B) in continuous flow MFC-Sorption system.

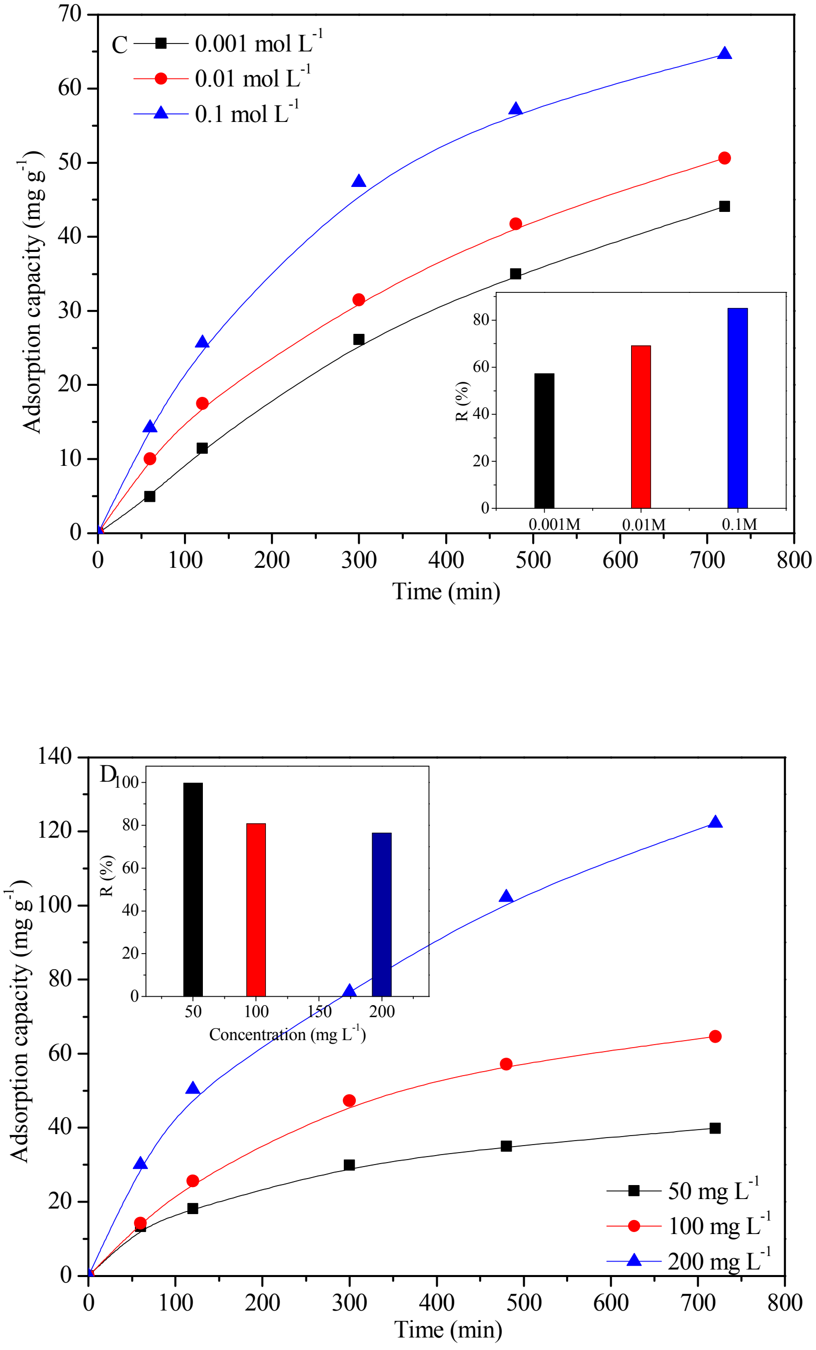
Fig. 6. The kinetics of batch flow MFC-Sorption system with different MFCs connected in series.


e-
(A)
e-
e-
Anode
Cathode
Anode
Cathode
MFC1
MFC2
Effluent
Influent
(B)
Anode
Cathode
Anode
Cathode

(Fig. 1)


A
Adsorption
MFC-sorption
Adsorption capacity (mg g^{-1})
0
10
20
30
40
50
60
70
Time (min)
0
100
200
300
400
500
600
700
800
R (%)
0
20
40
60
80
100
Adsorption
MFC-Sorption

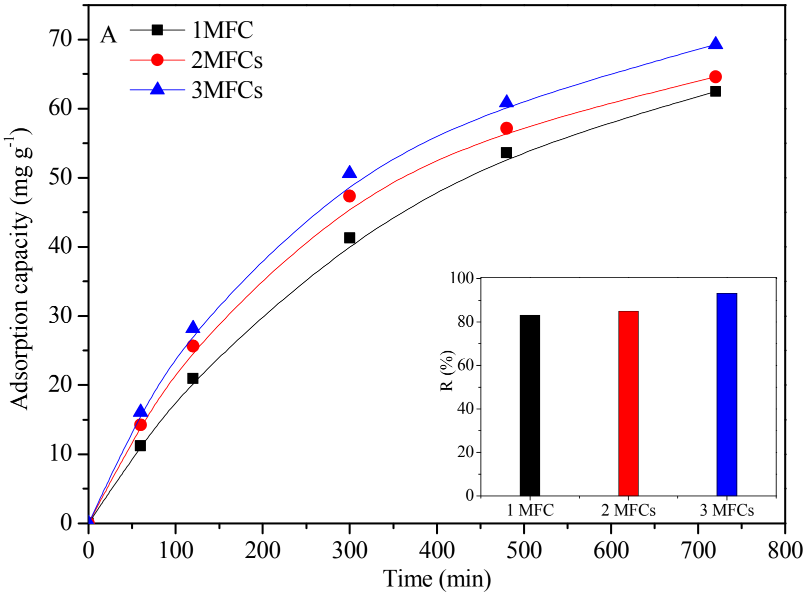

B
pH=3
pH=5
pH=7
pH=9
pH=11
Adsorption capacity (mg g^{-1})
0
5
10
15
20
25
30
35
40
Time (min)
0
100
200
300
400
500
600
700
800
R (%)
0
20
40
60
80
pH
2
3
4
5
6
7
8
9
10
11
12


C
0.001 mol L^{-1}
0.01 mol L^{-1}
0.1 mol L^{-1}
Adsorption capacity (mg g^{-1})
Time (min)
0
10
20
30
40
50
60
70
0
100
200
300
400
500
600
700
800
R (%)
0
20
40
60
80
0.001M
0.01M
0.1M
D
140
120
100
80
60
40
20
0
R (%)
100
80
60
40
20
0
50
100
150
200
Concentration (mg L^{-1})
50 mg L^{-1}
100 mg L^{-1}
200 mg L^{-1}

(Fig. 2)

433

434



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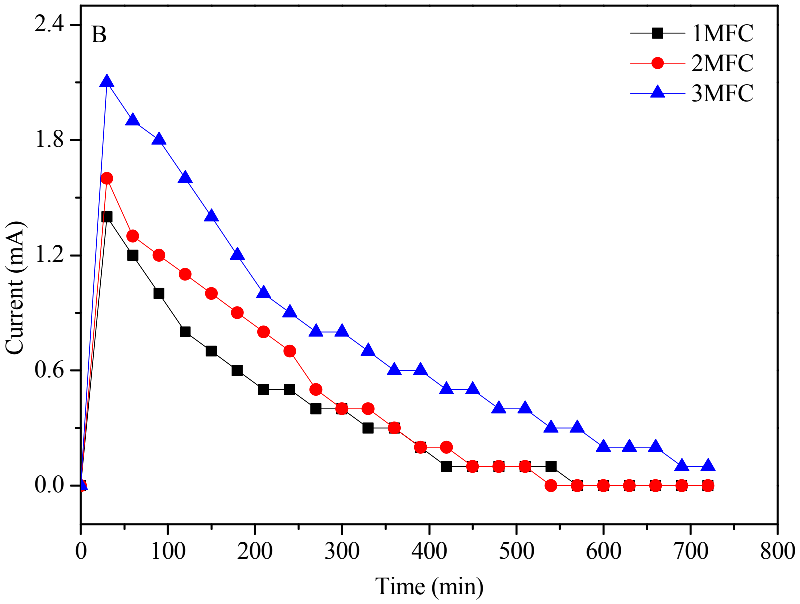

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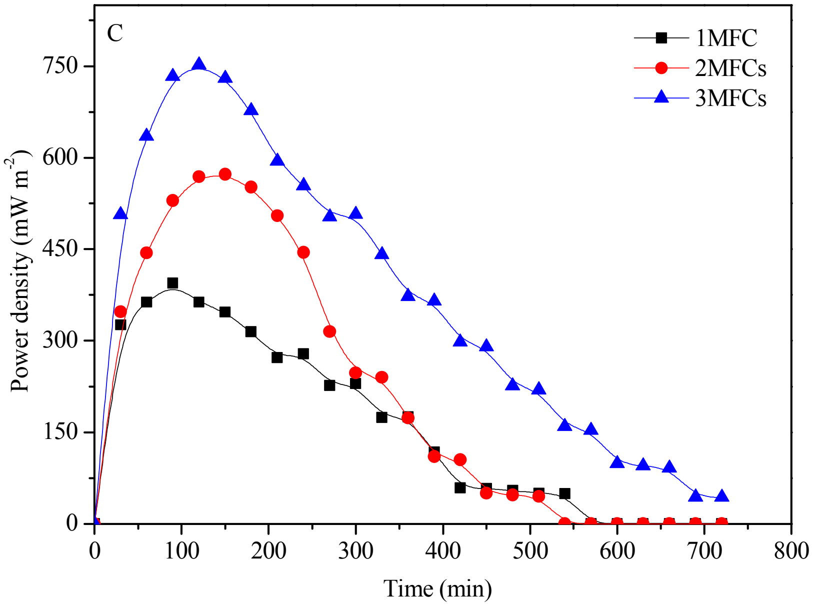
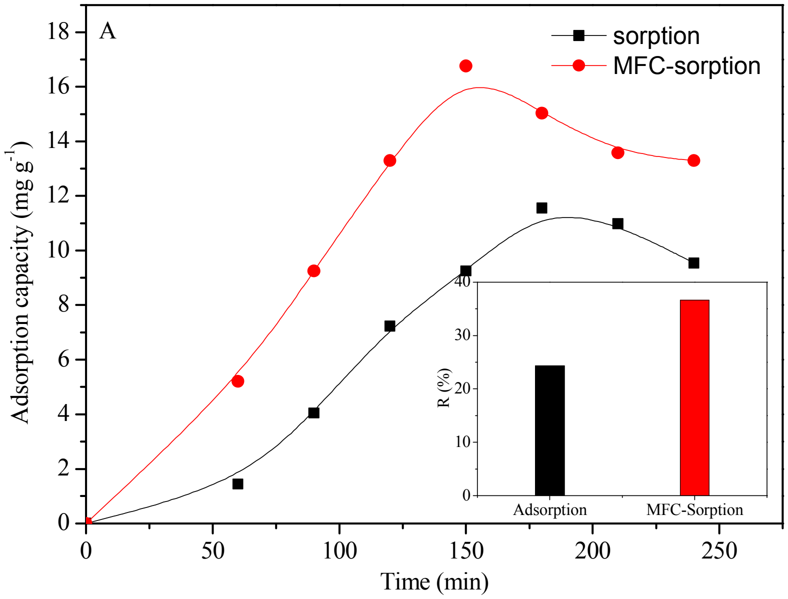
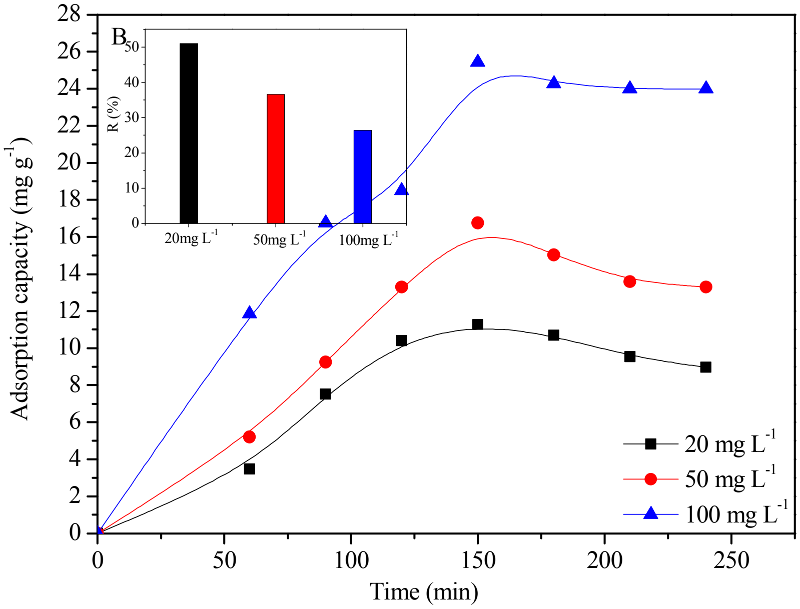
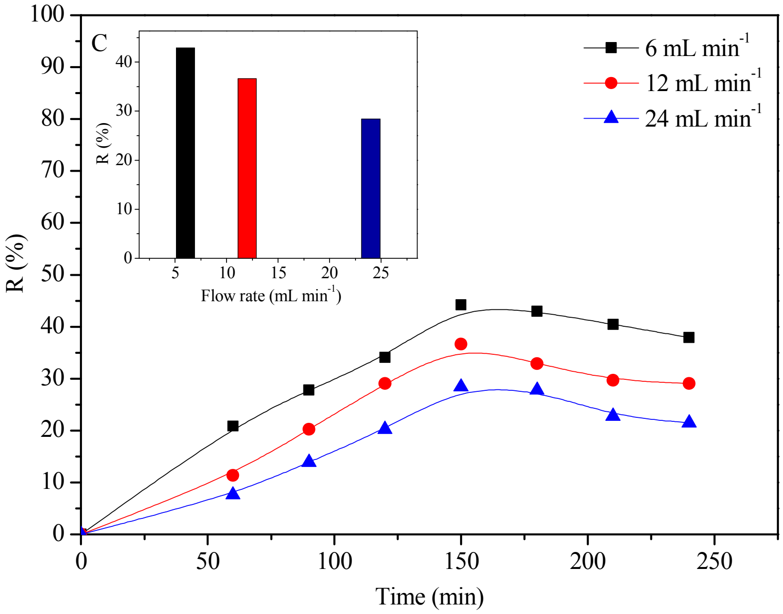

C
1MFC
2MFCs
3MFCs
Power density (mW m^{-2})
0
150
300
450
600
750
Time (min)
0
100
200
300
400
500
600
700
800

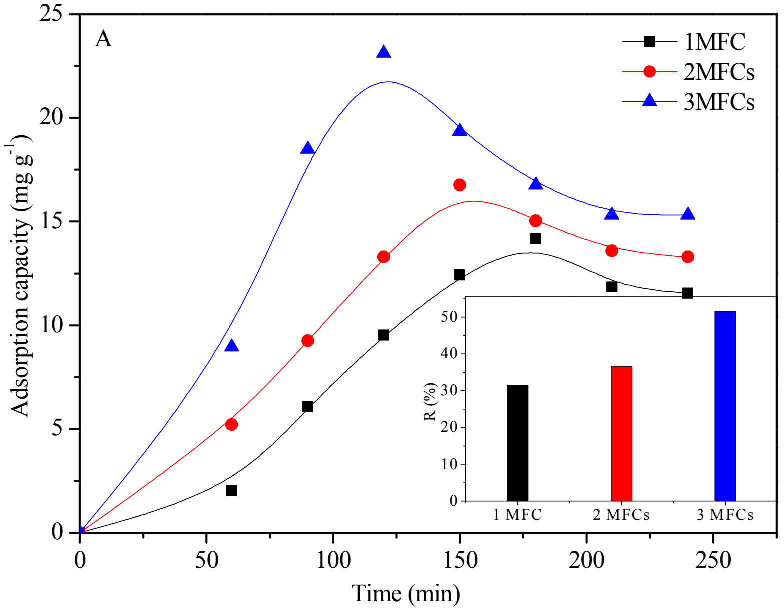
(Fig. 3)

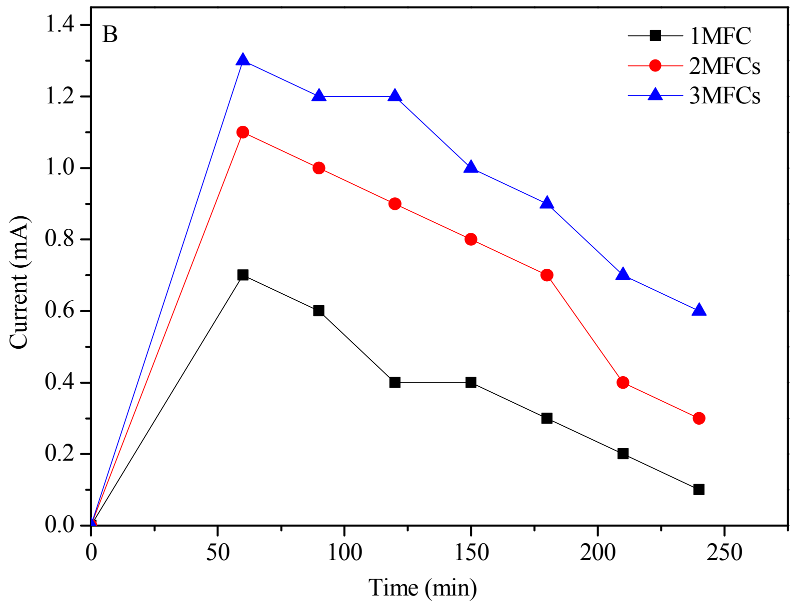

A
sorption
MFC-sorption
Adsorption capacity (mg g^{-1})
Time (min)
0
2
4
6
8
10
12
14
16
18
0
50
100
150
200
250
R (%)
0
10
20
30
40
Adsorption
MFC-Sorption


B
Adsorption capacity (mg g^{-1})
Time (min)
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
0
50
100
150
200
250
20 mg L^{-1}
50 mg L^{-1}
100 mg L^{-1}
R (%)
0
10
20
30
40
50
20mg L^{-1}
50mg L^{-1}
100mg L^{-1}

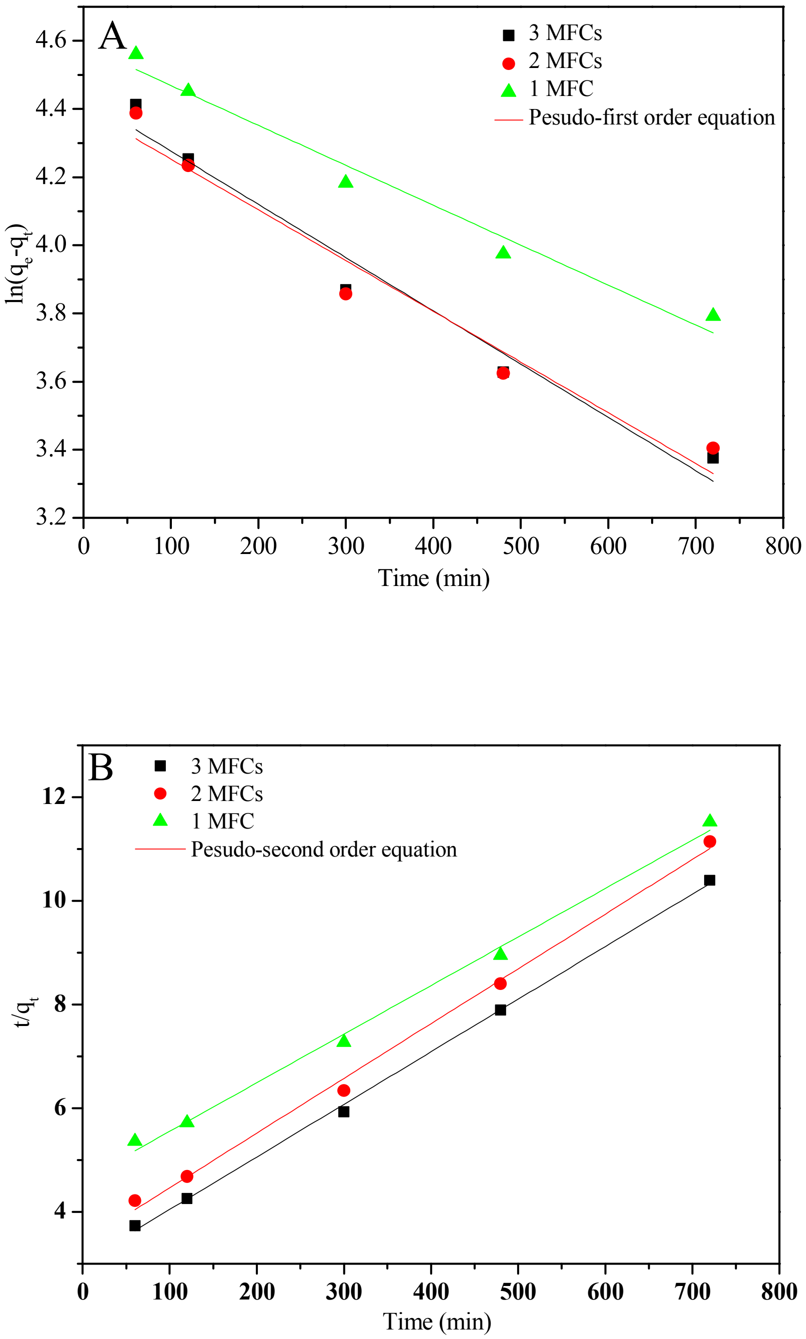

C
6 mL min^{-1}
12 mL min^{-1}
24 mL min^{-1}
R (%)
0
10
20
30
40
50
60
70
80
90
100
Time (min)
0
50
100
150
200
250
R (%)
0
10
20
30
40
Flow rate (mL min^{-1})
5
10
15
20
25

(Fig. 4)


A
1MFC
2MFCs
3MFCs
Adsorption capacity (mg g^{-1})
Time (min)
0
5
10
15
20
25
0
50
100
150
200
250
R (%)
0
10
20
30
40
50
1 MFC
2 MFCs
3 MFCs


B
1MFC
2MFCs
3MFCs
Current (mA)
Time (min)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
0
50
100
150
200
250

(Fig. 5)


A
■ 3 MFCs
● 2 MFCs
▲ 1 MFC
Pesudo-first order equation
$\ln(q_e\text{-}q_t)$
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
Time (min)
0
100
200
300
400
500
600
700
800
B
■ 3 MFCs
● 2 MFCs
▲ 1 MFC
Pesudo-second order equation
t/q_t
12
10
8
6
4
Time (min)
0
100
200
300
400
500
600
700
800

(Fig. 6)

Table 1

MFC-Sorption kinetic parameters of tetracycline removal under different experimental conditions.

	Pseudo-first-order model				Pseudo-second-order model			
	q_e	k_1 (10^{-3} min^{-1})	R^2	P	q_e	k_2 (10^{-5} g mg^{-1} min^{-1})	R^2	P
3 MFCs	84.12	1.56	0.960	21.4	98.52	3.4	0.999	1.16
2 MFCs	81.55	1.49	0.950	26.3	94.70	3.27	0.995	2.13
1 MFC	98.09	1.17	0.969	21.1	106.84	1.90	0.994	2.84