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High efficiency removal of 2-chlorophenol from drinking water by a hydrogen-based polyvinyl chloride membrane biofilm reactor

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ABSTRACT

A continuously stirred hydrogen-based membrane biofilm reactor (MBfR) with polyvinyl chloride (PVC) hollow fiber membrane was investigated for removing 2-chlorophenol (2-CP) from contaminated drinking water. The bioreactor startup was achieved by acclimating the microorganisms from a denitrifying and sulfate-reducing MBfR to the drinking water contaminated by 2-CP. The effects of some major factors, including 2-CP loading, H_2 pressure, nitrate loading, and sulfate loading, on the removal of 2-CP by the MBfR were systematically investigated. Although the effluent 2-CP concentration increased with its increasing influent loading, the removing efficiency of 2-CP by the MBfR could be up to 94.7% under a high influent loading (25.71 mg/L d). The removing efficiency of 2-CP by the MBfR could be improved by higher H_2 pressure, and lower influent nitrate concentration and sulfate concentration. A high H_2 pressure can assure enough available H_2 as the electron donor for 2-CP degradation. The competition in the electron donor made nitrate and sulfate inhibit the degradation of 2-CP in the MBfR. The electron flux analyses indicated that the degradation of 2-CP only accounted for a small part of electron flux, and the autohydrogenotrophic bacteria in the MBfR were highly efficient for the 2-CP removal.

1. Introduction

Chlorophenols (CPs) are chemicals widely used to manufacture insecticides, herbicides, fungicides, biocides and dyes [1]. The US Environmental Protection Agency (EPA) has compiled a list of nine phenol compounds considered as priority pollutants [2]. Among them, chlorophenols such as 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, pentachlorophenol, are the most toxic and carcinogenic [3,4]. According to the data from the EPA, 2-CP concentration in drinking water should be no more than 200 μg/L [5,6]. Removal of 2-CP from drinking water has gained significant attention in recent years because of its severe toxicity [7].

Some physicochemical methods, such as activated carbon adsorption, thermal degradation, hydrogen peroxide oxidation, and photocatalytic degradation, have been reported to remove 2-CP from wastewater [8–11]. Although these methods can also be used to remove 2-CP in drinking water, they were limited in application due to high capital and energy costs and subsequent disposal of problematic residues [12].

Microbial dechlorination is a common metabolic pathway for treating CPs [13]. Under anaerobic conditions, bacteria can dechlorinate various CPs to produce less-chlorinated phenol [14]. The reduction of CPs usually requires an addition of some electron donor substrates, which include organic carbon sources, such as methanol, ethanol or acetate (belonging to heterotrophic dechlorination) [15,16] and a few inorganic electron donors, such as hydrogen and sulfur (belonging to autotrophic dechlorination) [17,18]. However, the residual organic carbon sources would become pollutants when heterotrophic dechlorination was used in the treatment of drinking water [13]. For this reason, the use of autotrophic dechlorination, which is free of the donor-residual problem, will increase [19].

Hydrogen is a cheap and nontoxic electron donor. Generally, there are two ways to transfer hydrogen to the bulk fluid, i.e., sparging the gas or transferring hydrogen to the biofilm through bubbleless gas-permeable membrane [20]. With the danger of explosion and low hydrogen utilization rate for the sparging method, the bubbleless gas-permeable membrane technology has been developed to be a promising way to reduce 2-CP, and there are more highlighted advantages for the latter, such as effective gas transferring and utilization, and safe environment [21]. In our former research, a new polyvinyl chloride (PVC) hollow fiber membrane biofilm reactor (MBfR) has been developed and successfully applied to remove some familiar oxidized contaminants in drinking water, like nitrate, nitrite and sulfate [19,22]. To our best knowledge, no previous work about the treatment of 2-CP

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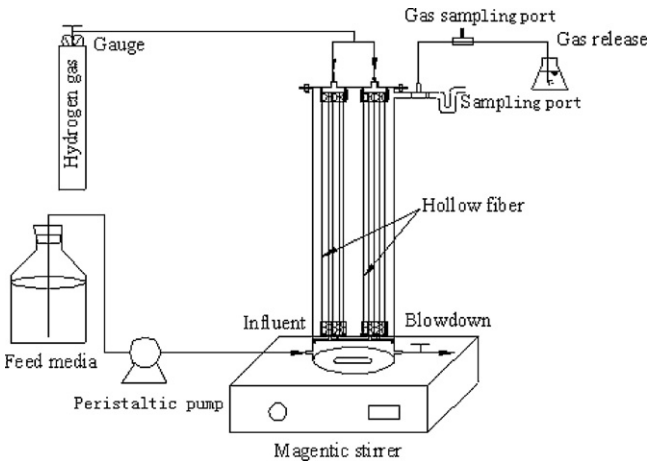

Fig. 1. Schematic of the continuously stirred hydrogen-based membrane biofilm reactor (MBfR) with polyvinyl chloride (PVC) hollow fiber membrane.

contaminated drinking water using MBfR has been reported to date.

This research, which focuses on H_2 as a clean and economical source of electronic donor, investigates the performance of the PVC hollow fiber membrane biofilm reactor for the removal of 2-CP from drinking water. The denitrifying and sulfate-reducing MBfR was firstly acclimated to the addition of 2-CP. After a steady removing efficiency of 2-CP by the MBfR was obtained, the effects of 2-CP loading, H_2 pressure, nitrate loading, and sulfate loading, on the removal of 2-CP was systematically investigated. Finally, the electron-equivalent fluxes of electron acceptors (2-CP, nitrate, and sulfate) and the percentage distribution of each flux were analyzed for revealing the removing mechanism of 2-CP by the MBfR.

2. Materials and methods

2.1. Experimental setup

The experimental set-up of the continuously stirred MBfR used in this study is shown in Fig. 1. A transparent plastic cylinder was used as a hollow fiber membrane reactor, in which two membrane modules were directly submerged in the bulk fluid and gas sealed with the plastic ring and the cap of the reactor. At the same time, the modules were easily disassembled from the reactor for rinsing or repairing the membranes when the membranes were polluted or damaged. The reactor was 22 cm in height and 6 cm in inner diameter. The system made the feed-media to be mixed well in the biofilm reactor because the stirring power was generated by a magnetic stirrer set on the bottom of the reactor. The hollow fibers were made of PVC with pore size of 0.01 μm, manufactured by Litree Company (Suzhou, China). The outside and inner diameters of the fiber are 0.15 and 0.085 cm, respectively, which provides 633.3 cm^2 of surface area with total 96 hollow fibers (each module consisted of 48 hollow fibers). The total available volume of the reactor system was 560 ml. The void ratio of the working reactor volume (volume of fiber was 23.7 ml) was 95.8%. A single peristaltic pump (Longer BT50-1J, Baoding, PRC) was used to keep a nitrate-medium-feed rate of 1.1 ml/min. Pure H_2 was supplied to the inside hollow fibers through a H_2 gas tank via a metering value.

2.2. Feed medium, stock solutions and mixed influent

The components of synthetic influent simulating drinking water were as follows (g/L): KH_2PO_4 0.128, Na_2HPO_4 0.434, $MgSO_4{\cdot}7H_2O$ 0.2, $CaCl_2{\cdot}2H_2O$ 0.001, $FeSO_4{\cdot}7H_2O$ 0.001, $NaHCO_3$ 0.252, and 1 ml of trace mineral solution. The trace mineral solution (mg/L) consisted of $ZnSO_4{\cdot}7H_2O$ 100, $MnCl_2{\cdot}4H_2O$ 30, H_3BO_3 300, $CoCl_2{\cdot}6H_2O$ 200, $CuCl_2{\cdot}2H_2O$ 10, $NiCl_2{\cdot}6H_2O$ 10, $Na_2MoO_4{\cdot}2H_2O$ 30, and Na_2SeO_3 30. The influent concentrations of nitrate, sulfate and 2-CP in the contaminated drinking water were 5 mg 2-CP/L, 10 mg NO_3^--N/L, and 50 mg SO_4^{2-}/L, respectively. Actual concentrations were measured daily. The feed medium was prepared in a 10.0 L (available volume) glass bottle under the purge by nitrogen gas to eliminate dissolved oxygen in the influent. $NaNO_3$ and $NaHCO_3$ were used as nitrogen source and carbon source for the growth of autotrophic microorganisms, respectively, and phosphate buffer ($KH_2PO_4 + Na_2HPO_4$) was used to keep initial pH value of the influent around 7.2 to prevent pH sharp variation during the biological process.

2.3. Inoculation and startup

Start-up of the continuously stirred MBfR began when hydrogen was supplied to the membrane under the hydrogen pressure of 0.02 MPa, and the MBfR was inoculated with mixed-culture biofilm collected from another bioreactor, in which the autohydrogenotrophic denitrifying bacteria had been acclimated for several months. At the beginning of start-up, the reactor had intermittently run for 2 days to establish a biofilm on the membrane surface. Then, the MBfR was run with the contaminated drinking

Table 1
Variable system conditions for the series of experiments.

Experimental name	Variable	H_2 pressure	Influent concentration (mg/L)		
			2-CP	Nitrate	Sulfate
Series 1	2-CP loading	0.02	1	10.0	50
		0.02	2	10.0	50
		0.02	3	10.0	50
		0.02	5	10.0	50
Series 2	H_2 pressure	0.02	5	10.0	50
		0.03	5	10.0	50
		0.04	5	10.0	50
		0.05	5	10.0	50
Series 3	Nitrate loading	0.02	5	2.5	50
		0.02	5	5.0	50
		0.02	5	10.0	50
		0.02	5	20.0	50
Series 4	Sulfate loading	0.02	5	10.0	10
		0.02	5	10.0	30
		0.02	5	10.0	50
		0.02	5	10.0	100

The influent pH value in all experiments was about 7.2.

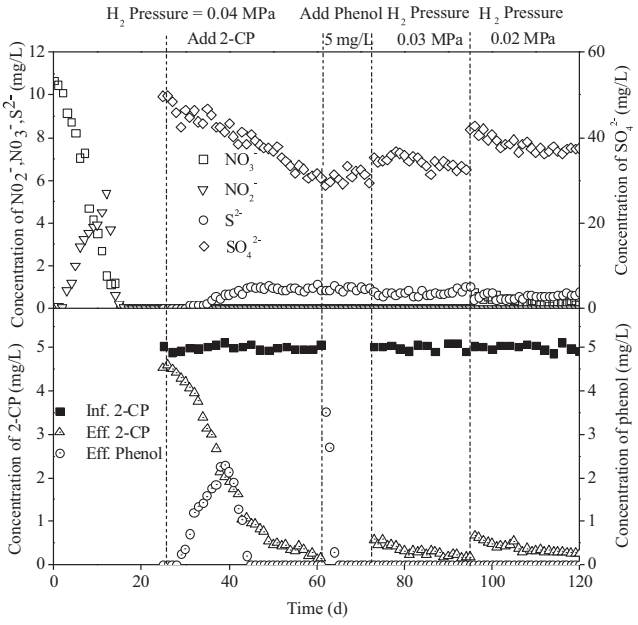

Fig. 2. Concentrations of nitrate, nitrite, sulfate, sulfide, 2-CP, phenol in the effluent of the MBfR. Influent concentrations were 5 mg/L of 2-CP, 10 mg/L of NO_3^--N, and 50 mg/L of SO_4^{2-}. The influent pH was about 7.2.

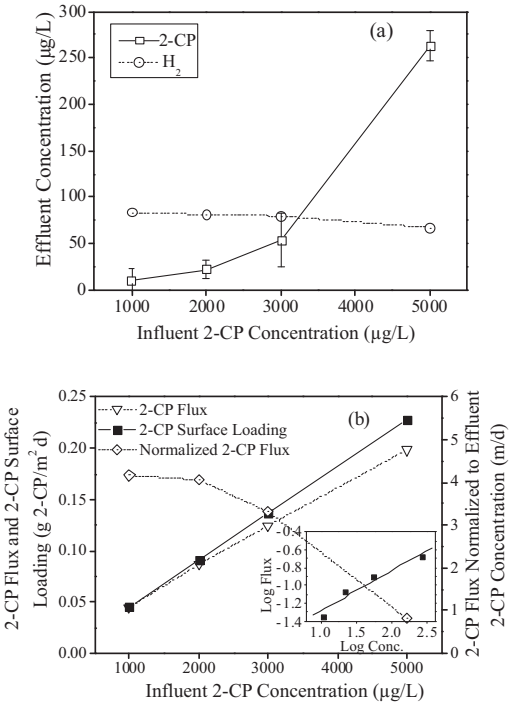

Fig. 3. Effect of 2-CP loading on 2-CP degradation by the MBfR: (a) 2-CP and H_2 concentration in the effluent; (b) 2-CP flux, 2-CP surface loading, and 2-CP flux normalized to its effluent concentration; (inset) logarithm of 2-CP flux vs. logarithm of effluent 2-CP concentration.

water (No 2-CP) at a flow rate of 2 ml/min until no nitrate in the effluent was detected (about 22 days). Afterward, the 2-CP contaminated drinking water was fed to the MBfR. After a steady state was reached, the phenol (5 mg/L) instead of 2-CP was added to the influent to examine whether phenol could be degraded by the biofilm or not. For the second steady state, the H_2 pressure was decreased from 0.03 to 0.02 MPa.

2.4. Short-term experiments

A series of experiments were designed to systematically investigate the effects of 2-CP loading, H_2 availability, nitrate loading, and sulfate loading, on the removal of 2-CP from drinking water by the MBfR. The experiments were organized into four series listed in Table 1. Prior to each experiment, the bioreactor was returned to the steady-state condition with an influent of 5 mg/L 2-CP, 10 mg NO_3^--N/L nitrate, 50 mg SO_4^{2-}/L, and 0.02 MPa H_2 pressure.

For each experiment, the change of system conditions lasted for 24 h before the effluent was sampled. With a hydraulic retention time of 4.67 h in the MBfR, 24 h (more than 5 hydraulic retention times) was long enough for the system to reach a pseudo-steady-state, which is defined as a condition in which the liquid concentration reached a stable state, while the biofilm accumulation and the biomass were not changed significantly from the actual steady state [23]. After a series test was completed, the reactor was returned to the steady state before the next one began.

2.5. Sampling and analysis

The performance of the reactor was monitored by analyzing influent and effluent samples taken on a daily basis and immediately filtered through a polyvinylidene fluoride (PVDF) syringe filter (Millipore, 0.45 μm). The 2-CP and phenol were determined by a high-performance liquid chromatography (HPLC) (Agilent 1200) equipped with diode-array detector and a Polaris C18 column. The mobile phase was a mixture of acetonitrile and distilled water in the proportion of 45/55. The HPLC pump was controlled at the flow rate of 1.0 ml/min, and the UV detector was set at 280 nm. Nitrate, nitrite and sulfate were measured by an ion chromatograph (ICS-1000, Dionex, USA) using an AS-11 column. A headspace-analysis method was used to determine dissolved H_2 concentrations in the effluent [24]. A 1 ml liquid sample was transferred from the reactor to a 50 ml serum vial with a thick butyl-rubber stopper previously out-gassed with nitrogen. The vial was shaken vigorously to liberate the dissolved H_2. A gas-tight syringe was used to sample the headspace (1 ml), and H_2 in the headspace was assayed by a gas chromatography (GC) (GC214B, Shimadzu). Once the headspace H_2 concentration was known, Henry's law and mass balance were used to determine the dissolved H_2 concentration [25].

3. Results and discussion

3.1. Startup and steady-state experiments

The experimental results of the bioreactor startup are shown in Fig. 2. In the first few days of the startup, nitrate was partially degraded to nitrite, and the effluent nitrite concentration gradually increased. Then the concentrations of both nitrate and nitrite in the effluent began to decrease after 14 days. On day 18, none of them was detected in the effluent. Then with the addition of 2-CP in the influent, phenol was detected in effluent and reached a maximum concentration (2360 μg/L) on day 40. A steady removing efficiency (about 97%) of 2-CP was achieved on day 60.

As can be seen from Fig. 2, phenol was detected as intermediate product during the degradation process of 2-CP. So the experiment about the degradation of phenol by the MBfR was also carried out. When phenol instead of 2-CP was added in the influent (5 mg/L), no phenol was detected in the effluent after 4 days. This indicated that the bioreactor contained phenol-degrading bacteria [14]. Then under a continuous-feeding operation, phenol was never detected during this experiment, because it would be instantly degraded as it was derived from 2-CP [14]. Phenol could be mineralized as the sole carbon substrate to carbon dioxide and methane under the

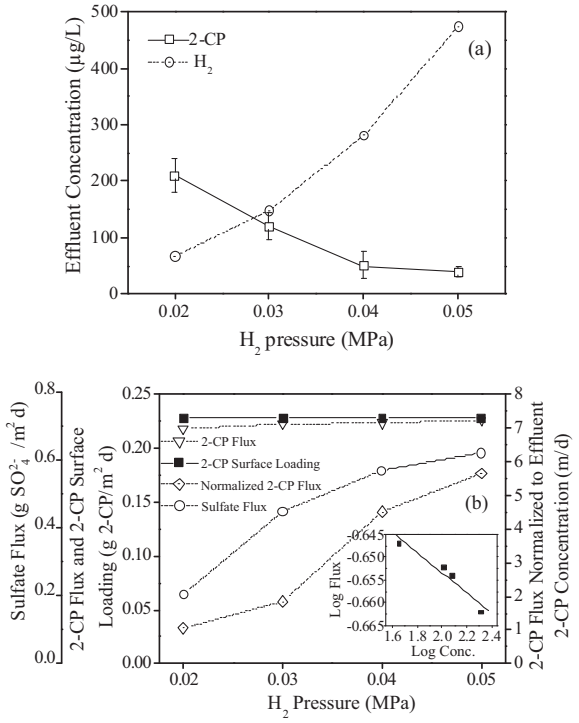

Fig. 4. Effect of H_2 pressure on 2-CP degradation by the MBfR: (a) 2-CP and H_2 concentration in the effluent; (b) 2-CP flux, 2-CP surface loading, and 2-CP flux normalized to its effluent concentration; (inset) logarithm of 2-CP flux vs. logarithm of effluent 2-CP concentration.

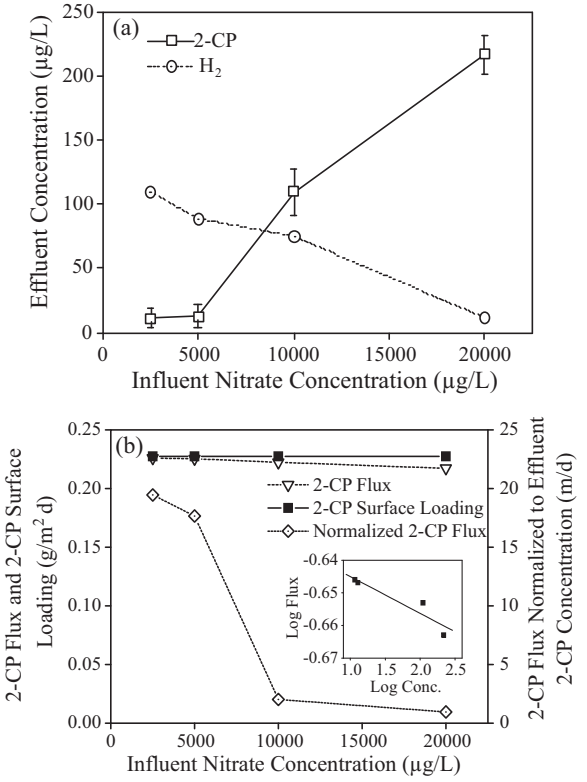

Fig. 5. Effect of nitrate loading on 2-CP degradation by the MBfR: (a) 2-CP and H_2 concentration in the effluent; (b) 2-CP flux, 2-CP surface loading, and 2-CP flux normalized to its effluent concentration; (inset) logarithm of 2-CP flux vs. logarithm of effluent 2-CP concentration.

anaerobic conditions [26,27]. This result indicates that 2-CP can be completely removed by the MBfR.

3.2. Effect of 2-CP loading on 2-CP degradation

The effect of the influent 2-CP loading on the removal of 2-CP by the MBfR was investigated by changing the influent 2-CP concentration. As shown in Fig. 3a, the effluent 2-CP concentration increased with its increasing influent loading. A higher removing efficiency (about 99%) of 2-CP was observed at a lower influent loading between 5.12 and 10.24 mg/L d. When its influent loading was increased to 25.71 mg/L d, the removing efficiency decreased to about 95%. Not affected by the influent 2-CP loading, the removing efficiency of nitrate by the MBfR was above 98.9% in all cases. With the increasing influent 2-CP loading, the removing efficiency of sulfate by the MBfR decreased from 13% to 6%. The effluent residual H_2 was steady at about 75 μg/L, which means that H_2 consumption was a constant in this series of experiments.

The substrate flux of the biofilm on the membrane (J) is usually used to reflect the removing performance of the bioreactors under various conditions. It can be calculated with Eq. (1) [19]. The flux normalized to the effluent concentration (k), which denotes the pseudo-first-order rate coefficient for the substrate degradation, can be calculated with Eq. (2) [19]. The reaction order of the substrate in the biofilm (k') can be calculated with Eq. (3) [19].

$$J = \frac{Q(S_i - S_e)}{A} \quad (1)$$

$$k = \frac{J}{S_e} \quad (2)$$

$$k' = \frac{d(\log J)}{d(\log S_e)} \quad (3)$$

where J refers to the flux, g/m^2 d; Q refers to the influent flow rate, m^3/d; S_i and S_e refer to the influent concentration and the effluent concentration of the substrate, respectively, g/m^3; A refers to the effective surface area of the membrane, m^2; k refers to the normalized substrate flux, m/d; k' refers to the reaction order of the substrate degradation.

According to the experimental results, 2-CP flux into the biofilm increased from 0.04 to 0.21 g/m^2 d when the influent 2-CP loading increased from 5.12 to 25.71 mg/L d. 2-CP flux in the MBfR is directly proportional to its influent loading, while the normalized 2-CP flux is inversely proportional to its influent loading. Therefore, the normalized 2-CP flux is dramatically high under the low influent 2-CP loading. Log J vs. log S_e is plotted in the inset of Fig. 3b, and the slope is 0.457. It is close to the well-known half-order kinetics, fitting for deep biofilms in which the reaction is zero order with respect to substrate concentration [28]. The impact of a reaction order smaller than one (<1) is that increase in S_e gives less than that in J, which means that removing efficiency will decline for higher loading [29]. This result is exactly confirmed by the phenomenon shown in Fig. 3b, which means that the proportional increase of 2-CP flux is less than that of influent 2-CP loading.

3.3. Effect of hydrogen pressure on 2-CP degradation

The effect of the hydrogen pressure on the removal of 2-CP by the MBfR was investigated. As shown in Fig. 4a, the effluent 2-CP concentration decreased with the increasing H_2 pressure. As H_2 pressure increased from 0.02 MPa to 0.03 MPa, the removing efficiency of 2-CP increased by 2.6%. Increasing the H_2 pressure to 0.04 MPa aroused a further increase in the removing efficiency of 2-CP. At the same time, the effluent H_2 concentration was up to 282 μg/L, much higher than that at 0.02 MPa (67 μg/L). When H_2 pressure was up to 0.05 MPa, the removing efficiency of 2-CP only showed a slight increase while effluent residual H_2 sharply

Table 2
Comparison of fluxes for 2-CP, sulfate, and nitrate from the series of experiments.

H_2 pressure (MPa)	2-CP conc. (mg/L)	Nitrate conc. (mg/L)	Sulfate conc. (mg/L)	Electron-equivalent flux (equiv./(m^2 d))			Sum up the fluxes in electron equivalent (equiv./(m^2 d))	Distribution of fluxes (%)		
				2-CP[a]	Nitrate[b]	Sulfate[c]		2-CP	Nitrate	Sulfate
0.02	1	10.0	50	0.0007	0.1542	0.0239	0.1788	0.39	86.25	13.36
0.02	2	10.0	50	0.0014	0.1551	0.0247	0.1812	0.97	85.41	13.62
0.02	3	10.0	50	0.0020	0.1599	0.0157	0.1776	1.57	89.63	8.80
0.02	5	10.0	50	0.0033	0.1606	0.0118	0.1757	1.91	91.36	6.73
0.02	5	10.0	50	0.0034	0.1616	0.0167	0.1817	1.86	88.92	9.21
0.03	5	10.0	50	0.0035	0.1622	0.0369	0.2026	1.70	80.08	18.22
0.04	5	10.0	50	0.0035	0.1620	0.0470	0.2125	1.65	76.25	22.10
0.05	5	10.0	50	0.0035	0.1622	0.0512	0.2170	1.62	74.76	23.62
0.02	5	2.5	50	0.0035	0.0406	0.0242	0.0683	5.14	59.40	35.46
0.02	5	5.0	50	0.0035	0.0812	0.0201	0.1048	3.35	77.44	19.21
0.02	5	10.0	50	0.0035	0.1622	0.0165	0.1821	1.90	89.07	9.04
0.02	5	20.0	50	0.0034	0.3241	0.0081	0.3356	1.01	96.57	2.42
0.02	5	10.0	15	0.0035	0.1616	0.0138	0.1788	1.97	90.34	7.69
0.02	5	10.0	30	0.0035	0.1555	0.0150	0.1740	1.99	89.37	8.64
0.02	5	10.0	50	0.0034	0.1603	0.0199	0.1835	1.84	87.31	10.85
0.02	5	10.0	100	0.0033	0.1573	0.0886	0.2492	1.32	63.12	35.56

[a] Calculated by $J_{e^-\text{-2-CP}}$ = (Influent flow rate(Q) × removed 2-CP($\Delta S_{2\text{-CP}}$))/(Total biofilm surface area(A) × $EW_{2\text{-CP}}$), where Q is in m^3/d, $\Delta S_{2\text{-CP}}$ is in g 2-CP/m^3, A is in m^2, and $EW_{2\text{-CP}}$ is 64.25 in g 2-CP/e^- equivalent for degradation of 2-CP to phenol.

[b] Calculated by $J_{e^-\text{-}NO_3^-\text{-N}}$ = (Influent flow rate(Q) × removed NO_3^--N ($\Delta S_{NO_3^-\text{-N}}$))/(Total biofilm surface area(A) × $EW_{nitrate}$), where Q is in m^3/d, $\Delta S_{NO_3^-\text{-N}}$ is in g NO_3^--N/m^3, A is in m^2, and $EW_{nitrate}$ is 2.8 in g NO_3^--N/e^- equivalent for reduction of nitrate to nitrogen gas.

[c] Calculated by $J_{e^-\text{-}SO_4^{2-}}$ = (Influent flow rate(Q) × removed SO_4^{2-} ($\Delta S_{SO_4^{2-}}$))/(Total biofilm surface area(A) × $EW_{sulfate}$), where Q is in m^3/d, $\Delta S_{SO_4^{2-}}$ is in g SO_4^{2-}/m^3, A is in m^2, and $EW_{sulfate}$ is 12 in g SO_4^{2-}/e^- equivalent for reduction of sulfate to sulfide.

increased to 475 μg/L. It suggests that H_2 pressure will not be the limiting factor of the 2-CP removal when it is above 0.04 MPa. Not affected by H_2 pressure, the denitrification was above 99%. On the other hand, sulfate reduction was significantly improved with the increased H_2 pressure, and the sulfate flux increased from 0.2 to 0.62 g SO_4^{2-}/m^2 d due to enough available electron donors.

As H_2 pressure increased from 0.02 MPa to 0.05 MPa, the normalized 2-CP flux increased from 1 to 5.6 m/d (Fig. 4b), suggesting that H_2 availability has a prominent effect on 2-CP degradation. Enough available H_2 can assure both the active depth of the biofilm and enough available electron donors for 2-CP degradation. This can also be confirmed by the negative reaction order (−0.025) shown in the inset of Fig. 4b.

3.4. Effect of nitrate loading on 2-CP degradation

The effect of the nitrate loading on the removal of 2-CP by the MBfR was shown in Fig. 5. At a low influent nitrate concentration (2.5–5.0 mg/L), a high removing efficiency of 2-CP can be achieved (99.8%). However, when influent nitrate concentration was up to 20.0 mg/L, the effluent 2-CP concentration quickly increased to 216 μg/L with the removing efficiency decreased to 95.7%. Nitrate can be easily utilized as an electron acceptor by the biofilm [14]. Thus, for a lower H_2 pressure (0.02 MPa) and a high nitrate loading, denitrification will inhibit the degradation of 2-CP by taking the place of 2-CP as electron acceptors [13]. The normalized 2-CP flux sharply decreased as the nitrate surface loading increased, which further demonstrated that the degrading speed of 2-CP obviously decreased.

3.5. Effect of sulfate loading on 2-CP degradation

The effect of sulfate loading on 2-CP degradation by the MBfR was shown in Fig. 6. When influent sulfate concentration was 10 mg SO_4^{2-}/L, the removing efficiency and the flux of 2-CP were 99.6% and 0.23 g/m^2 d, respectively. Increasing sulfate loading caused a decrease in the removing efficiency of 2-CP, which indicates that sulfate reduction also inhibits the degradation of 2-CP by taking the place of 2-CP as electron acceptors [13]. This may caused by that sulfate reduction to sulfide consumes 8e^- equiv./mol, while 2-CP dechlorination to phenol only consumes 2e^- equiv./mol, which means that the total demand for H_2 was controlled by sulfate reduction other than 2-CP dechlorination. For a lower H_2 pressure (0.02 MPa) and a high sulfate loading, there is also a competition for electron donor between 2-CP and sulfate. As shown in Fig. 6b,

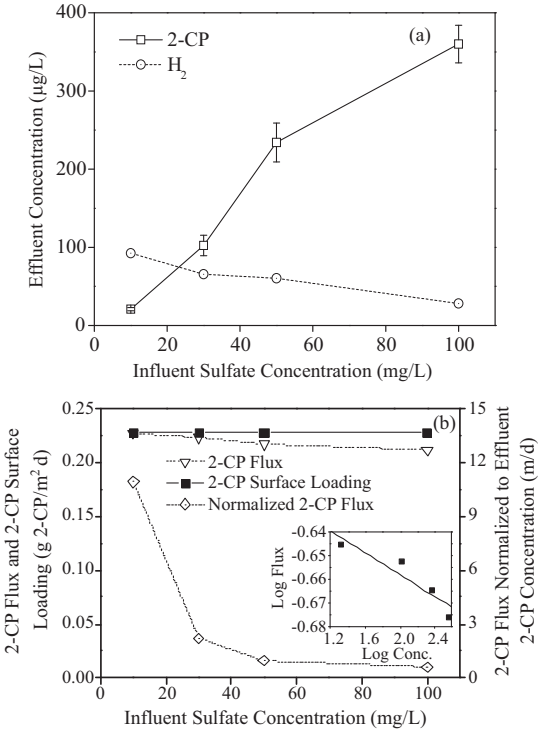

Fig. 6. Effect of sulfate loading on 2-CP degradation by the MBfR: (a) 2-CP and H_2 concentration in the effluent; (b) 2-CP flux, 2-CP surface loading, and 2-CP flux normalized to its effluent concentration; (inset) logarithm of 2-CP flux vs. logarithm of effluent 2-CP concentration.

Table 3
Removal performance of various systems for 2-CP degradation under anaerobic conditions.

Reactor	Influent 2-CP loading (mg/L d)	Average HRT (h)	2-CP removal efficiency (%)	Remark	Reference
AFBR	70–600	168	62.0	A selectively enriched, strictly anaerobic, dehalogenating mixed culture from sludge was used.	[27]
AFBR	50–1365	81.6	73.0	The stable removal rate achievable was 730 mg/L d.	[30]
UASB + RBC	45–120	30.8	97.5	3 g/L sodium acetate was used as co-substrate.	[31]
SMBR	26.47	15.0	92.8	Hydrogenotrophic conditions with silicone-tube membrane	[13]
MBfR	5.12–25.71	4.67	99.0	Hydrogenotrophic conditions with PVC hollow fiber membrane	This work

the normalized 2-CP flux decreased with the increased influent sulfate concentration, especially from 10 to 30 mg SO_4^{2-}/L, which also reflected that the degrading speed of 2-CP obviously decreased.

3.6. Electron-equivalent fluxes analyses

The analysis about the electron-equivalent fluxes of the electron acceptors (2-CP, nitrate, and sulfate) and the percentage distribution of each flux is shown in Table 2. Denitrification was insensitive to H_2 pressure and sulfate loading, since the nitrate fluxes were nearly invariant. With an average percentage of electron fluxes (83%), denitrification was the biggest consumer of electrons in all series experiments. On the other hand, 2-CP degradation took up a very small percentage of electron fluxes, less than 6%. So in the autohydrogenotrophic process, sulfate and nitrate were the first electron acceptors, which were the largest consumers of electrons for reduction, together accounted for at least 94% of the total electron fluxes. This means that the total demand for H_2 was largely controlled by nitrate and sulfate reduction, not by 2-CP degradation.

It is interesting to compare the removal performance of various systems for 2-CP degradation under anaerobic conditions (Table 3). In the continuously grown cultures in an anaerobic fixed-bed reactor (AFBR) with suspended cultures on Liapor clay beads, the degradation rates of 2-CP of up to 375 mg/L d were observed [27]. At a HRT of 52.8 h and a 2-CP loading rate of 2 g/L d, the average 2-CP removal rate in an AFBR was 0.87 mg/L d, accounting for 73% removal [30]. Combination of upflow anaerobic sludge blanket (UASB) and aerobic rotating biological contactor (RBC) reactors was applied for 2-CP removal [31]. At an influent 2-CP concentration of 30 mg/L, 12 h HRT of UASB and 28.8 h HRT of RBC were the optimum combination for the treatment of simulated wastewater containing 2-CP [31]. Under the condition of influent 2-CP 25 mg/L with HRT of 15 h, the respective 2-CP removal efficiency by the hydrogenotrophic biofilm cultivated in a silicone-tube membrane bioreactor (SMBR) was 95% in a denitrification reactor, 94% in a sulfate-reduction reactor, and 95% in a dechlorination reactor [13]. Compared to the above anaerobic reactors, the MBfR shows the shortest HRT and the highest efficiency for 2-CP removal.

4. Conclusions

The present paper investigated the removal of 2-CP from drinking water using a continuously stirred hydrogen-based MBfR with PVC hollow fiber membranes. The bioreactor startup was achieved by acclimating the microorganisms from a denitrifying and sulfate-reducing MBfR to the drinking water contaminated by 2-CP. A removal efficiency of about 99.0% could be obtained when the bioreactor was adjusted to a steady state. Increasing the H_2 pressure or reducing the competition for H_2 from denitrification and sulfate reduction could improve the removal efficiency of 2-CP by the MBfR. The dechlorination of 2-CP only accounted for a small part of electron flux, and the autohydrogenotrophic bacteria in the MBfR were highly efficient for 2-CP removal.

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