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Treatment of oilfield wastewater in moving bed biofilm reactors using a novel suspended ceramic biocarrier

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ABSTRACT

In this study, a novel suspended ceramic carrier was prepared, which has high strength, optimum density (close to water), and high porosity. Two different carriers, unmodified and sepiolite-modified suspended ceramic carriers were used to feed two moving bed biofilm reactors (MBBRs) with a filling fraction of 50% to treat oilfield produced water. The hydraulic retention time (HRT) was varied from 36 to 10 h. The results, during a monitoring period of 190 days, showed that removal efficiency of chemical oxygen demand was the highest in reactor 3 filled with the sepiolite-modified carriers, followed by reactor 2 filled with the unmodified carriers, with the lowest in reactor 1 (activated sludge reactor), at an HRT of 10 h. Similar trends were found in the removal efficiencies of ammonia nitrogen and polycyclic aromatic hydrocarbons. Reactor 3 was more shock resistant than reactors 2 and 1. The results indicate that the suspended ceramic carrier is an excellent MBBR carrier.

1. Introduction

Oilfield produced water (OPW), designated the wastewater generated after separation from crude oil during the primary separation process, accounts for the majority of the waste derived from oilfield development. Since OPW contains high concentrations of petroleum hydrocarbons, oilfield chemicals, different salts, suspended solids and heavy metals, it can cause considerable environmental impacts if discharged without effective treatment [1]. Nowadays, the petroleum industry faces a huge challenge in meeting increasingly stringent environmental standards.

During the past decades, various technologies such as membrane filtration [2], reverse osmosis [3,4], electrochemical oxidation [5], land disposal [6], and biological treatment [7,8], have been developed for treating OPW. Physical and chemical technologies cannot remove small suspended oil particles and dissolved elements. Besides, chemical treatments may produce hazardous sludge. Compared with physical and chemical processes, biological treatment of oily wastewater can be a cost-effective and environmental friendly method, and more compatible with existing plant facilities and operation [9]. As a prevalent biological wastewater treatment process, however, activated sludge process is unsatisfactory to remediate OPW because of filamentous bulking and foaming, high suspended solid content, and the presence of complex components in the wastewater [10].

Biofilm processes have been successfully used in wastewater treatment for over a century, and have proved to be reliable for contaminant removal without some of the problems encountered in activated sludge processes [11]. The moving bed biofilm reactor (MBBR) process has been employed successfully in treatment of drinking water, municipal and various types of industrial wastewater [12]. The MBBR has been devised to offer the advantages of the biofilm system (compact, stable removal efficiency and simplicity of operation) without its shortcomings (medium channeling and clogging) [13]. The core of MBBR is the supporting media for microbial adhesion. The properties of biocarrier can directly influence the ability to form biofilms, the quantity of biomass and the efficiency of treatment. A wide range of biofilm carriers, including polyethylene, polyurethane (PU), granular activated carbon, sand and diatomaceous earth, have been used in MBBR systems [14]. In general, polymer carriers have low density and excellent processability, and expansion can be obtained easily as the water circulates. However, the poor hydrophilicity and biocompatibility of plastic carriers often lead to some deficiencies in the rate and amount of biofilm culturing, and the adhesion extent of biofilm. In addition, biomass buildup and reactor head-loss may occur due to rapid clogging and jamming of the plastic carriers below the upper grid, inducing the upper retention grid to break [15]. Inorganic carriers such as limestone, zeolite, activated carbon, graystone, slag, and

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Table 1
Characteristics of the oilfield produced water.

pH	6.4–6.7
COD, mg/L	343–365
BOD_5, mg/L	82–95
TOC, mg/L	82–89
TPH, mg/L	24–28
NH_3-N, mg/L	41–48
Total nitrogen, mg/L	68–71
Total phosphorus, mg/L	0.19–0.22
$Fe^{2+}/^{3+}$, mg/L	9.5–9.8
Mg^{2+}, mg/L	25–26
Ca^{2+}, mg/L	165–167
S^{2-}, mg/L	1.5–1.6
SO_4^{2-}, mg/L	36–38
Total dissolved solids, mg/L	4950–5230

coke have good mechanical strength and biocompatibility. However, relatively high densities of inorganic carriers can increase the energy requirement for expansion.

Many efforts have been devoted to the development and application of novel biocarriers. Chen et al. [16] used a tube chip type of polymer mixed with nano-size inorganic materials as biocarrier to treat pesticide wastewater by integration of MBBR and Fenton-coagulation pretreatment. The results showed that the MBBR had excellent advantages such as flexibility, easy operation and strong resistance against loading impact. Delnavaz et al. [13] utilized light expanded clay aggregate (density 0.55 g/cm^3) as carrier for a toxic and hard biodegradable aniline removal, and up to maximum of 90% removal efficiencies were obtained for COD of 2000 mg/L after 3 days of treatment. The PU foam and biodegradable polymer polycaprolactone (PCL) particles were applied by Chu and Wang [15] to treating wastewater with a low C/N ratio using MBBRs. The results exhibited that total organic carbon and ammonium removal efficiencies were 90% and 65%, respectively, in the reactor filled with PU carriers, compared with 72% and 56% in the reactor filled with PCL carriers.

With the advance of technology, searching for novel, low-cost, long-life, and easily attached-growth biomass carriers becomes a research subject. In the present study, a novel suspended ceramic biocarrier was developed and employed as MBBR carrier to treat OPW. The performance of the carriers was investigated, and the characteristics of pollutant removal were evaluated.

2. Materials and methods

2.1. Chemicals

2,3,5-Triphenyltetrazolium chloride (TTC) was purchased from Sigma (St. Louis, MO, USA). All other chemicals and solvents used were of analytical or glass-distilled grade and were obtained from commercial supplier (Beijing Chemical Reagent Company, China).

2.2. Wastewater

The OPW was collected on 7 April 2010, from a water injection pipe of Henan Oilfield, Central China. The wastewater was allowed to settle for 24 h, and the floating crude oil was discarded. The wastewater was stored at 4 °C until required. Characteristics of the OPW sample are listed in Table 1.

2.3. Preparation and modification of suspended ceramic biocarriers

Fly ash, collected from Jingdezhen Power Plant in Jiangxi Province in China, was used as raw materials. The fly ash was crushed in a mortar, dehydrated at 120 °C for 2 h and then heated at 900 °C for 6 h until the fly ash had constant weight to remove remaining carbon and other decomposable components.

Preparation of suspended ceramic body was performed according to Sepulveda et al. [17–20]. Briefly, fly ash powder (16 g) was mixed with deionized water (16 mL), the monomer (acrylamide, 5 g), the cross-linker (*N*,*N*′-methylene bisacrylamide, 3 g), and the dispersant (2 drops) to produce a slurry. The mixture was then vigorously stirred to produce foam with the assistance of Triton X-100 (0.1 mL). Polymerization was triggered by the addition of the initiator (0.52 g/mL ammonium persulfate solution, 2 mL) and the catalyst (tetramethylethylene diamine, 3 mL). The foam was immediately cast into moulds prior to the gelation. The sample was dried at 150 °C, and then sintered in a gas furnace at 1250 °C for 2 h with heating rate of 5 °C/min.

In order to obtain higher porosity, the prepared suspended ceramic body was modified with sepiolite. Raw sepiolite powder was received from Leping, Jiangxi Province, China. Sepiolite samples were treated before using in the experiments as follows [21]: the raw sepiolite was sieved through a 20-mesh sieve to remove the impurity; then mixed with deionized water in proportion of 1:20 and stirred at 2000 rpm for 24 h; the suspension was centrifuged, and the supernatant was discarded and the clay particles on the top layer of the sediment was scraped off by using spatula; the solid sample was dried at 105 °C for 24 h, ground then sieved by 50 μm sieve; the particles below 50 μm were used in further experiments; the clay particles were then suspended in deionized water and acidified with 1 M HCl to pH 3.0 to remove the carbonates and then centrifuged, followed by calcination at 300 °C for 4 h. The ceramic foam body and refined sepiolite particles were mixed with distilled water, and then subjected to ultrasonic agitation (480 W; UR1, Retsch GmbH, Carl Stuart Limited, Germany) for 2 min. Afterwards, the mixture was dried at 120 °C and then mixed with the organic binder (5% aqueous PVA-1750 solution). After drying at 80 °C for 12 h, the granules were sintered between 550 and 650 °C in intervals of 50 °C for 2 h. The Brunauer–Emmett–Teller (BET) specific surface area of biocarrier was determined with ASAP 2020 M + C (Micromeritics, America). Flexure strength was determined by the three-point bending method. The bulk density was computed from the weight-to-volume ratio.

2.4. Set-up and operation of reactors

Three identical reactors made of pexiglas with a useful volume of 5-L were continuously fed. The first reactor (R1) contained only activated sludge taken from a wastewater treatment plant at Yanshan Petrochemical Co., Ltd., Beijing. The second reactor (R2) was filled with the suspended ceramic granules as biomedia. In the third reactor (R3) ceramic granules modified with sepiolite was added. The amount of carrier corresponded to a volume fraction of 50%, for both reactors. Fig. 1 shows a schematic representation of one MBBR system and the suspended ceramic biocarriers. The activated sludge reactor has the same configuration as shown in Fig. 1; the only difference is that there is no carrier in the activated sludge reactor.

The operation of the three reactors was started by inoculating 0.5 L of fresh activated sludge. After inoculation, OPW was introduced into the reactors to obtain a working volume of 5 L. Air was diffused in order to supply oxygen to the biomass and to mix the carriers. After aeration for 12 h, one-half of the mixed liquid was drained off and then the same volume OPW was introduced for the next 12 h of the operation. This procedure was repeated during the first week of the startup. After that, the feed mode of wastewater was changed into continuous flow mode during a period of 183 days. All laboratory experiments were conducted at room temperature and dissolved oxygen (DO) concentration was always controlled above 3 mg/L during the operation by

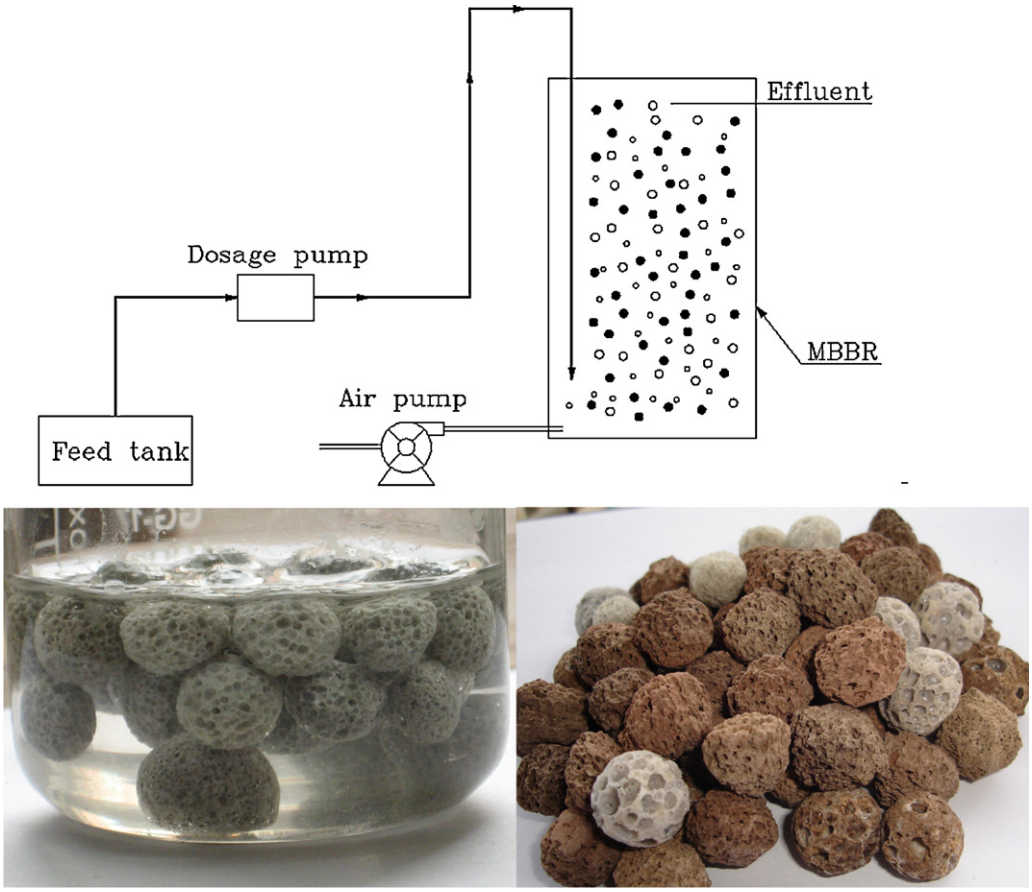

Fig. 1. Schematic diagram of the aerobic MBBR system (above) and photos of suspended ceramic biocarriers (below).

regulating the aeration rate. The variations in operational parameters are listed in Table 2.

As shown in Table 1, the content of N in the OPW was sufficient to support the COD removal. However, the amount of phosphorus was far below the conventional treatment standard of 100:5:1. Therefore, K_2HPO_4 used as a phosphorus source was added to the wastewater based on a COD:P ratio of 100:1.

2.5. Analytical methods

DO, pH, and temperature were monitored *in situ* daily using portable devices during the experiments. Water samples were centrifuged at 8000 rpm for 5 min, and then analyzed according to standard methods [22]. Briefly, COD was determined by titrimetric method after dichromate closed reflux. BOD_5 was measured via the oxygen consumption of bacteria breaking down organic matter in the sample over a 5-day period under standardized conditions. NH_3-N was determined by Nessler's reagent colorimetry. Water samples that could not be analyzed immediately were frozen at −20 °C prior to analysis. Biofilm thickness was measured in 10 different parts of a carrier and then averaged, using a dissecting microscope (Nikon, Japan) equipped with an ocular micrometer.

Table 2
Operational conditions during the experiment.

Phase	Operational days	HRT (h)
I	1–7	0
II	8–95	36
III	96–155	18
IV	156–190	10

Morphology of carriers was observed with a field emission scanning electronic microscope (SEM) (JSM-6700 F, JEOL, Japan).

2.6. Biochemical analyses

Influent and effluent samples were filtered through 0.22 μm membrane filter to obtain wastewater filtrate. Aliquots (20 μL) of the bacterial reagent (*Photobacterium phosphoreum*) were added to a series of dilutions of filtrates. The salinity of the samples was adjusted to 2% with reagent-grade NaCl. The luminescence of bacteria was measured after 15 min of exposure at 15 °C, using a SDI M500 analyzer (SDI, USA). Microtoxicity values were the average of five replicates of each filtrate sample, expressed as EC_{50}, which was defined as the effective nominal concentration of elutriate (volume percent) that reduces the intensity of light emission by 50%.

The activity of microorganisms attached to the biomedia was measured using the TTC dehydrogenase test adopting the method described elsewhere [23]. In brief, one entire ceramic carrier was taken from the reactors at regular intervals and immersed into the reagents. The mixture was incubated and microbial activity was measured. Results were expressed as μg triphenylformazan (TPF)/g, based on the mass of the carrier after sintering (550 °C, 24 h). Each measurement was made in triplicate, and the average of three independent measurements was presented.

2.7. Instrumental analyses

Analyses of saturated and aromatic fractions were carried out using a simplified sample clean-up and a gas chromatography–mass spectrometric (GC–MS) system. Briefly, wastewater samples were extracted three times by liquid–liquid

Table 3
Characteristics of synthesized suspended ceramic biocarriers with or without sepiolite modification.

Item	Original	Modified
Bulk density, g/cm^3	0.92–0.96	0.93–0.98
Flexure strength, MPa	2.5–3.0	2.5–3.0
BET specific surface area, m^2/g	3.8–4.1	5.6–5.9

technique with dichloromethane for pH 2, 7, and 12. The three extract layers were combined and condensed to 1 mL in a rotary evaporator, and then fractionated by silica-gel column chromatography to separate saturate and aromatic fractions. The fractions were analyzed by an Agilent7890-5975c GC–MS equipped with an Agilent HP-5MS fused silica capillary column (60 m × 0.25 mm × 0.25 μm). Concentrations were determined for the following 16 priority polycyclic aromatic hydrocarbons (PAHs): naphthalene; acenaphthene; acenaphthylene; fluorene; phenanthrene; anthracene; fluoranthrene; pyrene; benz[a]anthracene; chrysene; benzo[b]fluoranthene; benzo[k]fluoranthene; benzo[a]pyrene; indeno[1,2,3-cd]pyrene; dibenz[ah]anthracene; and benzo[ghi]perylene. An aliquot of the above-obtained extract without fractionation was examined by electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS). Additional details have been published elsewhere [24].

2.8. Statistical analysis

The data are presented in terms of arithmetic averages of three replicates values ± standard deviation. Statistical analysis (arithmetic average and standard deviation) was made using SPSS (Statistical Product and Service Solution) for Windows. The comparisons between treatments were done using the one-way analysis of variance (ANOVA). The statistical significance in this analysis was defined at $p < 0.05$.

3. Results and discussion

3.1. Characteristics of suspended ceramic biocarriers

Biocarriers for MBBR should be provided with large surface area, a certain strength, no blocking and congregation, and good expansion during the operation. The photos of synthesized ceramic biocarrier are shown in Fig. 1. The ceramic granule has a diameter of around 1.25 cm. The bulk density is slightly less than that of water (Table 3). The density of the ceramic granule would be close to that of water after biofilm growth, therefore only gentle agitation or aeration was needed to produce good carrier expansion. As shown in Table 3, the three-point flexure strength of the ceramic granule did not change after modification; however the BET specific surface area was increased significantly. Sepiolite, which has a $Si_{12}Mg_8O_{30}(OH)_4(OH_2)_4{\cdot}8H_2O$ unit-cell formula, is a magnesium hydrosilicate with a micro-fibrous structure and has a theoretical high surface area (more than 200 m^2/g) and high chemical and mechanical stability [25]. In the region of high temperature (>800 °C), however, the collapse of micro-fibrous structure of sepiolite will occur, and micropores will be destroyed [26]. Therefore the sintering temperature was controlled below 650 °C during the modification process.

The mechanical characteristics of the carriers are important in the MBBRs. The three-point flexure strength of the carriers was kept at 2.5–3.0 MPa after 190 days of reactor operation, indicating a good durability of the carriers. In addition, the average weight of the carriers after calcination (500 °C in air) only decreased by approximately 5% after 190 days of operation, indicating a good abrasion resistance of the carriers.

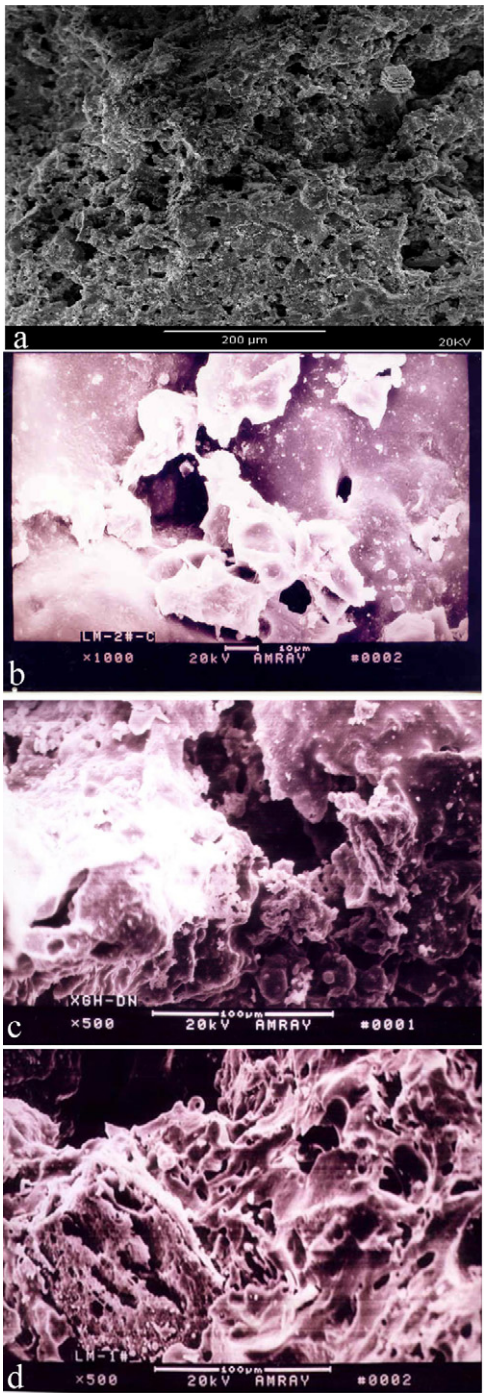

Fig. 2. Surface changes of biocarriers during the operation of R3 (filled with sepiolite-modified ceramic granules): (a) clear carrier; (b) carrier cultivated for 2 days; (c) carrier cultivated for 7 days; and (d) photo of a carrier at the end of the experiment (190 days).

3.2. Biomass and biofilm characteristics

The pH value of the feeding OPW was always kept at 6.4–6.7 and no further pH adjustment was used for the system. During the operation days, the pH stayed at the range 6.1–6.5 for the three reactors. The sludge retention time in the three reactors was maintained at 10 days by sludge withdrawal from the reactors once every day.

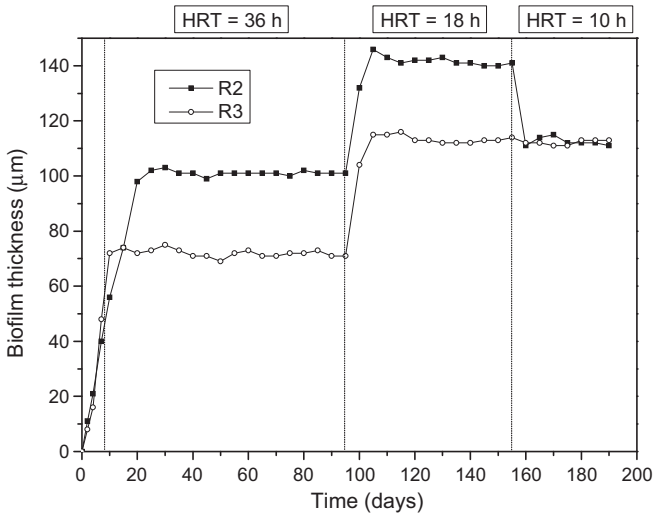

Fig. 3. Grow curves of biomass. R2: the MBBR filled with unmodified ceramic media and R3: the MBBR filled with sepiolite-modified ceramic media.

To visualize the presence of biofilm on the surface of support moving in the reactor, SEM images of clean and biofilm-containing carriers were prepared. The surface of clean biocarrier (Fig. 2a) was bare. On day 2 only a part of the carrier was covered with biofilms (Fig. 2b). One-week operation of the reactor led to the formation of biofilms with a thickness larger than 45 μm (Fig. 2c). After 190 days of cultivation, the structure of the biofilm was rather dense (Fig. 2d).

Thickness of biofilm attached on the carrier was measured on the 2nd, 4th, 7th, 10th days and every 5 days afterwards. Fig. 3 shows that the growth curves of biofilms in R2 and R3 varied with time. Biofilms in R2 and R3 vigorously grew at a transient condition from 4th to 10th and 20th days, respectively. Under a steady-state condition, biofilms reached a maximum growth rate and biofilm thickness in R2 was larger than that in R3. This is because that the sepiolite-modified media has a larger specific surface area than the unmodified ones. Under the same conditions (i.e. suspended biomass amount, organic loading), the amount of attached biomass was identical between R2 and R3. Larger the specific surface area, thinner was the biofilm. However, the time required to reach steady state was significantly reduced due to the modification of biocarrier with sepiolite (10 and 20 days for R2 and R3, respectively), which can be attributed to the powerful adsorbent properties of sepiolite. Hrenovic et al. [27] demonstrated that sepiolite was a good carrier of immobilized and metabolically active phosphate-accumulating bacteria, and the number of microorganisms immobilized onto sepiolite was higher in purified form than in original form.

It was also observed that biofilm thickness on media increased as the hydraulic retention time (HRT) was decreased from 36 to 18 h. When the HRT was further reduced to 10 h, biofilm thickness on sepiolite-modified media remained the same, whereas significantly decreased in the case of unmodified media. The decrease in biofilm thickness on media at higher HRT may be attributed to the lack of sufficient substrate and DO in inner layers and dominance of anaerobic conditions in the film, which led to the gradual sloughing of biofilm [28]. A steady state biofilm thickness is dependent on the comprehensive effects of biofilm growth rate, mechanical shearing, and subsequent detachment [29].

3.3. Performance of treatment systems

Considering that COD and NH_3-N are the two leading monitoring indices of emission of petrochemical wastewater, these two parameters were monitored every two days during the treatment process.

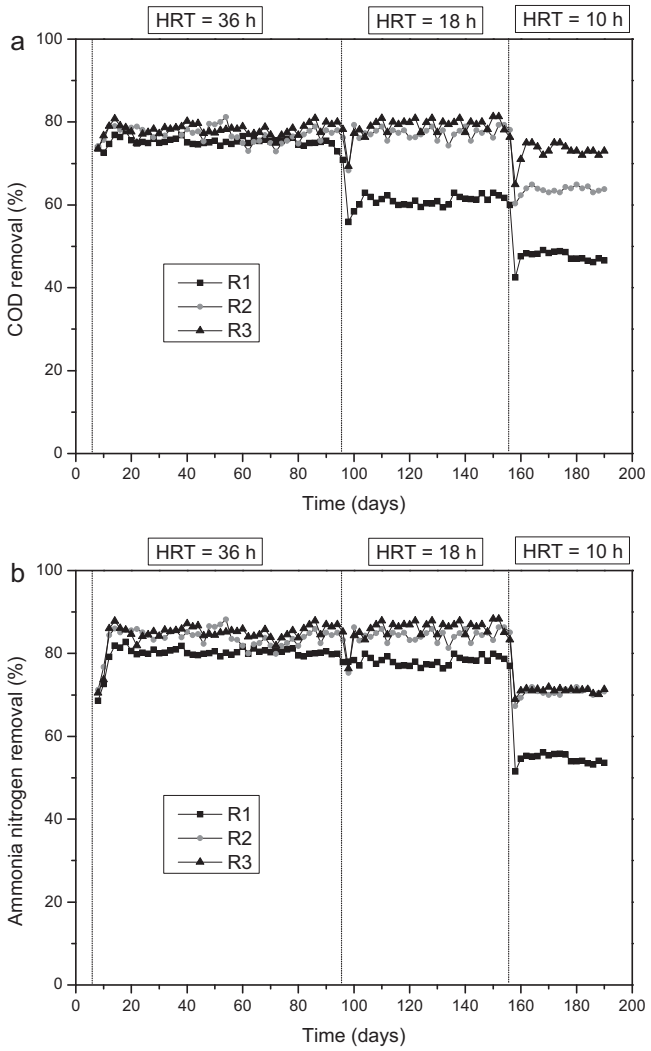

Fig. 4. COD (a) and NH3-N (b) removal efficiency variations at HRTs of 36, 18, and 10 h. R1: the activated sludge reactor; R2: the MBBR filled with unmodified ceramic media; and R3: the MBBR filled with sepiolite-modified ceramic media.

3.3.1. COD removal

According to HRT variations from 36 to 10 h, organic loading was increased from 1.17 to 4.21 kg COD/m^3 d. The average COD removal efficiencies in the three reactors during the operating period are shown in Fig. 4a. The results showed that at an HRT of 36 h, the average efficiencies for COD removal were consistently higher than 73% for the three reactors. It was also interesting to note that there was no significant difference ($p < 0.05$) in COD removal among the three processes at 36 h HRT. When the HRT decreased from 36 to 18 h, however, the COD removal efficiency decreased significantly from average 75.4% to 61.5% for R1 treatment. After a period of adaptation, the COD removal efficiency recovered to previous levels for both R2 and R3 treatment when the HRT was reduced to 18 h, indicating that the MBBRs had a strong capacity to resist shock loading caused by the change in influent flow rate. When the HRT was further reduced from 18 to 10 h, the COD removal efficiencies decreased from an average value of about 62% to 47% for R1, from 77% to 63% for R2, and from 79% to 74% for R3, respectively.

During the experiments, R3 exhibited the advantage over R2 at 10 h HRT. The sepiolite-modified ceramic carrier has a higher specific surface area than the unmodified ones (Table 3). At lower

substrate loadings, sepiolite-modified surfaces were not fully utilized by microorganisms as suggested above that biofilm thickness in R3 was less than in R2. This also indicates that the increasing extent in biofilm thickness was greater for sepiolite-modified media than for unmodified ones with the increase of substrate loading. The specific surface is an important factor influencing the performance of MBBRs. Andreottola et al. [30] found that MBBR and activated sludge pilot plants showed nearly comparable performances in COD removal during the treatment of municipal wastewater, which was attributed to the insufficient specific surface (160 m^2/m^3) of the MBBR plastic media used to overcome the activated sludge system in performance.

In recent years, a considerable number of studies have been published that purport to treat oilfield wastewater using microorganisms. Freire et al. [31] studied COD removal efficiency of acclimated sewage sludge in a sequencing batch reactor (SBR) with different percentages of produced water and sewage. In 45% and 35% (v/v) mixtures of wastewater, COD removal efficiencies varied from 30% to 50%. Baldoni-Andrey et al. [32] evaluated the feasibility of the biotreatment of saline produced water in SBR. Results showed that the biodegradability of the produced water can be obtained, though the salinity was up to 200 g/L. However, a loss of biomass occurred during continuous SBR operation. Pendashteh et al. [33] investigated the biological pretreatment of oilfield produced water in SBR. It was found that 90% COD removal was obtained at salt concentration of 35,000 mg/L and at an organic load rate of 1.8 kg COD/m^3 d. Lu and Wei [24] used the combined process of chemical oxidation and biological degradation to treat oilfield wastewater containing hydrolyzed polyacrylamide (HPAM) in a batch activated sludge reactor. The results showed that under the optimum conditions, the total removal efficiencies of HPAM, total petroleum hydrocarbons, and COD were 96%, 97% and 92%, respectively.

3.3.2. NH_3-N removal

The time course of NH_3-N variation is plotted in Fig. 4b. After the lapse of 4 days, the ammonia oxidation efficiencies were 79%, 84% and 86% for R1, R2 and R3, respectively. The NH_3-N removal of the three reactors remained practically constant in the first two runs. However, NH_3-N removal efficiencies dropped when the HRT was reduced to 10 h. The evidence of nitrification process was confirmed through the determination of effluent nitrate content (data not shown). For phase IV, nitrate concentrations in the reactor effluent decreased significantly, revealing the nitrification collapse for the highest range of applied organic loadings. During wastewater treatment processes NH_3-N can be removed in two ways: (a) assimilation into biomass; (b) ammonia volatilization; and (3) biological nitrification under aerobic conditions and denitrification process under depleted oxygen levels or anoxic conditions [34].

3.4. Biofilm dehydrogenase activity

Dehydrogenase activity (DHA) provides a measure of overall microbial activity and consequently indicates whether stimulation or inhibition of the microbial communities is present. The DHA of attached microorganisms was measured on the 8th, 60th, 120th, and 180th days. The DHA measurements over the time period under different HRT conditions are plotted in Fig. 5. On average, the highest biofilm activity occurred on the 120th day (18 h HRT), followed by that on the 180th day (10 h HRT), with the lowest on the 8th day. In addition, it is also observed that the biofilm in R3 had slightly higher DHA than that in R2. It should be noted that the MBBRs had been operated in continuous flow mode since the 8th day. Wijeyekoon et al. [35] demonstrated that the lower loaded biofilms exhibited the highest DHA, followed by the higher loaded biofilms, with the medium loaded biofilms having the lowest activity. It was also pointed out that the biofilm metabolic activity was affected not only by substrate loading, but also by other physical and biological factors.

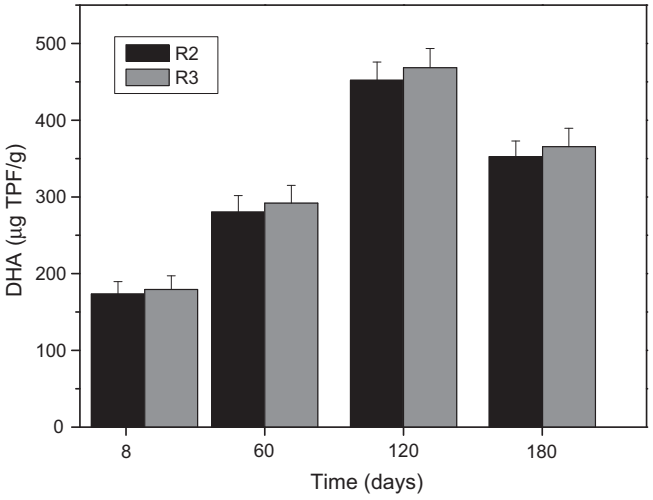

Fig. 5. Time course of changes in dehydrogenase activity of biofilm. R2: the MBBR filled with unmodified ceramic media; and R3: the MBBR filled with sepiolite-modified ceramic media.

Table 4
Biodegradation extents (%) of saturated hydrocarbons in the produced water as determined on the 180th day at 10 h HRT. R1: the activated sludge reactor; R2: the MBBR filled with unmodified ceramic media; and R3: the MBBR filled with sepiolite-modified ceramic media.

	Linear	Branched	Cyclic
R1	58.4 ± 2.9	34.6 ± 3.5	15.2 ± 1.8
R2	71.3 ± 3.1	58.2 ± 3.1	30.6 ± 1.7
R3	82.6 ± 2.7	67.1 ± 2.3	41.2 ± 2.1

3.5. Microtoxicity tests

Microtoxicity assessment gives refined information on the changes in wastewater quality undergoing treatment. Microtox analysis was performed on the 8th, 60th, 120th, and 180th days, to monitor toxicity levels of the bioremediated OPW and the results are shown in Fig. 6. It can be found that the acute toxicity to the

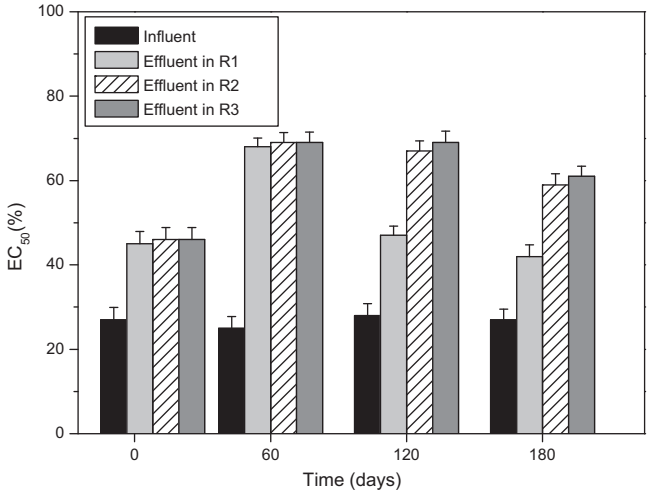

Fig. 6. Time course of changes in microtoxicity of influents and effluents. R1: the activated sludge reactor; R2: the MBBR filled with unmodified ceramic media; and R3: the MBBR filled with sepiolite-modified ceramic media.

Table 5
Concentrations of the 16 priority PAHs in influent and effluent as determined on the 180th day at 10 h HRT. R1: the activated sludge reactor; R2: the MBBR filled with unmodified ceramic media; and R3: the MBBR filled with sepiolite-modified ceramic media.

Concentration (μg/L)				
	Influent	Effluent of R1	Effluent of R2	Effluent of R3
Naphthalene	125.3 ± 4.9	43.9 ± 1.7	25.6 ± 1.8	26.4 ± 1.6
Acenaphthylene	14.2 ± 1.2	5.6 ± 0.4	4.3 ± 0.5	4.6 ± 0.6
Acenaphthene	18.5 ± 1.6	8.3 ± 0.7	6.9 ± 0.8	6.7 ± 0.8
Fluorene	78.4 ± 4.2	42.6 ± 2.8	31.5 ± 2.7	30.6 ± 3.1
Phenanthrene	329.3 ± 8.4	116.5 ± 7.4	84.3 ± 6.5	67.4 ± 5.3
Anthracene	32.4 ± 2.1	11.9 ± 1.1	8.5 ± 0.9	7.6 ± 0.9
Fluoranthrene	46.8 ± 2.5	15.3 ± 1.0	9.6 ± 0.8	7.5 ± 0.9
Pyrene	55.6 ± 2.4	37.1 ± 2.0	25.7 ± 1.6	22.5 ± 1.4
Benz[a]anthracene	18.5 ± 1.3	11.6 ± 0.9	8.5 ± 0.6	7.3 ± 0.7
Chrysene	216.8 ± 11.3	147.3 ± 8.3	106.5 ± 7.4	93.3 ± 7.8
Benzo[b]fluoranthene	54.3 ± 5.8	32.8 ± 4.5	24.9 ± 3.6	18.6 ± 3.3
Benzo[k]fluoranthene	8.1 ± 0.9	5.4 ± 0.6	3.6 ± 0.4	3.5 ± 0.4
Benzo[a]pyrene	11.4 ± 1.3	6.5 ± 0.6	4.8 ± 0.6	4.3 ± 0.5
Indeno[1,2,3-cd]pyrene	2.2 ± 0.3	1.3 ± 0.2	0.8 ± 0.1	0.7 ± 0.1
Dibenz[ah]anthracene	3.5 ± 0.4	2.4 ± 0.1	1.5 ± 0.2	1.3 ± 0.1
Benzo[ghi]perylene	7.4 ± 1.1	4.9 ± 0.4	3.4 ± 0.4	3.1 ± 0.3

bacterium *P. phosphoreum* decreased after the start-up of reactors. However, as the HRT decreased from 18 to 10 h, the reductions in the toxicity of treated wastewater declined. This may be due to the less extent of biodegradation of some toxic intermediates under high HRT conditions. Overall, R3 treatment showed the greatest reductions in microtoxicity, followed by R2 treatment, with R1 treatment having the lowest reductions. In addition, the differences in microtoxicity reduction of treated wastewater between the activated sludge process and the MBBR treatment were significant on the 120th and 180th days (18 and 10 h HRT, respectively) ($p < 0.05$). Therefore, it is concluded that the MBBR was a quite efficient process for decontaminating the OPW. It has been reported that the attached biomass can be up to 500 times more resistant to antibacterial agents than freely suspended ones [36].

3.6. Biodegradation of petroleum hydrocarbons

GC analyses taken on days 180 showed the degradation extents of linear, branched and cycloalkanes in the OPW by the three processes (Fig. S1, Supporting Information). It can be observed from Table 4 that most of linear alkanes were removed after biotreatment, with relatively low degradation of cycloalkanes. The extent of biodegradation was significantly higher in R2 and R3 than in R1 ($p < 0.05$).

The degradation of PAHs was confirmed by monitoring the disappearance of the 16 priority PAHs in the influent and effluent streams. Table 5 lists the concentration changes of the 16 priority PAHs during treatment. The total content of the 16 PAHs were: 1022 μg/L in the influent stream; 493 μg/L in the effluent stream of R1 corresponding to a degradation efficiency of 52%; 351 μg/L in the effluent stream of R2 corresponding to a degradation efficiency of 65%; and 306 μg/L in the effluent stream of R3 corresponding to a degradation efficiency of 70%. Naphthalene, phenanthrene and chrysene were the three major constituents, representing 12%, 32%, and 21%, respectively, of the total 16 PAHs found in the influent oil field wastewater that was the characteristic of Henan Oilfield. Of the minor constituents, indeno[1,2,3-cd]pyrene, dibenz[ah]anthracene, and benzo[ghi]perylene were also degraded with respective efficiencies of 41%, 30%, and 34% for R1, 64%, 57%, and 54% for R2, and 68%, 63%, and 58% for R3.

3.7. Analysis of biodegradation extent

Since its introduction in 1974 by Comisarow and Marshall [37], FT-ICR MS has advanced to become an extraordinarily versatile mass spectrometric technique, which affords ultrahigh mass resolving powers $m/\Delta m_{50\%} > 400{,}000$ and mass accuracy < 0.5 ppm, allowing the molecular formula assignment of 10,000+ ions in a single mass spectrum [38].

In this study, the calibrated negative-ion FT-ICR mass spectra of the oils extracted from the influent and effluents taken on days 120 are presented in Fig. S2, Supporting Information. In each spectrum, more than 8000 peaks with a signal to noise ratio of 3 were detected in the range. The broadband mass spectra clearly showed that the molecular weight distribution of polar compounds was greatly altered by biodegradation. The weight-average molecular weight was 483 Da for the influent samples, and decreased with biodegradation to 425, 403 and 392 Da for the effluent samples in R1, R2, and R3, respectively.

Kim et al. [39] devised an index to estimate the extent of biodegradation in crude oil (Fig. S3, Supporting Information). This index is based on the ratio of acyclic to cyclic naphthenic acids (A/C ratio) and is calculated as follows:

$$A/C \text{ ratio} = \frac{\sum O_2 \;_{z=0}}{\sum O_2 \;_{z=-2,-4,-6}} \quad (1)$$

The A/C ratio decreases as the extent of biodegradation increases. For O_2-containing compounds with the molecular formula $C_nH_{2n+z}O_2$, n is the number of carbon atoms, z is the number of hydrogen atoms that are lost as the structures become more compact. In this study, the oils extracted from the effluents on the 180th day have an Acid Biodegradation Index of 2.6 (moderately degraded), 3.5 (moderately degraded), and 4.1 (severely degraded), for R1, R2, and R3, respectively. It can be concluded, therefore, that the MBBR treatment has a major advantage in terms of biodegradation degree of oils indicated by the Acid Biodegradation Index. In addition, the MBBR filled with sepiolite-modified ceramic biomedia exhibited a higher degree of oil biodegradation than that filled with unmodified ones. This can be attributed to unique properties of sepiolite such as high surface area, and great adsorptive capacity. However, further research is needed to reveal the concrete mechanism of sepiolite-enhanced petroleum biodegradation.

4. Conclusions

This investigation demonstrated that MBBR filled with the suspended ceramic biocarrier was an effective and feasible process for removal of COD, petroleum hydrocarbons, and ammonium nitrogen from the OPW in the tested organic loading range of 1.17–4.21 kg COD/m^3 d, compared to the conventional activated

sludge treatment. The modification of ceramic biocarrier with sepiolite produced positive outcomes in the wastewater treatment efficiency. At HRT of 18 h, the concentrations of NH_3-N and COD of effluent in the MBBRs could satisfy the professional emission standard (grade one) (NH_3-N < 15 mg/L, COD_{Cr} < 100 mg/L) of petrochemical industry of PR China (GB4287-92).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.09.001.

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