Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.20180

64 (2017) 40–47
February

Waste tire chunks as a novel packing media in a fixed-bed sequence batch reactors: volumetric removal modeling

Zahra Derakhshan[a], Mohammad Hassan Ehrampoush[a], Mohammad Faramarzian[b], Mohammad Taghi Ghaneian[a], Amir Hossein Mahvi[c,d,*]

[a]*Environmental Science and Technology Research Center, Department of Environmental Health Engineering, Shahid Sadoughi University of Medical Sciences, Yazd, Iran, emails: derakhshan63@ssu.ac.ir (Z. Derakhshan), ehrampoush@ssu.ac.ir (M.H. Ehrampoush), mtghaneian@yahoo.com (M.T. Ghaneian)*
[b]*Department of Environmental Health Engineering, Faculty of Health, Shiraz University of Medical Sciences, Shiraz, Iran, email: mfaramarzi1985@yahoo.com*
[c]*Center for Solid Waste Research (CSWR), Institute for Environmental Research (IER), Tehran University of Medical Sciences, Tehran, Iran. Tel. +982144729729; Fax: +982188950188; email: ahmahvi@yahoo.com*
[d]*Department of Environmental Health Engineering, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran*

Received 24 February 2016; Accepted 21 August 2016

ABSTRACT

Waste tires feature environmentally sensitive and new recycling techniques are necessary. The present study evaluated waste tire chunks (WTCs) as a novel media for biological growth and biofilm development in fixed-bed sequence batch reactor (FBSBR) as an alternative method of recycling scrap tires. To assess WTCs as a biofilm carrier, two types of operation means sequencing batch reactor (SBR) and adding WTCs into SBR (FBSBR) were used to treat municipal wastewater. The FBSBR was fed with four concentrations synthetic wastewater at four hydraulic retention times (HRTs). An experimental model was used to study the kinetics of substrate consumption in biofilm. Soluble chemical oxygen demand (SCOD) removal efficiency was 90%–96% for the FBSBR compared with 85%–95% in an SBR. The use of WTCs as a media for biomass production was assessed by monitoring the mixed liquor suspended solid (MLSS) concentrations vs. COD removal for both reactors. The results revealed that the sludge production yield (Y_{obs}) was significantly less in the FBSBR compared with the SBR. It also produced less sludge and recorded a lower stabilization ratio (volatile suspended solids/total suspended solids). The findings show that the Stover–Kincannon model was the best fit ($R^2 > 99\%$).

Keywords: Waste tire; Packing media; FBSBR; Biofilm; Modeling; Sludge yield

1. Introduction

Waste tires are a major environmental problem worldwide. The current waste tire recycling market is small compared with the annual number of waste tires generated globally (17 million T) [1,2]. Waste tires are nearly nondegradable and take up landfill space. If not properly disposed of, they can hold water that provides a breeding ground for mosquitoes and facilitate the spread of mosquito-borne disease. It is essential to develop new markets for waste tires [3,4].

Tire fires are common occurrences and cause serious air, water, and soil pollution; however, waste tire has a high heat value and is used as supplemental fuel in cement kilns and paper mills [5,6]. Waste tires can also be recycled as a roadway pavement material, refuse-derived fuel, or reproduced as tires. They are also used to produce rubber mats, roadway guardrails, as engineered protective cushions or bumpers,

* Corresponding author.

and for building and construction materials [7]. In marine applications, they are used as a wave breaking material, as ship/dock protective bumpers, and to construct artificial reefs in the ocean farming industry [4]. Nevertheless, these markets are small compared with the number of tires generated each year. It is of interest to explore new applications/markets for the scrap tire industry [1,4].

Removal of organic materials by biological oxidation is a foundation technology in wastewater treatment [8–10]. Among these technologies, the sequencing batch reactor (SBR) offers uniquely flexible operation, compact structure, and simple construction [11,12]. An attached growth system, however, provides different perimeters for various types of microorganisms so that each can find its niche. Such a system offers a higher substrate removal rate, greater system stability, simplicity of operation, handling of shock loads, reduced need for power, lower sludge production, and overall efficiency that clearly exceeds conventional methods of wastewater treatment. A hybrid system combining SBR and biofilm has been proposed to realize the compact structure and flexible operation with high efficiency [13].

One type of hybrid system is the fixed-bed sequence batch reactor (FBSBR) developed based on conventional activated sludge and biofiltering processes. Studies have proven that FBSBR possesses attractive properties such as high biomass, high chemical oxygen demand (COD) loading, strong tolerance of loading, and no sludge bulking problem [12]. The FBSBR can maximize sludge retention time (SRT) in the biofilm and has the potential for operating a suspended activated sludge system with a relatively short hydraulic retention time (HRT). Moreover, in FBSBR, microorganisms with different SRTs can be developed in a single reactor [12,14,15].

Several materials have been tested as carriers (media) in sequencing batch biofilm reactors (SBBR). Soltani et al. investigated the effects of peach pits as media on the efficiency of a FBSBR. Their study showed that when organic loading was 12 kg COD/m^{3}d, organic matter removal in the FBSBR and SBR was 71.84% and 56.57%, respectively, and SRT decreased from 40 to 19.8 d [16]. Dutta et al. studied the effects of granular activated carbon and natural zeolite as attached carriers in anaerobic SBBR and showed that the addition of carriers improved both the COD removal efficiency and biogas production [17]. A summary of research on the SBBR is presented in Table 1. This study was conducted to compare discrepancies in operation efficiency when waste tires directly added into SBR and the effects of this carrier in the SBR under organics shock loading were tested. The present study evaluated the use of waste tire chunks (WTCs) as a suitable biocarrier for biological attached growth and biofilm development in FBSBRs and as an alternative form of recycling scrap tires. Also, this study intended to investigated the removal of different concentrations of organic pollutants from aqueous environments at different HRTs using a consortium of microorganisms in an FBSBR with WTCs as packing media.

2. Materials and methods

Two reactors (SBR and FBSBR) were operated in parallel under the same conditions to determine the effectiveness of WTCs as a media for biological removal of organic carbon, to improve sludge quality, and to reduce sludge production yield.

2.1. Preparation of media

The WTCs were obtained from Yazd Tire Company (Yazd, Iran). The tire chunks were measured using a ruler to determine the approximate average size. Physicochemical characterization studies were performed to verify the chemical resistance of the novel packing medium by placing it in glass beakers containing tap water, acidic (pH = 4.9), and basic (pH = 9.2) solutions for 30 d. The media were then removed from the solution, rinsed repeatedly with distilled water, dried in an oven at 60°C for 24 h, cooled in a desiccator, and then reweighed. Weight loss of 1.8% and 2.5% were recorded with the samples placed in acidic and basic solutions, respectively.

2.2. Experimental setup and operating conditions

The experiment was carried out in the SBR and FBSBR at a total volume of 4.7 l, a diameter of 0.1 m, and a height of 0.6 m (Fig. 1). In the FBSBR, WTCs with a porosity of 90%, specific surface area of ~370 m^{2}m^3 and a total volume of 2 l (40%) were fixed to the bottom of the reactor. The air was introduced into the reactors with a microbubble air diffuser, and the air flow rate was controlled with an air flow-meter.

2.3. Pilot start-up

Activated sludge from the Yazd wastewater treatment plant was used to seed the pilot start-up at a volume of ~3.5 l per reactor and a COD of 500 ± 7.54 mg/l. The floc was established over 3 week of aeration and reaction. At this stage, food was added each day. The COD, dissolved oxygen (DO), pH, and temperature of the wastewater were recorded and compared with the results of samples collected at 3 week after pilot start-up. The effluent COD values were similar to

Table 1
Results of research on fixed-bed sequencing batch reactors

Type of reactor	Media	Environment	Efficiency (%)	Reference
Anaerobic/aerobic fixed-bed sequencing	Volcanic pumice stone	Synthetic wastewater	92–94	[18]
batch biofilm reactor	plastic media (polyethylene)		95–96	
FBSBR	Plastic media (polyethylene)	Synthetic wastewater	90–96	[19]
SBBR	Fibrous carrier	Synthetic wastewater	90–95	[20]
Sequencing batch reactor biofilm	Polypropylene carriers	Wastewater	95	[21]

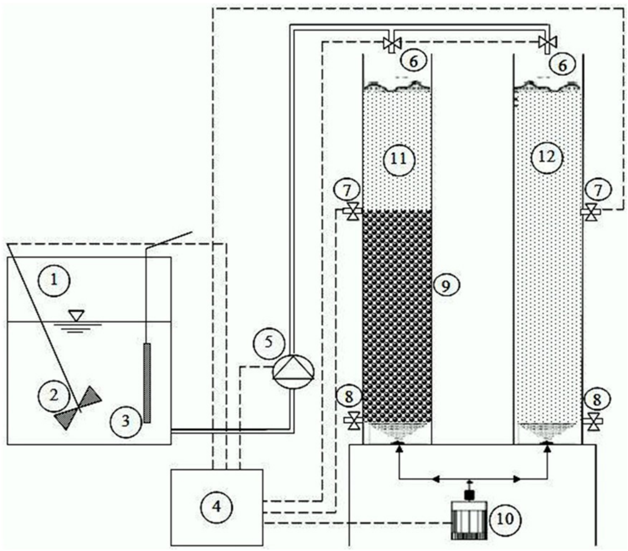

Fig. 1. Schematics of SBR and FBSBR.
Note: 1 – feed tank, 2 – mixer, 3 – heater, 4 – control unit, 5 – peristaltic pump, 6 – feed control valve, 7 – decanter (sampling) valve, 8 – discharge sludge port, 9 – novel packing media, 10 – air compressor, 11 – FBSBR, and 12 – SBR.

each other, which indicates the end of the start-up period. Biofilm had also formed on the media in the FBSBR.

The exchangeable volume of each reactor was 2 l. The reactors were maintained at a fixed temperature of 30°C ± 2.4°C (average temperature of Yazd from January through June is 30°C) using a thermostatic heater. The reactors were operated in cycles of 10, 8, 6, and 4 h. The system was controlled using timer switches (Theben; Germany). Each cycle comprised 4 phases. In phase 1, the reactor was continuously fed for 15 min. In phase 2, the reactor was aerated for 525, 405, 285, and 165 min, depending on cycle duration. In phase 3, settling occurred for 45 min. In phase 4, effluent was discharged for 15 min. Fluctuations in pH were controlled using 0.5 mol/l sodium bicarbonate for an operational pH of 7.31 ± 0.32.

Testing was conducted using synthetic wastewater at concentrations of 500 ± 4.1, 1,000 ± 8.2, 1,500 ± 5.6, and 2,000 ± 4.1 mg COD/l to avoid fluctuations in the feed concentration, provide a continuous source of biodegradable organic carbon, and simulate domestic wastewater (low to high strength). The constituents of the synthetic wastewater are given in Table 2.

The reactors were acclimatized for about 21 d prior to monitoring. Synthetic wastewater was fed into both reactors with a pump. Decanting to remove supernatant was carried out from electric valves. Air was supplied by an electromagnetic blower (Resun; model ACO-018; China), and air diffusers were controlled by a DO meter (model Mi605; Martini Instruments, Hungary). To prevent interference from light (photocatalysis) and algae growth, the columns were covered with aluminium foil. The operational scheme of the system for 16 phases (runs) is shown in Tables 3 and 4. The FBSBR was operated at 4 HRTs using municipal sewage from Yazd (COD = 539 ± 16.6 mg/l) to assess the ability of this system under real conditions.

Table 2
Chemical composition of synthetic wastewater [22,23]

Component	Concentration (mg/L)
Sodium acetate (NaCOOH)	100–200
Ammonium sulfate ($(NH_4)_2SO_4$)	150–700
Potassium phosphate (KH_2PO_4)	150–600
Calcium chloride ($CaCl_2.2H_2O$)	0.37
Magnesium sulfate ($MgSO_4.7H_2O$)	5
Manganese chloride ($MnCl_2.4H_2O$)	0.28
Zinc sulfate ($ZnSO_4.7H_2O$)	0.45
Anhydrous iron chloride ($FeCl_3$)	1.45
Copper sulfate ($Cu_2SO_4.5H_2O$)	0.4
Cobalt chloride ($CoCl_2.6H_2O$)	0.4
Sodium molybdate ($Na_2MoO_4.2H_2O$)	1.25
Sodium bicarbonate ($NaHCO_3$)	20
Sucrose ($C_{12}H_{22}O_{11}$)	Variable (100–800)

Table 3
Operational scheme of runs at 30°C in FBSBR

Run	Cycle time (h)	Initial conc. of SCOD (mg/L)	DO (mg/L)	pH
1	10	500 ± 4.783	4.783 ± 4.783	7.178
2		1,000 ± 6.495	4.243 ± 0.221	7.197
3		1,501 ± 6.509	4.247 ± 0.124	7.315
4		2,002 ± 4.408	4.538 ± 0.201	7.196
5	8	502 ± 3.927	4.263 ± 0.217	7.200
6		998 ± 6.647	4.284 ± 0.108	7.274
7		1,500 ± 5.692	4.237 ± 0.087	7.291
8		1,999 ± 5.209	4.340 ± 0.260	7.331
9	6	500 ± 4.11	4.278 ± 0.198	7.207
10		1,003 ± 8.98	4.305 ± 0.113	7.279
11		1,498 ± 5.43	4.192 ± 0.131	7.273
12		2,000 ± 4.44	4.360 ± 0.339	7.311
13	4	499 ± 4.08	4.348 ± 0.298	7.181
14		997 ± 9.15	4.355 ± 0.128	7.253
15		1,500 ± 5.60	4.264 ± 0.245	6.968
16		2,000 ± 3.25	4.337 ± 0.301	7.391

2.4. Analytical methods

All results were obtained from the bioreactors at steady state. The supernatant from one complete cycle was collected in a container, and the mixed liquor was sampled at the end of aeration time. The DO concentration was measured using a DO meter (model Mi605; Martini Instruments, Hungary) and the pH using a pH meter (HACH; Germany). COD was measured using a spectrophotometer (DR-2000; HACH; Germany). The mixed liquor suspended solids (MLSS), total suspended solids (TSS), volatile suspended solids (VSS), and COD content were determined using standard methods for the examination of water and wastewater [24].

The parameters measured were soluble chemical oxygen demand (SCOD), pH, DO, MLSS, VSS, TSS, and temperature. At a specific run, the pH, DO, and temperature were measured of each sample. These parameters were included in the

Table 4
Operational scheme of runs at 30°C in SBR

Run	Cycle time (h)	Initial conc. of SCOD (mg/L)	DO (mg/L)	pH
1	10	500 ± 4.783	4.328 ± 0.147	7.146
2		1,000 ± 6.495	4.422 ± 4.422	7.142
3		1,501 ± 6.509	4.205 ± 0.119	7.260
4		2,002 ± 4.408	4.163 ± 0.145	7.221
5	8	502 ± 3.927	4.299 ± 0.144	7.319
6		998 ± 6.647	4.344 ± 0.146	7.380
7		1,500 ± 5.692	4.248 ± 0.132	7.339
8		1,999 ± 5.209	4.420 ± 0.152	7.124
9	6	500 ± 4.11	4.275 ± 0.131	7.267
10		1,003 ± 8.98	4.231 ± 0.110	7.297
11		1,498 ± 5.43	4.284 ± 0.123	7.258
12		2,000 ± 4.44	4.191 ± 0.119	7.415
13	4	499 ± 4.08	4.212 ± 0.119	7.408
14		997 ± 9.15	4.316 ± 0.139	7.276
15		1,500 ± 5.60	4.276 ± 0.161	7.378
16		2,000 ± 3.25	4.322 ± 0.104	7.362

list of measurements to ensure the proper operation of the system and the stability of the reactors. The data presented is the average of two or more replicates, and the figures were drawn by using Excel and MATLAB.

2.5. Scanning electron microscopy

The biomass attached to the media was analyzed by scanning electron microscopy (SEM) from samples taken at the end of testing. The samples were prepared by fixing with 2.5% glutaraldehyde in 0.1 M phosphate buffer at pH 7.2 at 4°C overnight. They were then dehydrated with ethanol from 60% to 100% at 20% increments for 10 min at each concentration. The samples were then dried at critical point (equilibrium between gas and liquid phase of CO_2), mounted, coated with gold, and examined by SEM [6,17].

2.6. Modeling

Biological and mathematical models were used to determine relationship between the variables and evaluate the experimental results. The models were also used to monitor and predict performance and optimize plant build at bench and pilot scales. It was confirmed that the criterion for biological growth system design was the volumetric organic load (VOL). The rate of substrate removal was obtained using the hyperbolic relations of the Stover–Kincannon function (Eq. (1)):

$$r_{\text{SCOD}} = r_{\max} \frac{B_{\text{SCOD}}}{k + B_{\text{SCOD}}} \quad (1)$$

where r_{SCOD} is the volumetric SCOD removal; $r_{\max}$ is the maximum rate of volumetric SCOD removal; B_{SCOD} is the SCOD load per unit volume of the reactor; and k is the constant of half velocity. All the parameters are in $\text{kg}_{\text{SCOD}}/\text{m}^3\text{d}$. B_{SCOD} and r_{SCOD} were obtained as follows:

$$B_{\text{SCOD}} = \frac{Q}{V} C_i \quad (2)$$

$$r_{\text{SCOD}} = \frac{Q}{V}(C_i - C_e) \quad (3)$$

where C_i is the SCOD concentration in the influent ($\text{kg}_{\text{SCOD}}/\text{m}^3$), and k is the SCOD concentration in the effluent ($\text{kg}_{\text{SCOD}}/\text{m}^3$) [22,23]. Eqs. (2) and (3) and Tables 3 and 4 were used to compute B_{SCOD} and r_{SCOD} under different conditions. The values for k and $r_{\max}$ were obtained using Curve Expert software.

3. Results and discussion

3.1. Statistical analysis

In this study, analysis of samples was performed for each parameter using variance. The data from the various effluent samples were analyzed in duplicate. If an F-test proved significant at $P < 0.05$ level, the means of each plot were compared by least significant difference. The standard statistical parameters used were mean and standard deviation. The nonparametric Mann–Whitney U test was used in SPSS (version 21) to identify relationships between reactors (Table 5).

3.2. SCOD removal

During system operation, the length of the runs was reduced from 10 to 8 to 6 to 4 h. The most important parameters monitored were VSS, TSS, and SCOD. The trend of SCOD removal in the reactors is shown in Figs. 2 and 3.

3.3. COD removal rate vs. COD loading

Both reactors showed high COD removal efficiency at steady state throughout the study period (Fig. 5); however,

Table 5
Comparison of reactors

Parameter	SCOD	SVI	Yield	VSS/TSS
Sig. (2-tailed)	0.015	0.158	<0.01	<<0.001

Note: Correlation is significant at the 0.05 level (2-tailed).

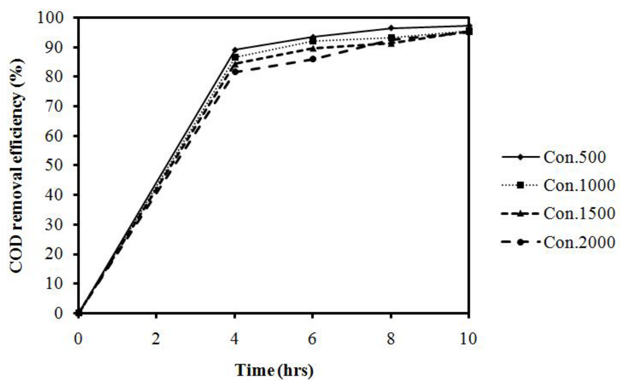

Fig. 2. SCOD removal in FBSBR.

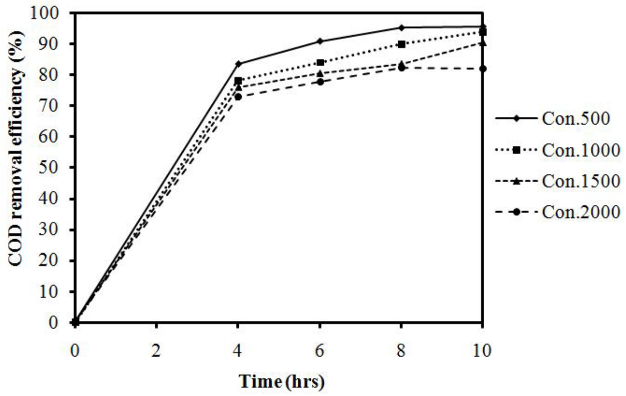

Fig. 3. SCOD removal in SBR.

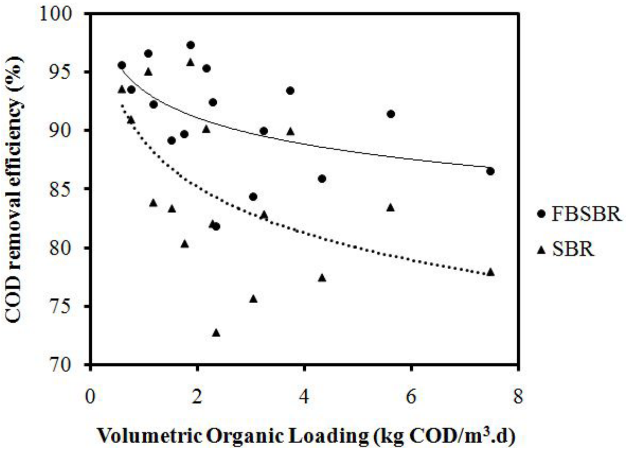

Fig. 4. COD removal efficiency vs. organic loading rate.

no significant differences were observed at lower organic loading rates. The FBSBR showed higher COD removal rate at higher loading rates and the best performance at loadings of 0.5–8 kg_{COD}/m^3 per d. This indicates that the microorganisms in the biofilm combined with the suspended growth sludge in the FBSBR had a greater ability to remove organic carbon and better resistance to shock loading than the single suspended growth sludge in the SBR. Similar findings have been reported for biofilm application in integrated fixed film activated sludge, a moving bed bioreactor, biofilm membrane bioreactor. To better understand the fate of organic carbon in reactors, the initial COD concentration and retention time were plotted vs. COD removal efficiency. Fig. 4 shows that the initial COD concentration positively affected FBSBR performance. This is likely the result of the increase in exposure of the microbial consortium to the contaminants.

3.4. Sludge quantity and quality

3.4.1. Sludge production yield

The sludge production yield vs. organic loading rate in the FBSBR and SBR is shown in Fig. 5. Analysis (Table 6) revealed that the biomass production rate (Y_{obs}) in the FBSBR was significantly lower than in the SBR ($P < 0.01$).

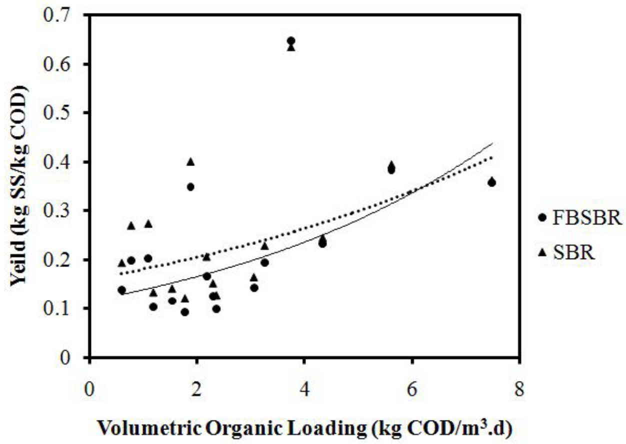

Fig. 5. Sludge production rate vs. organic loading rate.

Table 6
Coefficients k and r_{max} at 30°C for Stover–Kincannon model

Reactor	R^2	SE	r_{max} (kg_{SCOD}/m^3d)	k (kg_{SCOD}/m^3d)
FBSBR	0.996	0.121	5.88	2.39
SBR	0.992	0.169	5.59	2.60

Y_{obs} varied from 0.22 to 0.53 kg SS/kg COD in the SBR and 0.16 to 0.47 kg SS/kg COD in the FBSBR. This means that the sludge production rate was lower in the FBSBR than SBR. This can be attributed to the high cell retention time in the biofilm and to the DO and substrate gradient in the biofilm layer that caused endogenous respiration.

3.4.2. Sludge volume index

Both FBSBR and SBR showed good settling characteristics. Statistical analysis (Table 6) showed no significant difference between reactors in terms of the sludge volume index (SVI) ($P > 0.05$). The SVI for the FBSBR was 83.78–143.61 ml/mg and for the SBR was 80.81–148 ml/mg.

3.4.3. Sludge stabilization ratio

The sludge stabilization ratio (VSS/TSS) varied from 0.67 to 0.89 in the SBR and 0.64 to 0.82 in the FBSBR. VSS/TSS with the loading rates are shown in Fig. 6.

It can be seen that biofilm plays a very important role in the sludge stabilization ratio. Statistical analysis showed that VSS/TSS in the FBSBR was significantly lower than in the SBR ($P < 0.05$). This can be attributed to the higher solid retention in the FBSBR than in the SBR. The effect of SRT on sludge stabilization has been proven. VSS/TSS is inversely related to SRT.

3.5. Modeling of data

The values for k and r_{max} were obtained using Curve Expert software and are presented in Table 6.

Figs. 7 and 8 show modeling of the data from the reactors. The figures and Table 6 indicate that the data obtained from

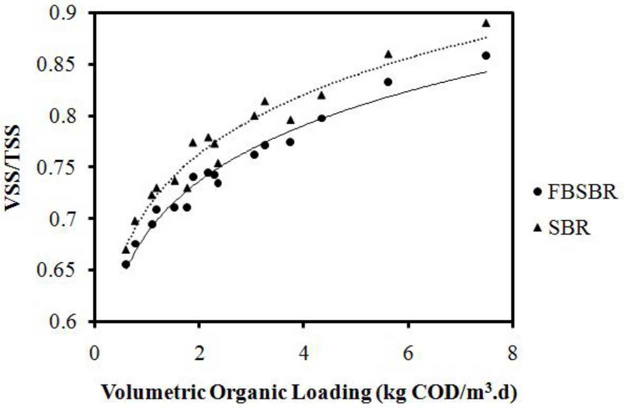

Fig. 6. Sludge characteristics vs. sludge stabilization ratio.

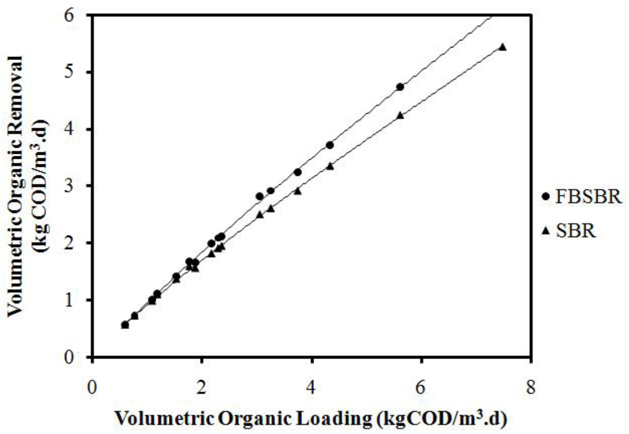

Fig. 7. Organic loading of bioreactors for 0–8 kg COD/m^3.d at 30°C.

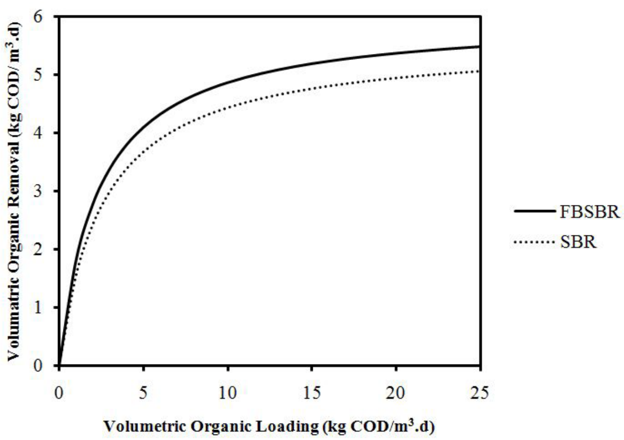

Fig. 8. Organic loading of bioreactors for 0–25 kg COD/m^3.d at 30°C.

the reactors was a good fit ($R^2 > 99\%$), but that the FBSBR had greater potential for removal organic carbon from aquatic environment. This is related to the growth of biofilm on the media. Comparison of the results of the previous studies (Table 1) and the present one shows that this system has high

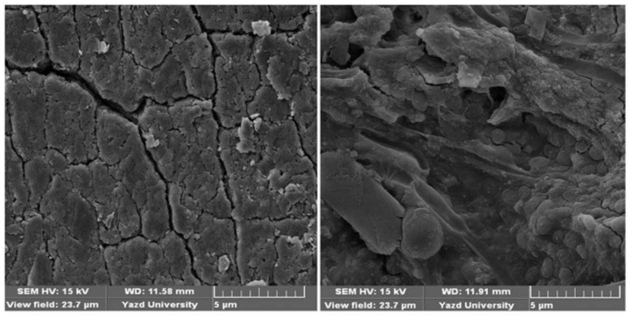

Fig. 9. SEM images of a sample of virgin surfaces of WTCs (left) and WTCs after biofilm formation (right).

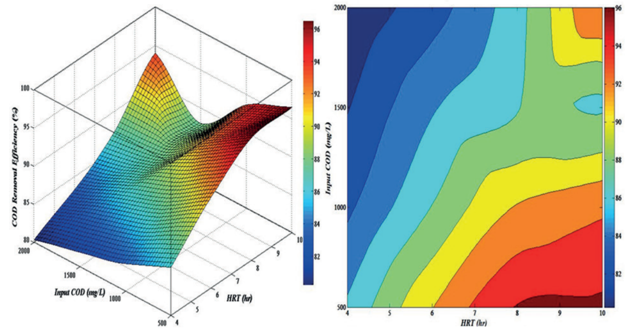

Fig. 10. Effect of initial COD concentration and HRT on COD removal efficiency in FBSBR.

ability for removing organic and inorganic pollutant from aqueous solutions.

3.6. Biofilm morphology

Biofilm is a metabolically active matrix of cells and extracellular compounds. The SEM photographs of biofilm grown on surfaces of the packing media are shown in Fig. 9. A variety of bacterial morphologies were observed in all samples. The increase in density was a result of both colonization and growth dense cell clumping. Microorganisms colonized a significant portion of the surface, which can be attributed to the mixture of a bacterial layer and embedded particles.

The potential for removal of the organic load by the SBR and FBSBR was evaluated at different SCOD concentrations and HRTs. Both reactors showed acceptable SCOD removal efficiencies in all experiments. Figs. 10 and 11 showed the effect of the initial concentration and HRT on reactor efficiency. It can be seen in the SBR that SCOD efficiency decreased as the organic load increased. In the FBSBR, it decreased 2%–4% when the COD concentration increased to 1,500 mg/l, but after adaptation, efficiency again increased with as the COD concentration increased.

3.7. COD removal efficiency of real wastewater

The results of FBSBR operation with real sewage is shown in Fig. 12. As seen, WHO output standards for COD influent (60 mg/l) [25] at 10 and 8 h were achieved with 93.93%

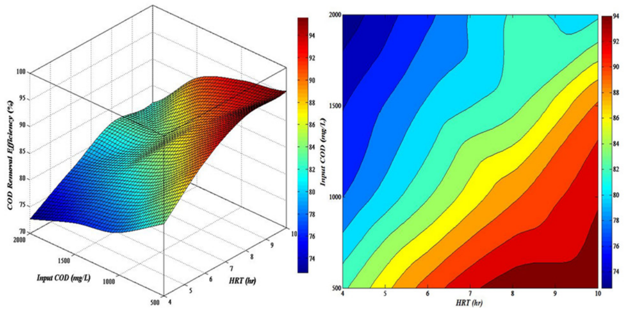

Fig. 11. Effect of initial COD concentration and HRT on COD removal efficiency in SBR.

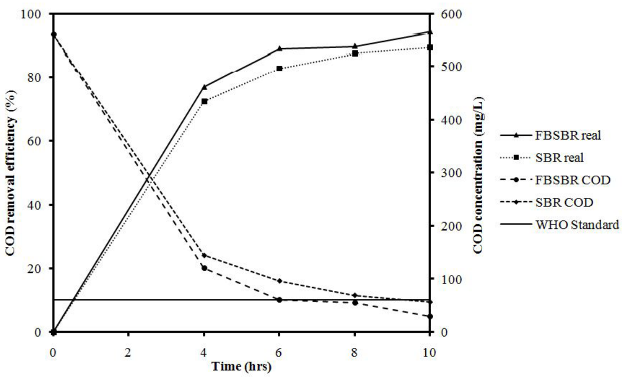

Fig. 12. Results of operation of FBSBR using real sewage.

and 90.87% efficiency, respectively; however, technical and economic aspects of the operation of this reactor mean that optimum operation time for the FBSBR for local usage is 8 h.

4. Conclusion

The present study investigated the effect of the addition of scrap tire as a carrier material in an FBSBR for the treatment of synthetic and real municipal wastewater. The results demonstrate the feasibility of using WTCs as a substitute media and biofilm carrier in attached growth. The addition of WTCs could improve the activity of the activated sludge, and COD could be removed in a shorter cycle time in SBR. The results suggest that the addition of carriers improved COD removal efficiency. This illustrates the high potential of WTCs to support biological activity for a variety of wastewater treatment applications. SEM showed that a greater amount of biomass was attached to the scrap tire.

Both FBSBR and SBR showed excellent performance for organic substance removal; however, the FBSBR was more efficient than the SBR at higher organic loading rates. The sludge production rate for the FBSBR was lower (13%–29%) than for the SBR, and the excess sludge better stabilized, meaning that the FBSBR sludge has greater potential for use as fertilizer. The addition of WTCs could also improve the settling property of activated sludge, which is helpful to inhabit the sludge bulking and to enhance the performance of biological organic pollutant removal.

Acknowledgment

The authors would like to thank the Research Vice-chancellor of Yazd University of Medical Sciences for funding the study (Grant 3612).

Abbreviations

BOD_5	—	Biochemical oxygen demand
COD	—	Chemical oxygen demand
DO	—	Dissolved oxygen
FBSBR	—	Fixed-bed sequence batch reactor
HRT	—	Hydraulic retention time
MLSS	—	Mixed liquor suspended solids
OLRs	—	Organic loading rates
SBR	—	Sequencing batch reactor
SBBR	—	Sequencing batch biofilm reactor
SCOD	—	Soluble chemical oxygen demand
SEM	—	Scanning electron microscopy
SRT	—	Solids retention time
TSS	—	Total suspended solids
VOL	—	Volumetric organic loads
VOR	—	Volumetric organic removal
VSS	—	Volatile suspended solids
WTCs	—	Waste tire chunks

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