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A new recycling technique for the waste tires reuse

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ABSTRACT

In this series of laboratory experiments, the feasibility of using fixed bed biofilm carriers (FBBC) manufactured from existing reclaimed waste tires (RWTs) for wastewater treatment was evaluated. To assess polyamide yarn waste tires as a media, the fixed bed sequence batch reactor (FBSBR) was evaluated under different organic loading rate (OLRs). An experimental model was used to study the kinetics of substrate consumption in biofilm. Removal efficiency of soluble chemical oxygen demand (SCOD) ranged by 76–98% for the FBSBR compared to 71–96% in a sequencing batch reactor (SBR). Removal efficiency of FBBC was significantly increased by inoculating these RWTs carriers. The results revealed that the sludge production yield (Y_{obs}) was significantly less in the FBSBR compared to the SBR ($p < 0.01$). It also produced less sludge and recorded a lower stabilization ratio (VSS/TSS). The findings show that the Stover-Kincannon model was the best fit ($R^2 > 99\%$) in a FBSBR. Results from this study suggest that RWTs to support biological activity for a variety of wastewater treatment applications as a biofilm carrier have high potential that better performance as COD and TSS removal and sludge settling properties and effluent quality supported these findings.

1. Introduction

Scrap tires are a major environmental problem worldwide. The current scrap tire recycling market is too small compared to the annual number of waste tires generated globally (17 million T) (Herrera-Sosa et al., 2015; Mehdiabadi et al., 2013). Waste tires are nearly non-degradable and take up large landfill space. If not properly disposed of, they can hold water that provides a breeding ground for mosquitos and facilitate the spread of mosquito-borne disease. It is essential to develop new markets for waste tires (Lin et al., 2008; Selbes et al., 2015).

An improper management of waste tires, as the combustion, unfortunately still a common phenomenon and it produces serious air, water, and soil pollution issues (Sciacca and Conti, 2009; Derakhshan et al., 2017; Oliveri Conti et al., 2017a; Dehghani et al., 2017; Oliveri Conti et al., 2017b); however, waste tire has a high heat value and is used as supplemental fuel in cement kilns and paper mills (Chyan et al., 2013; Naz et al., 2014). Waste tires can also be recycled as: roadway pavement material, refuse-derived fuel, or reproduced as tires, but also to produce rubber mats, roadway guard rails, protective cushions or bumpers, and building materials (Gupta et al., 2014). In marine applications, they are used as a wave breaking material, ship/dock protective bumpers, and to construct artificial reefs in the offshore fish farming industry (Lin et al., 2008). Nevertheless, these markets are small compared to the number of tires generated each year. It is of great interest to explore new applications/markets for the scrap tire industry (Herrera-Sosa et al., 2015; Lin et al., 2008).

Among the biological technologies, the sequencing batch reactor (SBR) is unique for its flexible operation, compact structure and simple

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Abbreviations: BOD_5, Biochemical Oxygen Demand; COD, Chemical Oxygen Demand; DO, Dissolved Oxygen; FBBC, Fixed Bed Biofilm Carriers; FBSBR, Fixed-Bed Sequence Batch Reactor; HRT, Hydraulic Retention Time; MLSS, Mixed Liquor Suspended Solids; OLRs, Organic Loading Rates;; RWTs, Reclaim Waste Tires; SEM, Scanning Electron Microscopy; SBR, Sequencing Batch Reactor; SRT, Solids Retention Time; SCOD, Soluble Chemical Oxygen Demand; TSS, Total Suspended Solids; VSS, Volatile Suspended Solids; VOL, Volumetric Organic Loads; VOR, Volumetric Organic Removal

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construction (Kulkarni, 2013; Mahvi et al., 2011; Takdastan et al., 2009). But also, the hybrid system combining suspended and biofilm process to realize the compact structure and flexible operation with high efficiency is well accepted in current literature (Mahvi, 2008; Maranon et al., 2008; Rodríguez et al., 2011; Santos and Boaventura, 2015).

Among the hybrid process, FBSBR method is an effective method for the wastewater treatment for its high efficiency in organic material's deletion by wastewater and it is able to quickly reduction the biodegradable organic materials. A highest use of this system is justified by more stringent provisions to the higher quality for output wastewater finalized to protect and preserve the resources water. Several 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 (Santos and Boaventura, 2015). 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 (Chen et al., 2015; Moghaddam and Sargolzaei, 2015; Santos and Boaventura, 2015).

Several materials have been tested as carriers (media) in sequencing batch biofilm reactors. Soltani et al. (2013) investigated the effects of peach pits as media on the efficiency of a fixed-bed sequencing batch reactor (FSBR). Their study showed that when organic loading was 12 $\mathrm{kg_{COD}/m^3.d}$, organic matter removal in the FSBR and SBR reactors was 71.84% and 56.57%, respectively, and SRT decreased from 40 to 19.8 d (Soltani et al., 2013). Dutta et al. (2014) studied the effects of granular activated carbon and natural zeolite as attached carriers in anaerobic sequencing batch biofilm reactors and showed that the addition of carriers improved both the COD removal efficiency and biogas production. A summary of researches on the sequencing batch biofilm reactors is presented in Table 1.

The main objective of present study was to explore the feasibility of using reclaim waste tires (RWTs) as a suitable media for biological growth and biofilm development in wastewater treatment system. More specifically, the study focused on using RWTs as a biofilm carrier in FBSBRs. In addition, the possibility of an alternative form of recycling of RWTs was also evaluated.

2. Materials and methods

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

2.1. Preparation of media

The RWTs were obtained from Yazd Tire Company. The RWTs were measured using a ruler to determine the approximate average size. Physicochemical characterization studies were performed to verify the chemical resistance of the novel biofilm carrier by placing it in glass beakers containing tap water, acidic (pH = 4.9), and basic (pH = 9.2) solutions for 30 days. 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 (Natarajan et al., 2015). Weight loss of 1.8% and 2.5% were recorded for samples placed in acidic and basic solutions, respectively.

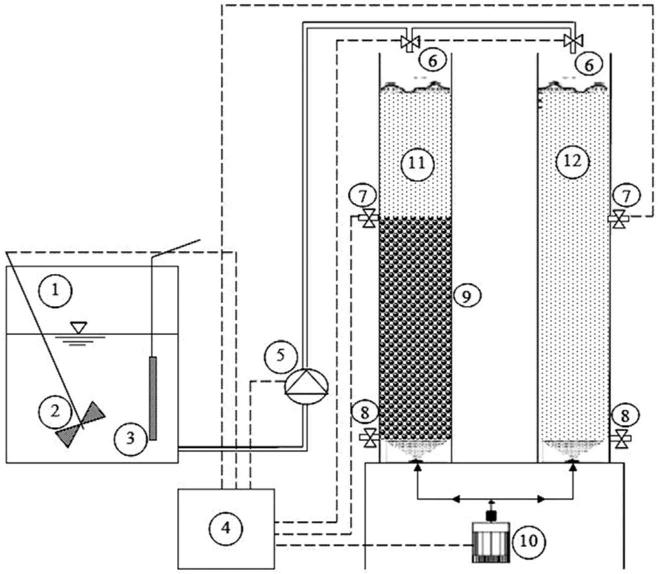

Fig. 1. Schematics of SBR and FBSBR. 1- Feed Tank, 2- Mixer, 3- Heater, 4- Control Unit, 5- Peristaltic Pump, 6- Feed Control Valve. 7- Decanter(Sampling) Valve, 8- Discharge Sludge Port, 9- Novel Packing Media, 10-Air compressor, 11- FBSBR Reactor, 12- SBR Reactor.

2.2. Experimental set-up 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, RWTs with a porosity of 90%, specific surface area of ~370 $\mathrm{m^2\ m^3}$ and a total volume of 2 l (40%) were fixed to the bottom of the reactor.

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 wk. 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 wk. after pilot start-up. The effluent's COD values were similar to 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 ± 2.4 °C (average temperature of Yazd from January through June is 30 °C) using a thermostaticheater. The reactors were operated in cycles of 10, 8, 6 and 4 h. The system was controlled using the timer switches (Theben; Germany).

Each cycle comprised 4 phases.

Table 1

Estimated Efficiency of some researches on fixed-bed sequencing batch reactors.

Type of reactor	Media	Environment	Efficiency (%)	Reference
Anaerobic/aerobic fixed-bed sequencing batch biofilm reactor	Volcanic pumice stone	Synthetic wastewater	92–94	(Hosseini Koupaie et al., 2013)
	Plastic media (polyethylene)		95–96	
FBSBR	Plastic media (polyethylene)	Synthetic wastewater	90–96	(Rahimi et al., 2011)
SBBR	Fibrous carrier	Synthetic wastewater	90–95	(Zhang et al., 2009)
Sequencing batch reactor biofilm	Polypropylene carriers	Wastewater	95	(Yin et al., 2015)

Table 2
Chemical composition of used synthetic wastewater (Baghapour et al., 2013; Nasseri et al., 2014).

Component	Concentration (mg/L)
Sodium acetate (NaCOOH)	100–200
Ammonium sulfate ((NH4)$_2$SO$_4$)	150–700
Potassium phosphate(KH_2PO_4)	150–600
Calcium chloride ($CaCl_2 \cdot 2H_2O$)	0.37
Magnesium sulfate ($MgSO_4 \cdot 7H_2O$)	5
Manganese chloride ($MnCl_2 \cdot 4H_2O$)	0.28
Zinc sulfate ($ZnSO_4 \cdot 7H_2O$)	0.45
Anhydrous Iron chloride ($FeCl_3$)	1.45
Copper sulfate ($Cu_2SO_4 \cdot 5H_2O$)	0.4
Cobalt chloride ($CoCl_2 \cdot 6H_2O$)	0.4
Sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$)	1.25
Sodium Bicarbonate ($NaHCO_3$)	20
Sucrose ($C_{12}H_{22}O_{11}$)	Variable (100–800)

- 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, 1000 ± 8.2, 1500 ± 5.6, and 2000 ± 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 priorto monitoring. Synthetic wastewater was fed into both reactors with a pump. Decantation 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 (MI-65; Martini Instruments). To prevent interference from light (photocatalysis) and algae growth, the columns were covered with aluminum foils. The operational scheme of the system for 16 phases (runs) is shown in Tables 3, 4. The FBSBR was operated at 4 HRTs using municipal sewage from Yazd (COD = 539 ± 16.6 mg/l, BOD_5 = 241 ± 7.81 mg/l, pH = 7.83 ± 0.37 and temperature = 34.8 ± 4.21 °C) to assess the ability of this system under real conditions.

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

Run	Cycle time (hr)	Initial conc. of SCOD (mg/L)	DO (mg/L)	pH
1	10	500 ± 4.783	4.378 ± 0.483	7.048
2		1000 ± 6.495	4.342 ± 0.122	7.261
3		1501 ± 6.509	4.724 ± 0.214	7.205
4		2002 ± 4.408	4.385 ± 0.102	7.317
5	8	502 ± 3.927	4.213 ± 0.127	7.443
6		998 ± 6.647	4.427 ± 0.118	7.427
7		1500 ± 5.692	4.349 ± 0.107	7.192
8		1999 ± 5.209	4.302 ± 0.209	7.133
9	6	500 ± 4.11	4.342 ± 0.189	7.507
10		1003 ± 8.98	4.403 ± 0.134	7.291
11		1498 ± 5.43	4.216 ± 0.235	7.327
12		2000 ± 4.44	4.291 ± 0.397	7.306
13	4	499 ± 4.08	4.276 ± 0.462	7.174
14		997 ± 9.15	4.437 ± 0.267	7.352
15		1500 ± 5.60	4.346 ± 0.309	7.016
16		2000 ± 3.25	4.218 ± 0.421	6.981

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

Run	Cycle time (hr)	Initial conc. of SCOD (mg/L)	DO (mg/L)	pH
1	10	500 ± 4.783	4.328 ± 0.147	7.146
2		1000 ± 6.495	4.422 ± 4.422	7.142
3		1501 ± 6.509	4.205 ± 0.119	7.260
4		2002 ± 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		1500 ± 5.692	4.248 ± 0.132	7.339
8		1999 ± 5.209	4.420 ± 0.152	7.124
9	6	500 ± 4.11	4.275 ± 0.131	7.267
10		1003 ± 8.98	4.231 ± 0.110	7.297
11		1498 ± 5.43	4.284 ± 0.123	7.258
12		2000 ± 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		1500 ± 5.60	4.276 ± 0.161	7.378
16		2000 ± 3.25	4.322 ± 0.104	7.362

2.4. Analytical methods

All results were obtained from the bioreactors at steadystate. 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 (MI-65; Martini Instruments) 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 (APHA, 2007).

The parameters measured were 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 list of measurements to ensure the proper operation of the system and the stability of the reactors. The data presented is the average of minimum 2 times 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% glutaraldehydein 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 ateach 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 (Dutta et al., 2014; Naz et al., 2014).

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)):

$$r_{SCOD} = r_{max} \frac{B_{SCOD}}{k + B_{SCOD}} \tag{1}$$

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 kg_{SCOD}/m^3d. B_{SCOD} and r_{SCOD} were obtained as:

Table 5
Comparison of reactors.

Parameter	SCOD	SVI	Yield	VSS/TSS
Sig. (2-tailed)	0.023	0.137	< 0.01	0.033
Correlation is significant at the 0.05 level (2-tailed).				

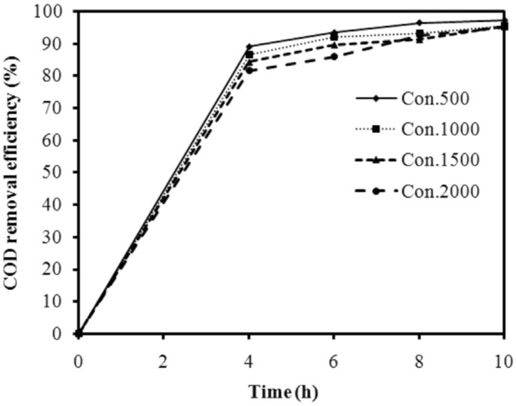

Fig. 2. SCOD removal in FBSBR.

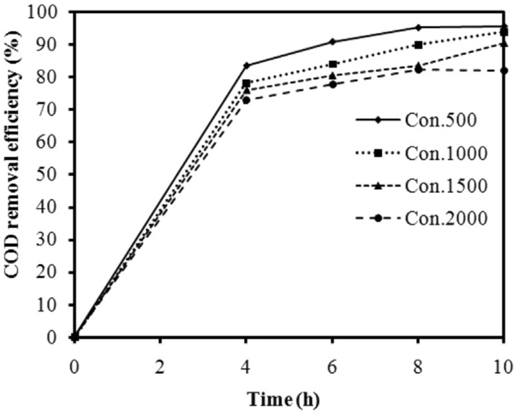

Fig. 3. SCOD removal in SBR.

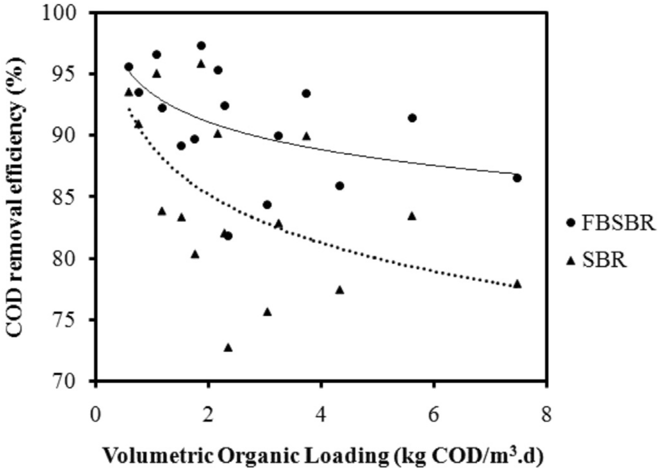

Fig. 4. COD removal efficiency vs. organic loading rate.

$$B_{SCOD} = \frac{Q}{V} C_i \tag{2}$$

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

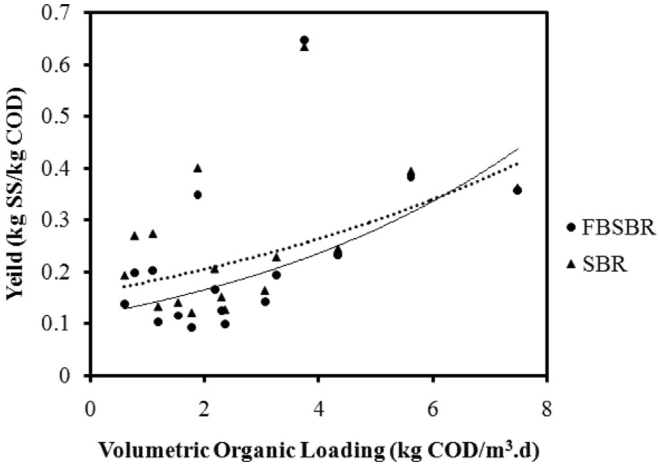

Fig. 5. Sludge production rate vs. organic loading rate.

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	0.995	0.140	6.00	2.31
SBR	0.992	0.169	5.59	2.60

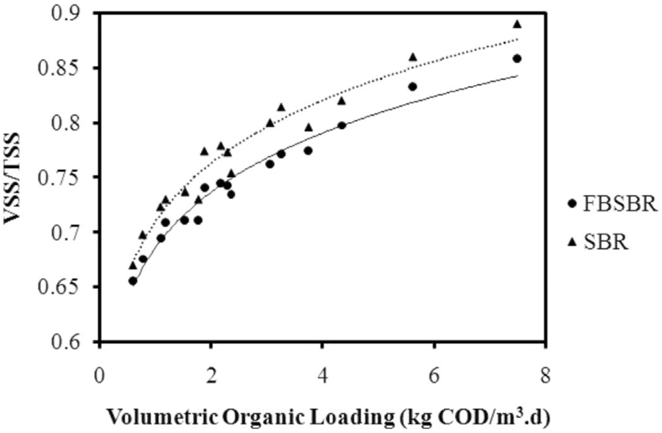

Fig. 6. Sludge characteristics vs. sludge stabilization ratio.

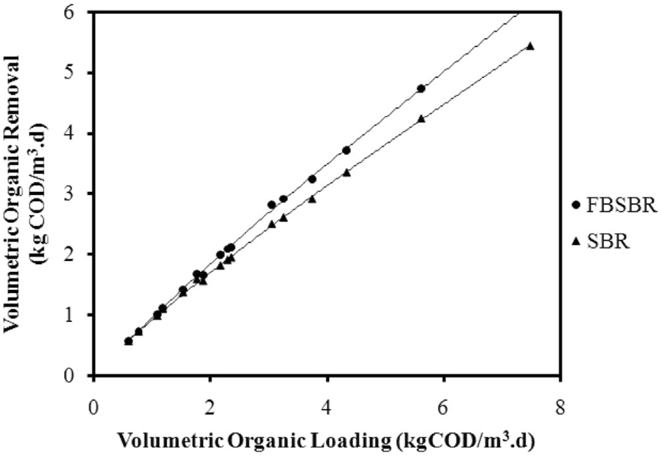

Fig. 7. Organic loading of bioreactors for 0–8 kgCOD/m^3.d at 30 °C.

where C_i is the SCOD concentration in the influent (kg_{SCOD}/m^3) and k is the SCOD concentration in the effluent (kg_{SCOD}/m^3) (Baghapour et al., 2013; Nasseri et al., 2014). Eqs. (2) and (3) and Tables 3, 4 were used to

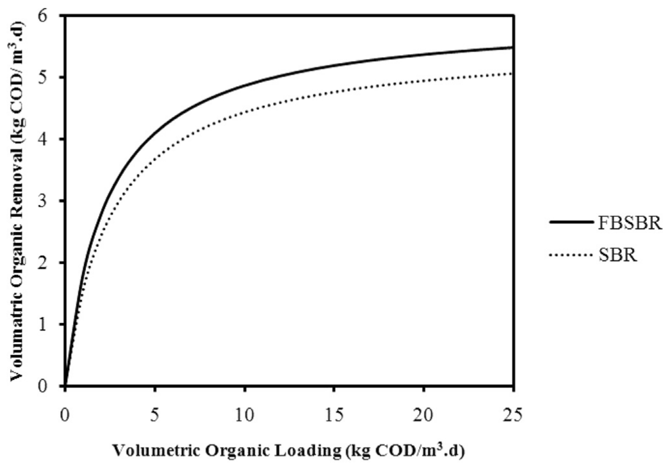

Fig. 8. Organic loading of bioreactors for 0–25 gCOD/m^3.d at 30 °C.

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

The statistical parameters used were mean and standard deviation (for more than two data points). The nonparametric Mann-Whitney U test was used in SPSS (version 21) to identify relationships between reactors (Table 5).

3.2. SCOD removal

COD reduction is one of the most common challenges faced by any facility that needs to comply with wastewater treatment regulations, and if it isn't properly addressed it can result in non-compliance fines. During system operation, the length of the runs was reduced from 10–8 to 6–4 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 versus COD loading

Both reactors showed high COD removal efficiency at steady state throughout the study period (Fig. 5); however, 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.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 versus 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 versus 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 ($p < 0.01$). Y_{obs} varied from 0.22 to 0.53 kg_{SS}/kg_{COD} in the SBR and 0.16–0.47 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 dissolved oxygen 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 0.64–0.82 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

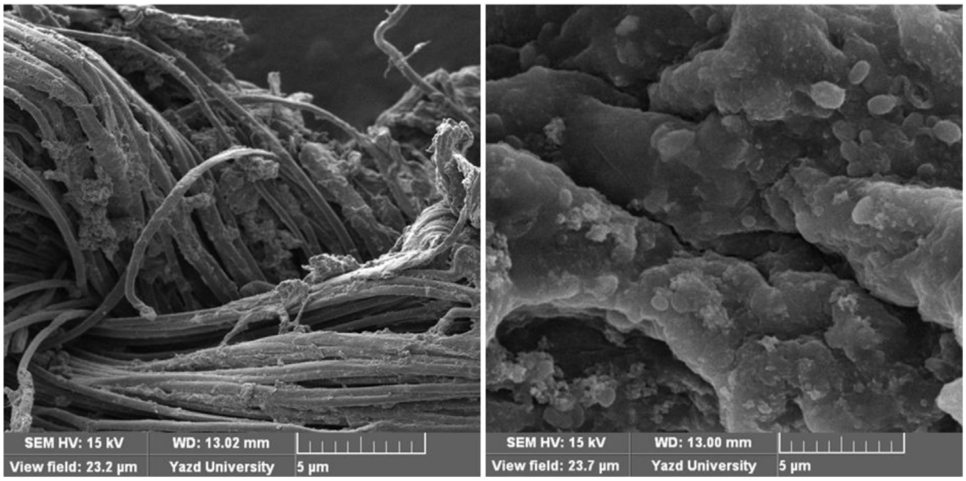

Fig. 9. SEM images of a sample of virgin surfaces of RWTs (left) and RWTs after biofilm formation (right).

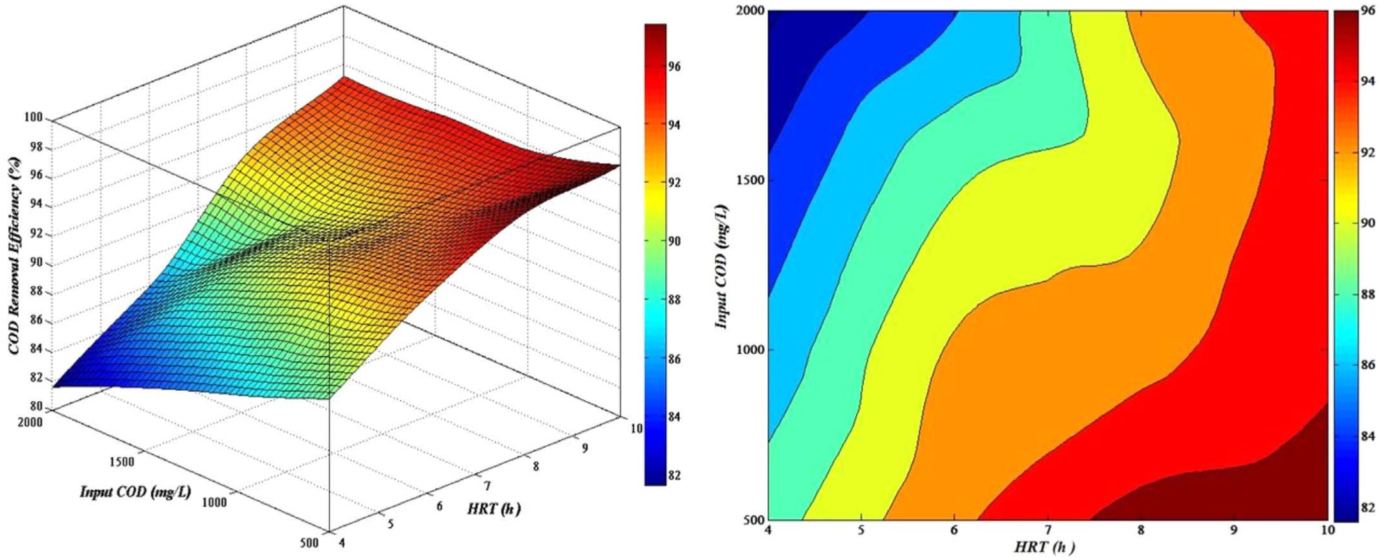

Fig. 10. Effect of initial COD concentration and HRT on COD removal efficiency in FBSBR.

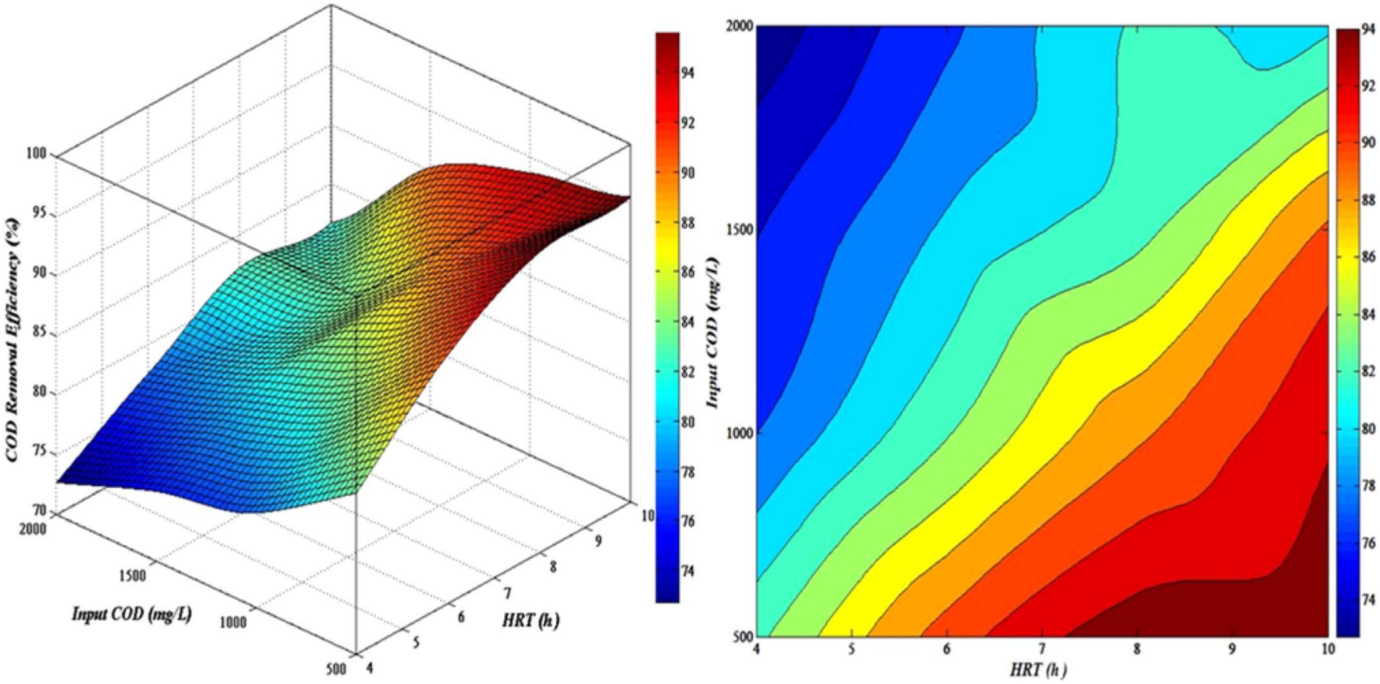

Fig. 11. Effect of initial COD concentration and HRT on COD removal efficiency in SBR.

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 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.

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 large variety of bacteria 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 1500 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 process with real sewage is shown in Fig. 12. As seen, WHO output standards for COD influent (60 mg/l) (Mahvi et al., 2009) at 10 and 8 h were achieved with 93.93% and 90.87% efficiency, respectively; however, technical and economic aspects of

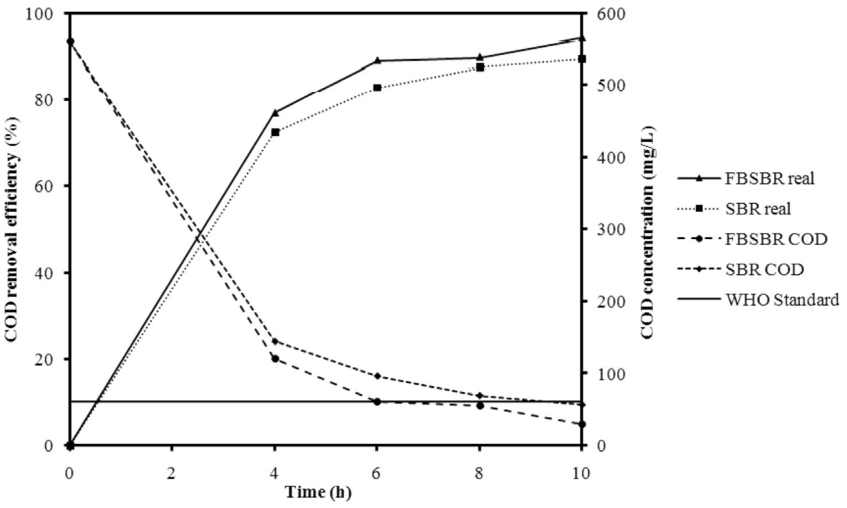

Fig. 12. Results of operation of FBSBR using real sewage.

this reactor's process indicates that the optimum operation time for the FBSBR for local usage is 8 h.

4. Conclusion

The results suggest that the addition of carriers improved COD removal efficiency. We showed the high potential of RWTs to support biological activity for a variety of wastewater treatment applications. SEM analysis results showed that a greater amount of biomass was attached to the RWTs. Both bioreactors 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% to 29%) than for the SBR and the excess sludge better stabilized, meaning that the FBSBR sludge has greater potential for use as fertilizer. Finally, we showed that this process represent a good alternative for the reuse of RWTs.

Competing interests

The authors declare that they have no competing interests.

Financial disclosure

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