Chemical Engineering Journal 158 (2010) 498–504

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

The removal of high concentrations of phenol from saline wastewater using aerobic granular SBR

Gholamreza Moussavi*, Behnam Barikbin, Maryam Mahmoudi

Department of Environmental Health, Faculty of Medical Sciences, Tarbiat Modares University, Tehran, Iran

ARTICLE INFO

Article history:
Received 11 August 2009
Received in revised form 16 January 2010
Accepted 19 January 2010

Keywords:
Saline wastewater
Phenol
Biological process
Granular biomass
SBR

ABSTRACT

The treatment of saline wastewater containing phenol is a challenge faced in the application of biological pollution control technologies. Phenol-laden saline wastewater is generated from various industrial and manufacturing activities. The aerobic granular sequencing batch reactor (GSBR) was investigated in this work in order to assess its performance for the degradation and chemical oxygen demand (COD) removal of phenol as the sole substrate from saline wastewater. The effect of inlet concentration (100–2000 mg phenol/L), cycle time (14–24 h), filling cycle time (1–4 h), shock loading, and total dissolved solids (TDS) concentration (3–8%) were evaluated on the performance of a bench scale GSBR seeded with granules containing mixed phenol-degrading consortia acclimatized to salt. The results showed that the investigated reactor could remove more than 99% of phenol from the feed saline wastewater at inlet phenol concentrations of up to 1000 mg/L, total cycle time of 17 h (15.5 h aerating, 1 h filling, and 30 min settling, decanting and idle) and TDS concentrations up to 8%. A high percent of COD removal and phenol mineralization obtained at these operational conditions. The GSBR could also withstand and absorb the strong phenol shock. Furthermore, the granular biomass in the GSBR indicated high quality in terms of sludge settleability. Overall, the results of this work revealed that establishing a granular biomass containing high concentration of active mixed microbial populations in the GSBR system can achieve complete degradation of high concentrations of phenol in saline wastewater. This makes it a very efficient and flexible technology for treating such waste streams in full-scale applications.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Industrialization has led not only to an increase in water demand, but also to an increase in water pollution due to industrial discharges. Many industries such as meat canning, olive oil mills, petroleum, petrochemical, agro-food, seafood processing, vegetable canning, pickling and cheese processing generate effluents with high salt content [1], most of which contain some amount of various organic compounds [2]. One common organic compound found in saline wastewater generated in industries like olive oil mills, petroleum refineries, petrochemical plants and oil field operations is phenol and its derivates [3]. For instance, olive oil mills, which are mostly concentrated in the Mediterranean area [4], produce an acidic wastewater with high salt and phenol content (0.1–1%). Furthermore, characteristics of olive oil mill wastewater vary widely and depend on the oil production method. In addition, concentrations of phenol in refineries and petrochemical plants are in the ranges of 6–500 mg/L and 2.8–1220 mg/L, respectively [5].

Phenol is listed as a toxic substance and is included in the priority list of hazardous substances as well, which demonstrates its serious health and ecological effects [6]. This makes it a major focus of environmental and health pollution control. In order to protect the environment against the adverse effects of phenol, wastewaters containing this toxic compound need to be treated in an effective and environmentally benign process before the wastewater can be discharged into the environment. Reviewing the literature indicated that most investigations reported on phenol removal has focused on its removal from fresh (low TDS) wastewaters using a range of processes [7]. Busca et al. [6] have recently published a short review on the separation and destruction techniques of phenol removal from wastewater. However, in spite of its importance, few works have been published on removal of phenol from saline wastewaters. This lack of published research is despite the fact that several industries such as olive oil mills, oil refinery, petrochemical, pharmaceutical, pesticides and oilfields [5,8] generate saline effluents containing several organic compounds such as phenol. Biological processes are considered to be environmentally benign, efficient, and cost effective treatment techniques in comparison to other processes [9] and offer effective removal of a wide range of contaminants in wastewater treatment. It is known that high salinity can seriously inhibit the effectiveness of aerobic and

* Corresponding author. Tel.: +98 21 82883827; fax: +98 21 82883825.
E-mail address: moussavi@modares.ac.ir (G. Moussavi).

1385-8947/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2010.01.038

anaerobic biological treatment of wastewater [10]. Although using halophilic microorganisms such as *Halobacter halobium*, etc. is the best approach for the biological treatment of saline wastewater [1], a biomass acclimated to a desired salt concentration can also mitigate the detrimental effects of salinity on the overall bioprocess performance.

Woolard and Irvine [11] investigated the removal of phenol from synthetic wastewater containing 15% salt in a sequencing batch biofilm reactor inoculated with moderated halophilic bacteria. They observed a removal efficiency of higher than 99% for phenol at inlet concentrations of 120 mg/L. They repeated the experiment in 1995, with a sequencing batch reactor (SBR) seeded with pure halophil culture and found a removal efficiency of 99.5% for phenol [12]. Hinteregger and Streichsbier [13] reported almost 100% removal of phenol in wastewater containing 14% NaCl. Li et al. [14] evaluated the effect of nutrients on the rate of phenol biodegradation in synthetic saline wastewater in a sequencing batch biofilm reactor. They observed an important role for nutrient content on phenol removal. Other investigations that have dealt with biological treatment of saline wastewaters containing phenol are those reported by Freire et al. [15], Alva and Peyton [16], Gómez et al. [17], and Ramos et al. [18], who showed the effectiveness of biotreatment of phenol-laden saline wastewaters. However, most of these studies have involved either single microbial species or low inlet phenol concentrations; both of which may have limitations in field application due to the presence of different and/or high concentrations of contaminants in the targeted wastewater.

The primary objective of this work was to investigate the biological treatment of saline wastewater containing high concentrations of phenol using a mixed culture and improvement of the biomass separation. Among the bioreactors invented for biological wastewater treatment, the SBR confers greater advantages, including flexibility, robustness, single basin operation, better control of shock loads, simplicity of operation, relatively low cost, and no sludge loss in the reaction period (and hence no need to return activated sludge) [19,20]. Therefore, SBR is the most common type of bioprocess used for industrial wastewater treatment [21]. A recent advantage reported for SBR is the possible formation of granules of biomass without using media, which can improve the reactor performance and sludge settleability [22,23]. On the other hand, one of the most frequently encountered problems in biological treatment of saline wastewater is gravity separation of solid-liquid phases in sedimentation unit operation. This is caused by a difference in saline water and biomass density, cell plasmolysis, reduced quantity of the filamentous bacteria and lack of protosoans [1,12]. Exploring the granulation ability in SBR systems might be a solution to mitigate the settling problems encountered in conventional suspended biological processes in treating saline wastewaters for several reasons. In addition to settleability improvement, biomass granulation increases the concentration of the biomass into the reactor and improves the resistance to toxicity [23,24], resulting in an enhancement of bioreactor performance. Although the ability of aerobic granules to be effective in the removal of toxic compounds like phenol [24], p-nitrophenol [25] and 2-4,dichlorophenol [23] has been previously published, no report could be found on phenol removal from saline wastewaters. Accordingly, the basic aim of this parametric study is investigating the performance of an aerobic granular sequencing batch reactor (GSBR) to explore the above-mentioned benefits in the treatment of a synthetic saline phenolic wastewater. To achieve this goal, the effect of inlet phenol concentration, wastewater salt content, aeration cycle time, filling cycle time and contaminant shock loading was evaluated in the removal of phenol from saline wastewater in a bench scale GSBR. It will be indicated that the GSBR can efficiently remove the phenol from saline wastewater.

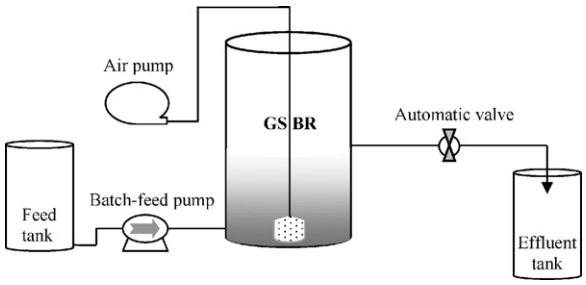

Fig. 1. The schematic of the GSBR experimental set up.

2. Materials and methods

2.1. Reactor setup

In this investigation, a cylindrical bench scale reactor, the schematic of which is shown in Fig. 1, was constructed and studied for the treatment of saline wastewater containing phenol under laboratory conditions. The reactor was made from glass and consisted of a 7 L total volume column (internal diameter (D) × height (H), 15 cm × 40 cm), 4 L of which served as the working volume. A peristaltic pump (WATSON MARLOW 101U/R) injected the synthesized wastewater into the reactor. The pumping rate of the wastewater to the reactor was regulated based on the fill volume and filling time. The reactor was aerated using an air pump (RESUN® AC-9908) and the air entered into the mixed liquor through two air stone diffusers placed at the bottom of the reactor. The inlet air flow rate to the GSBR was controlled by a valve mounted on the pump to meet the oxygen demand corresponded to the inlet organic loading rate. Two sampling ports were provided on the influent and effluent lines of the reactor for taking samples and monitoring the performance of the system in removal of phenol. In addition, a valve was located at the bottom of the reactor to withdraw the sludge and drain the reactor, as needed.

2.2. Reactor operation

The GSBR used in this work was operated in cyclic mode for 275 days, so that each operating cycle comprised of filling (with aeration), aerating, settling and decanting with various cycle times. The fill volume of the reactor was kept constant at 2 L during the entire course of the experiment, meaning that 50% of the full volume was replaced during the filling period with new synthetic wastewater in each cycle. Table 1 gives the operational conditions of the investigated GSBR. Following start up, the reactor was run to investigate the effects of operational variables on phenol removal and the corresponding chemical oxygen demand (COD) removal at steady state operational conditions. Table 2 illustrates the phases of the study and the purpose considered in each phase of the experiment along with the range of investigated variables. The steady state condition was assumed to have occurred at each operational run when change in the removal efficiency was within ±5% for 10–15 consec-

Table 1
Basic operation parameters of the GSBR.

Parameter	Unit	Value
Phenol concentration	mg/L	100–2000
COD concentration	mg/L	227–4540
Salt concentration	g/L	30–80
Cycle time	h	14–24
Filling	h	1–4
Aerating	h	9.5–19.5
Settling, decanting and idle	h	0.5

Table 2
Experimental phases and GSBR operation schedule.

Phase	Day	Operation	Inlet concentration, C_{in} (mg/L)		TDS (g/L)	Cycle time[a] (h)	
			Phenol	COD		Fill	React
0	0–50	Biomass acclimation	100	227	5–50	–	–
1	51–115	Effect of C_{in}	100–2000	230–4540	50	4	19.5
2	116–165	Effect of aerating time	1000	2270	50	4	19.5–9.5
3	166–220	Effect of filling time	1000	2270	50	4–1	15.5
4	221	Effect of shock loading	–	–	50	Shock-feed	15.5
5	222–275	Effect of salt content	1000	2270	30–80	1	15.5

[a] Settling, decanting and idle cycle times kept constant at 5, 10, and 15 min, respectively, during the time course of the experiment.

utive cycles. The concentration of biomass over the whole period of the experiment stayed steady at 9500 ± 500 mg/L.

The wastewater fed to the GSBR was prepared daily by adding phenol and nutrient stock solutions to the tap water. It should be noted that throughout this experiment, phenol was the sole carbon source for microorganisms in the reactor. The nutrient stock solution was prepared by dissolving given amounts of KH_2PO_4, K_2HPO_4, and NH_4Cl and 1 mL of trace element solution into 1 L of distilled water. A stock phenol solution was made by dissolving 35 g of phenol crystals into 1 L of distilled water. Feed wastewater was produced by mixing sufficient volumes of phenol and nutrient stock solutions with tap water in the synthetic wastewater tank. The ratio of COD:N:P in the feed wastewater was kept constant at 100:5:1 throughout the investigation. The salt content of the prepared wastewater was controlled at the required value based on total dissolved solids (TDS) via adding a sufficient amount of NaCl and $Ca(Cl)_2$. To keep from limiting the phenol biodegradation, the concentration of dissolved oxygen (DO) in the mixed liquor was maintained around 2 mg/L during all areration cycles. In addition, the pH of the feed wastewater was set at a neutral range. All chemicals were of analytical grade except for NaCl, which was purchased commercially.

2.3. Inoculum preparation

To prepare an acclimatized salt-tolerant phenol-degrading inoculum, the granular activated sludge taken from a bioreactor treating synthetic phenol-laden wastewater with removal efficiency of over 99% was used as the initial seed. The granules were averagely 2 mm in diameter, dense in structure and appeared brownish in color. The adaptation of biomass granules to salt was performed in the batch reactor, during which time the synthetic wastewater containing 100 mg/L phenol was fed to the reactor. The salt content (based on TDS parameter) in the feed wastewater was increased step-wise up to 50 g/L of salt during the 50 days of acclimation phase. In each TDS concentration, the reactor was operated until the removal efficiency of phenol became greater than 95%; thereafter the salt concentration was increased. Acclimation to salt was assumed to be achieved when the removal efficiency of phenol exceeded 95% at the target salt content of 50 g/L. Upon attaining the acclimation of phenol-degrading granular biomass to salt, the reactor was operated for 20 more days to enrich the salt-tolerant granular consortia. The obtained biomass was applied as inoculum to the reactor. Microscopic observations revealed that the granules could preserve their firmness and shape during exposure to salt.

2.4. Analysis

To evaluate performance of the GSBR, samples were taken in each operation cycle from inlet, settled effluent as well as the content of the reactor during reaction phase. Inlet samples were analyzed as taken for phenol, COD, NH_4-N, phosphate, pH and TDS. The mixed liquor samples were analyzed for phenol, COD, and suspended solids. Mixed liquor and effluent samples were filtered before analysis through a filter with a 0.45 μm pore size to remove particles. The effluent samples were analyzed for phenol, COD and turbidity. Phenol concentrations were measured spectrophotometrically by the chlorimetric 4-aminoantipyren procedure as detailed in the Standard Methods [26], using a Unico-UV 2100 UV/VIS Spectrophotometer. DO and pH of the reactor mixed liquor were monitored by specific electrodes. Turbidity was measured using a nephlometric turbidimeter (Hach, 2100N Turbidimeter). All other parameters were analyzed according to the Standard Methods [26] with correction for chloride anion in the COD test. The morphology of the granules was evaluated using scanning electron microscopy (SEM) images from a Philips-XL30 Electron Microscope.

3. Results and discussion

3.1. Effect of inlet phenol concentration

The effect of the initial phenol concentration over a wide rage (100–2000 mg/L) on the performance of the GSBR in phenol and COD removal was evaluated over seven runs. In this phase, the GSBR was operated for 64 days under the conditions given in Table 2. The reactor was operated at each concentration until steady state performance in phenol removal was attained. Fig. 2 illustrates the variation of phenol and COD removal efficiency versus the operation time at this step of the study. As shown in Fig. 2, once the phenol was fed to the reactor, its complete removal was observed. Observing no lag phase for phenol elimination could be due to the use of enriched biomass granules adapted to phenol in saline medium. The effect of phenol concentration in the range of 100–1700 mg/L was observed to be insignificant on the performance of the GSBR in its removal. Although further increasing the phenol concentration to 2000 mg/L resulted in a slight decrease in its removal efficiency,

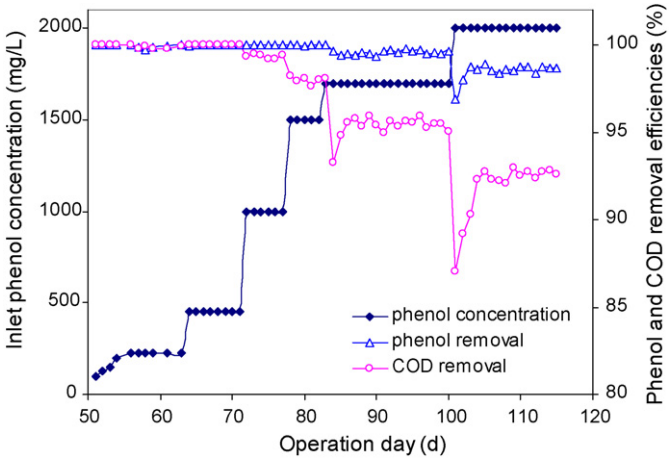

Fig. 2. Performance of the GSBR in removal of phenol and COD at various inlet concentrations at cycle time of 24 h.

Table 3
Mean of inlet and outlet concentrations and removal efficiencies of phenol and COD in the GSBR at different inlet phenol concentration under steady state performance.

Performance	Inlet phenol (COD) concentration (mg/L)						
	100 (230)	225 (510)	450 (1020)	1000 (2270)	1500 (3400)	1700 (3860)	2000 (4540)
Phenol							
Outlet concentration (mg/L)	ND[a]	ND	ND	ND	0.2	7.6	27.3
Removal efficiency (%)	100	100	100	100	100	99.6	98.6
COD							
Outlet concentration (mg/L)	<10	<10	<10	15	25	154	331
Removal efficiency (%)	>96	>98	>99	99.3	99.3	96.0	92.5
Organic metabolites (mg COD/L)	–	–	–	–	24.5	136.7	269

[a] Not-detected.

the reactor recovered quickly after passing one cycle. This suggests that the GSBR with the acclimated biomass could absorb the phenol load fluctuation caused by switching the concentration to an earlier step in the saline wastewater treatment.

The profile of COD removal efficiency at various inlet concentrations was also assessed and the results are shown in Fig. 2. This figure indicates that the removal efficiency of COD was not markedly affected by inlet concentrations up to around 2270 mg/L (1000 mg phenol/L). When phenol was increased to 2000 mg/L in three steps, corresponding to an increase of COD to 4540 mg/L, COD removal efficiency reduced at a higher rate than that of the phenol. It can also be seen from Fig. 2 that upon switching from COD 3400 to 3860 and then to 4540 mg/L, the COD removal efficiency first dropped and then recovered to a steady state performance. The removal efficiency was further reduced and the time to attain steady state further increased at higher inlet COD concentrations.

The mean of the results from the steady state performance of the reactor under different phenol concentrations is given in Table 3. Based on the results presented in Table 3, GSBR could effectively remove over 99% of phenol from saline wastewater at inlet concentrations up to 1700 mg/L under the selected experimental conditions. For COD removal, the critical inlet concentration, at which the mean steady state removal efficiency was greater than 99%, was 3400 mg/L (1500 mg phenol/L). Therefore, the critical loading rate based on inlet concentration (at a cycle time of 24 h) on the GSBR at which the removal efficiencies of phenol and COD were over 99% was found to be 0.75 kg phenol/m^3 day (1.7 kg COD/m^3 day). Increasing the COD concentration to 3860 and then 4540 mg/L led to gradually decreasing COD removal efficiency to 96% and 92.5%, respectively. Accordingly, the GSBR could effectively remove both phenol and its COD from the synthetic saline wastewater. It has also been indicated by other researchers that SBRs are very efficient at removing phenol from saline wastewaters. Woolard and Irvine [11,12] reported removal of phenol from a 15% saline wastewater by a moderate halophile using a SBR as well as a biofilm SBR, and observed up to 99% removal efficiency for phenol at a concentration of 100 mg/L.

By definition, the difference between the COD equivalent of phenol and COD measurements in the effluent represents the quantity of the organic intermittent (metabolites) produced during the phenol biodegradation. The concentration of phenol biodegradation metabolites were also calculated and included in Table 3. As illustrated in Table 3, the degradation of phenol at concentrations of up to 1000 mg/L was complete; no intermediates were observed, meaning that the part of phenol utilized in catabolism had been mineralized. As phenol was the sole substrate entered to the GSBR, any reduction of COD, except for those incorporated in new cells, denoted the mineralization of the compound. Therefore, as long as the phenol concentration in the feed wastewater was lower than 1000 mg/L, complete mineralization had occurred. Thus, this value was adopted as the optimum phenol concentration for the next phases of the experiment. Nonetheless, the degree of mineralization reduced and the intermittent concentrations increased to 269 mg/L as COD at a maximum investigated phenol concentration of 2000 mg/L. This can be explained by the fact that during the bio-oxidation of an inhibitory organic compound such as phenol, the compound may be partially degraded to intermediate organic metabolite(s), which can still be measured in COD tests. This is particularly true in high phenol concentrations. Furthermore, as the higher concentration of phenol caused higher inhibition for microorganisms [27], the increase of inlet phenol concentration led to incomplete degradation occurring with increased intermediate concentrations remaining in the mixed liquor. This reveals that the biomass needs a longer reaction time to attain complete oxidation (phenol and its COD removal) at higher phenol loadings, which may not be economically reasonable.

Such behavior and conclusions have also been reported by other researchers; although at lower phenol concentrations and for pure cultures [28,29]. Better performance of phenol removal and higher capacity of the investigated bioreactor to complete oxidation of phenol could be related to the use of high concentrations of adopted granular mixed biomass consortia compared to the cited researchs where the pure culture were investigated.

From the above results, it can be concluded that the phenol in the feed saline wastewater up to optimum determined concentration had no toxic effect on the biomass activity. This high performance can be attributed to providing a granular biomass containing high concentration of initially acclimated and active microbial consortia in the reactor, which is needed for phenol degradation [30], as well as to the reactor configuration.

3.2. Effect of aeration time

The effect of aeration time as one of the critical phases in the GSBR operation was evaluated on removal of phenol and its related COD at four periods: 19.5, 15.5, 12.5 and 9.5 h. Other operational conditions were as given in Table 2. Fig. 3 demonstrates the variation of phenol and its COD removal efficiencies in the GSBR at various aeration times, while the mean of steady state results are presented in Table 4. Fig. 3 depicts that the aeration time down to 15.5 h had no significant effect on phenol and its COD removal, such that the removal efficiencies of both parameters at aeration phase time of 15.5 h was at least 99%. However, when the duration of aeration phase was reduced to 12.5 and subsequently to 9.5 h, the removal efficiency of both phenol and COD was reduced. In addition, the removal efficiency of phenol and COD when the aeration time was transitioned from 15.5 to 12.5 h, decreased down to 89.1% and 84.6%, respectively (Fig. 3). However, after passing 5 cycles, removal efficiency recovered to an average of 96.6% for phenol and 90.2% for COD (Table 4). As observed in Table 4, the transition of aeration time from 12.5 to 9.5 h resulted in a drop of phenol and COD removal mean values to around 93.2% and 78.6%, respectively. This, in turn, implies that there is greater sensitivity of the GSBR to aeration time at lower values. A greater reduction in the value

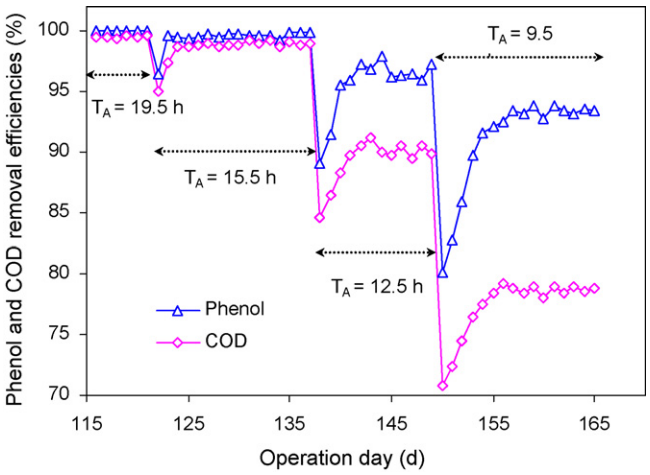

Fig. 3. Variations of phenol and COD removal efficiencies of the GSBR at different aeration cycle times (T_A).

of the COD removal efficiency was observed in comparison to that of phenol. Tsang et al. [31] and Çınar et al. [32] have also reported the adverse effect of aeration time on COD removal efficiency in the SBR system. It can be inferred from above that the optimum reaction time period for the GSBR under the selected operational conditions was 15.5 h, at which time the phenol and COD removal efficiencies were at least 99%. These results indicate that the GSBR seeded with a granular biomass containing adopted phenol-degrading consortia rather than a pure culture can efficiently remove high phenol concentrations and associated COD.

According to Table 4, since there was no considerable accumulation of intermediate metabolites up to aeration time of 15.5 h (phenol loadings of 0.6 kg/m^3 day), it can be concluded that no phenol (as a single substrate) inhibition occurred under these operating conditions. Furthermore, the phenol biodegradation metabolites fraction has continued to increase with the decrease of aeration cycle time below 15.5 h. This behavior of the GSBR could be explained by the reduction in the reaction (bio-oxidation) time, as well as the increase of applied inlet load due to the increased number of cycles per day (and thus the daily feed wastewater volume). The inlet phenol load applied to the GSBR at this phase of the work was 0.5, 0.6, 0.71 and 0.86 kg/m^3 day at total cycle periods of 24, 20, 17 and 14 h, respectively. As an enzymatic inhibitor [33], the increase of phenol load over the degradation capacity of the biomass in the reactor might inhibit the complete metabolic pathway that, in turn, resulted in the formation of intermediates. Hence, the higher the inlet phenol load, the larger the inhibitory effect and the greater the reaction time that is required to attain complete degradation or mineralization.

As previously discussed, no experiments dealing with removal of phenol from saline wastewater by using mixed cultures in GSBR were found in the literature, and only a few were found for pure cultures in SBR. Woolard and Irvin [11] investigated the performance of a biofilm SBR for treating phenol in a saline wastewater at hydraulic retention time (HRT) of 24 h, inlet COD concentration of 290 mg/L and volumetric loading rate of 0.29 kg COD/m^3 day, and reported the efficiency of 99% for COD removal. They repeated their work on phenol removal from saline wastewater with SRB [12] under operational condition of HRT of 24, inlet COD of 250 mg/L and organic loading rate of 0.29 kg COD/m^3 day, finding a 99.5% removal efficiency of COD. The GSBR experimented in this research operated at loading rate around three times greater than that reported by Woolard and Irvine [11,12], attained complete removal of phenol and had the same performance for COD elimination. The greater performance of the GSBR in this research could be specifically due to the existence of a high concentration of biomass granules containing an acclimated and active mixed culture capable of metabolizing high concentrations of phenol and its metabolites.

Table 4
Mean of inlet and outlet concentrations and removal efficiencies of phenol and COD in the GSBR at different aeration cycle time under steady state performance.

Performance	Aeration time (h)			
	19.5	15.5	12.5	9.5
Phenol				
Outlet concentration (mg/L)	0	3.8	34.5	67.6
Removal efficiency (%)	100	99.6	96.6	93.2
COD				
Outlet concentration (mg/L)	10.5	20.4	223	486.6
Removal efficiency (%)	99.5	99.1	90.2	78.6
Organic metabolites (mg COD/L)	–	11.8	144.7	333.2

3.3. *Effect of filling time*

A unique feature of SBR when treating an inhibitory compound is the mitigation of the inhibitory and toxicity effects of the substrate on the microorganisms' activity due to batch feeding and dilution of entering compound(s). This results in a reduction of the concentration peak of the inhibitory compound [34,35] and an increase in the reaction rate [19]. In this step of the experiment, the effect of filling time ranging from 4 h down to 1 h was evaluated on the behavior of the GSBR under previously optimized conditions, including aeration time of 15.5 h and a phenol concentration of 1000 mg/L (COD of 2270 mg/L). Other conditions were as presented in Table 2. This step was design to study the filling time as one of the components of a GSBR operation cycle. At each filling time, the GSBR was operated until a steady state in performance was achieved and then continued for at least 5 consecutive days to gather the reportable data. Fig. 4 illustrates the changes in removal efficiencies of phenol and COD as a function of number of operated cycles under different filling periods. The data plotted in Fig. 4 indicates that the phenol removal efficiency decreased from 99.6% to 99%, when the time of filling phase was decreased from 4 to 1 h, denoting no improper effect of the filling time on the phenol removal at the tested conditions. Fig. 4 also shows that lowering the filling time from 4 to 1 h resulted in decrease of the removal of COD from around 99% to 97.5%, corresponding to increase of COD concentration of the decanted effluent from around 20 to 56 mg/L. The relatively low COD concentration at a filling time of as low as 1 h reveals that

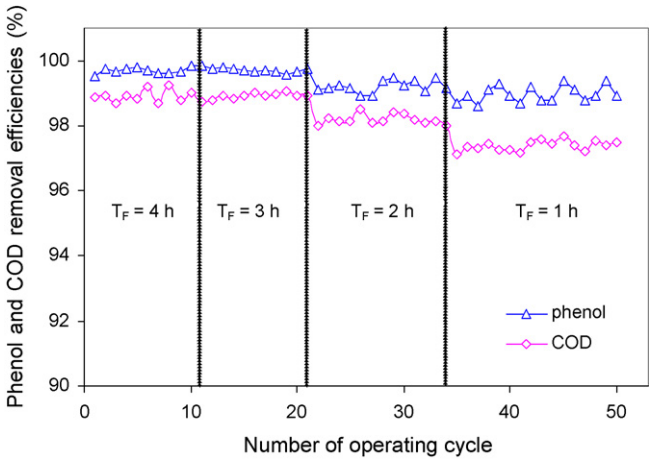

Fig. 4. Changes of phenol and COD removal efficiencies of the GSBR at different filling times (T_F).

the bio-oxidation of the phenol has been almost complete without intermediate production. The value of COD measured can be attributed to the biomass lyses [34,35]. Accordingly, the duration of the filling phase in the GSBR under tested operating conditions has little, if any, role in phenol removal from saline wastewater.

3.4. Effect of shock loading

Some industries discharge the processed wastewater sporadically, imparting shock to the biological processes in the treatment system. The bioreactor has to be able to handle these undesirable conditions in order to maintain stable performance. Therefore, a part of this investigation was spent to determine if the GSBR could handle the shock phenol loads and if shock loading affects the system performance. To study the behavior of the developed GSBR, 100 mL of wastewater containing 1750 mg phenol, was added into the reactor working at full volume while mixing by aeration. Other conditions are presented in Table 2. Upon adding the solution and mixing, the mixed liquor was sampled at time zero and at several intervals throughout the experiment. The samples were analyzed for phenol and COD. The concentrations of phenol and COD at the beginning of the run, just after pouring the phenol solution into the reactor and mixing, were measured 320 and 725 mg/L, respectively, which is lower than the theoretical values. If no process other than dilution affected the concentration, the initial phenol concentration in the mixed liquor would have been around 435 mg/L. The difference of initial phenol concentration measurement to theoretical value was 115 mg/L. Owing to the high concentration of the biomass in the reactor and relatively high octanol–water partition coefficient of phenol (1.46), the deficit amount of phenol might have been immediately adsorbed onto the granules in the reactor. This further confirms that the GSBR containing a high concentration of biomass is very advantageous for treatment of industrial wastewaters containing inhibitor compounds, because of conferred advantages in reducing shock, not only via dilution but also via initial biosorption onto the biomass granules. Fig. 5 depicts the profile of phenol and COD cumulative removal efficiencies during one cycle of the GSBR under shock feeding. As seen in Fig. 5, the removal of phenol started to increase immediately after injection and reached to above 99% after 12 h aeration. The COD was also removed, with the highest rate between hours 4 and 9 of operation, and reached to 10 mg/L after 15 h reaction time (98.6% removal). Therefore, the GSBR was resistant to the shock phenol loading and rapidly recovered from it, and removed phenol and its corresponded COD effectively in a relatively short period. These features present the GSBR as an efficient, reliable and stable process for removal of phenol from saline wastewaters.

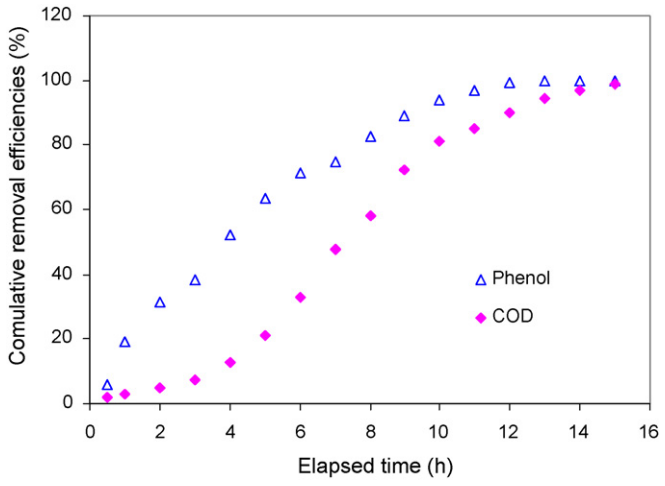

Fig. 5. Performance of the GSBR at slug feed condition for phenol and COD removal.

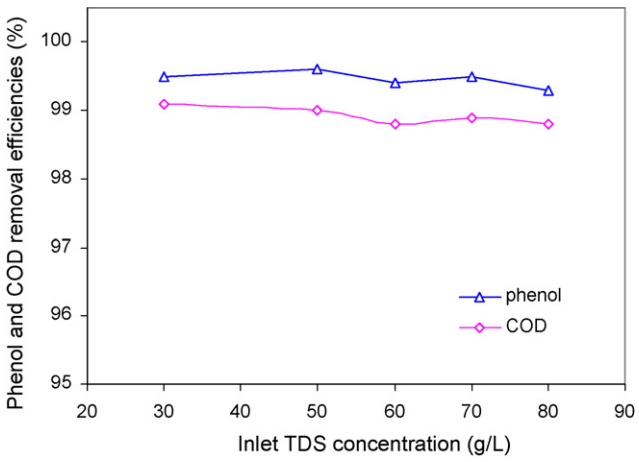

Fig. 6. Average of phenol and COD removal efficiencies in the GSBR at various wastewater TDS concentrations.

3.5. Effect of TDS concentration

The effect of salt content of the feed stream ranging from 3% to 8% was assessed on performance of the GSBR for removal of phenol and COD. The GSBR was operated at each TDS concentration under predetermined optimum condition listed in Table 2. The average of phenol and COD removal efficiencies as a function of TDS concentration in the feed wastewater is illustrated in Fig. 6. Each point in Fig. 6 represents the mean result of 10 cycles of GSBR operation under steady state conditions. It seems that the performance of GSBR was not sensitive to TDS up to a concentration of 80 g/L, so that the mean efficiencies stayed around 99% for both COD and phenol. Again, stability of the GSBR versus the variation of the salt content in range of 3–8% can be related to establishing the biomass granules containing high concentration of salt-adapted and/or halophilic microorganisms. It can be concluded from above that operating SBR with granular acclimated biomass with a mixed consortium can achieve high performance for saline phenolic wastewater in terms of phenol and COD removal under various operational conditions. Ludzack and Noran [36] and Oren et al. [37] stated that high concentration of salt in the influent has detrimental effects on the performance of aerobic treatment processes. Nonetheless, Woolard and Irvine [12] showed high phenol removal efficiency at salt contents up to 15% using a SBR inoculated with the halophilic cultures.

3.6. Sludge settling quality

The sludge volume index (SVI) was used to evaluate the sludge settling quality of the biomass granules at the various operational conditions, and to determine whether the salt content of wastewater had a detrimental effect on effluent quality. The SVI of the granules for TDS concentrations up to 80 g/L was between 15 and 25 mL/g, a value lower than the 50 mL/g that is usually accepted as the lower limit for sludge bulking [38]. The effluent turbidity was below 30 NTU during all experimental runs. In spite of the detrimental effects of salt on sludge quality and settleability of the suspended cells in the bioreactors [1], the granular biomass in the investigated GSBR indicated high quality in terms of SVI. Figueroa et al. [39] also determined a SVI of 30 mL/g VSS in an aerobic granular SBR treating saline wastewater with the salt content up to 30 g NaCl/L. The lower SVI and effluent turbidity in the present work can be related to granular nature of the biomass, and to the

presence of a high concentration of calcium ion (200 mg/L) in the feed wastewater, which accelerates the granulation process and maintains the integrity of granules structure [40,41]. The improved settleability of granules facilitates the separation of biomass from the mixed liquor suspension and thus mitigates the separation problems encountered in biological treatments of saline streams using suspended growth bioreactors.

4. Conclusion

This work describes the performance of the GSBR for phenol removal from saline wastewater. A bench scale GSBR was operated to investigate the effect of operational variables including inlet phenol and COD concentrations, filling and aerating cycle times, TDS concentration, and shock feeding on the performance of the reactor. The conclusions drawn from this study are summarized as follows:

- The performance of GSBR was not significantly affected by inlet phenol concentrations up to 1500 mg/L with cycle time of 24 h, where the removal efficiencies of both phenol and COD were over 99%.
- Aeration time is an important variable affecting the phenol removal from saline wastewater in the GSBR, such that reducing the aeration time below 15.5 h led to reduction of the phenol and COD removal.
- Filling phase period did not have a notable effect on the performance of the GSBR as very high removal efficiency was achieved with 1 h filling time.
- The GSBR could effectively remove phenol and its corresponding COD from the feed saline wastewater with TDS concentrations up to 8%.
- The SVI of the granules for TDS concentrations up to 80 g/L was between 15 and 25 mL/g, indicating high sludge settling quality.

Acknowledgment

The authors would like to express their gratitude to Tarbiat Modares University for providing financial and technical support.

References

[1] R. Lefebvre, R. Moletta, Treatment of organic pollution in industrial saline wastewater: a literature review, Water Res. 40 (2006) 3671–3682.
[2] N.P. Dan, C. Visvanathan, B. Basu, Comparative evaluation of yeast and bacterial treatment of high salinity wastewater based on biokinetic coefficients, Bioresour. Technol. 87 (2003) 51–56.
[3] X. Zhao, Y. Wang, Z. Ye, A.G.L. Borthwick, J. Ni, Oil field wastewater treatment in biological aerated filter by immobilized microorganisms, Process. Biochem. 41 (2006) 1475–1483.
[4] F.J. Benitez, J. Beltran-Heredia, J. Torregrosa, J.L. Acero, Aerobic degradation of olive mill wastewater, Appl. Microbiol. Biotechnol. 47 (1997) 185–188.
[5] N. Azbar, A. Bayram, A. Filibeli, A. Muezzinoglu, F. Sengul, A. Ozer, A review of waste management options in olive oil production, Crit. Rev. Environ. Sci. Technol. 34 (2004) 209–247.
[6] G. Busca, S. Berardinelli, C. Resini, L. Arrighi, Technologies for the removal of phenol from fluid streams: a short review of recent developments, J. Hazard. Mater. 160 (2008) 265–288.
[7] G. Moussavi, M. Mohseni, The treatment of waste air containing phenol vapors in biotrickling filter, Chemosphere 72 (2008) 1649–1654.
[8] S.H. Lin, C.T. Shyu, M.C. Sun, Saline wastewater treatment by electrochemical method, Water Res. 32 (1998) 1059–1066.
[9] M. Karthik, N. Dafale, P. Pathe, T. Nandy, Biodegradability enhancement of purified terephthalic acid wastewater by coagulation–flocculation process as pretreatment, J. Hazard. Mater. 154 (2008) 721–730.
[10] T. Panswad, C. Anan, Impact of high chloride wastewater on an anaerobic/anoxic/aerobic process with and without inoculation of chloride acclimated seeds, Water Res. 33 (1999) 1165–1172.
[11] C.R. Woolard, R.L. Irvine, Biological treatment of hypersaline wastewater by a biofilm of halophilic bacteria, Water Environ. Res. 66 (1994) 230–235.
[12] C.R. Woolard, R.L. Irvine, Treatment of hypersaline wastewater in the sequencing batch reactor, Water Res. 29 (1995) 1159–1168.
[13] C. Hinteregger, F. Streichsbier, Halomonas, sp. a moderately halophilic strain, for biotreatment of saline phenolic wastewater, Biotechnol. Lett. 19 (1997) 1099–1102.
[14] Y. Li, Z. Lei, Z. Zhang, N. Sugiura, Effects of nutrient addition on phenol biodegradation rate in biofilm reactors for hypersaline wastewater treatment, Environ. Technol. 27 (2006) 511–520.
[15] D.D.C. Freire, M.C. Cammarota, G.L. Sant'Anna, Biological treatment of oil field wastewater in a sequencing batch reactor, Environ. Technol. 22 (2001) 1125–1135.
[16] V.A. Alva, B.M. Peyton, Phenol and catechol biodegradation by the haloalkaliphile *Halomonas campisalis*: influence of pH and salinity, Environ. Sci. Technol. 37 (2003) 4397–4402.
[17] M.A. Gómez, E. Hontoria, J. González-López, Nitrogen removal from saline high nitrate industrial wastewater containing phenol, Fresenius Environ. Bull. 13 (2004) 326–331.
[18] A.F. Ramos, M.A. Gómez, E. Hontoria, J. González-López, Biological nitrogen and phenol removal from saline industrial wastewater by submerged fixed-film reactor, J. Hazard. Mater. 142 (2007) 175–183.
[19] G. Tchobanoglous, F.L. Burton, H.D. Stensel, Wastewater Engineering: Treatment and Reuse, 4th ed., McGraw-Hill, New York, 2003.
[20] Y. Shengquan, W. Hui, Z. Chaohua, Q. Xiaoming, Study of the hydrolytic acidification-SBR process in aquatic products processing wastewater treatment, Desalination 222 (2008) 318–322.
[21] E. Marañón, I. Vaïzquez, J. Rodrıĭguez, L. Castrilloĭn, Y. Fernaĭndez, H. Loĭpez, Treatment of coke wastewater in a sequential batch reactor (SBR) at pilot plant scale, Bioresour. Technol. 99 (2008) 4192–4198.
[22] Z. Hu, R.A. Ferraina, J.F. Ericson, A.A. MacKay, B.F. Smets, Biomass characteristics in three sequencing batch reactors treating a wastewater containing synthetic organic chemicals, Water Res. 39 (2005) 710–720.
[23] S.-G. Wang, X.-W. Liu, H.-Y. Zhang, W.-X. Gong, X.-F. Sun, B.-Y. Gao, Aerobic granulation for 2,4-dichlorophenol biodegradation in a sequencing batch reactor, Chemosphere 69 (2007) 769–775.
[24] H.L. Jiang, J.H. Tay, S.T.L. Tay, Changes in structure, activity and metabolism of aerobic granules as a microbial response to high phenol loading, Appl. Microbiol. Biotechnol. 63 (2004) 602–608.
[25] S. Yi, W.Q. Zhuang, B. Wu, S.T.L. Tay, J.H. Tay, Biodegradation of p-nitrophenol by aerobic granules in a sequencing batch reactor, Envion. Sci. Technol. 40 (2006) 2396–2401.
[26] APHA, AWWA, WEF, Standard Methods for the Examination of Water and Wastewater, 20th ed., APHA, AWWA, WEF, Washington, DC, 1998.
[27] K. Vidya Shetty, R. Ramanjaneyulu, G. Srinikethan, Biological phenol removal using immobilized cells in a pulsed plate bioreactor: effect of dilution rate and influent phenol concentration, J. Hazard. Mater. 149 (2007) 452–459.
[28] C.S.A. Sá, R.A.R. Boaventura, Biodegradation of phenol by *Pseudomonas putida* DSM 548 in a trickling bed reactor, Biochem. Eng. J. 9 (2001) 211–219.
[29] M. Afzal, S. Iqbal, S. Rauf, Z.M. Khalid, Characteristics of phenol biodegradation in saline solutions by monocultures of *Pseudomonas aeruginosa* and *Pseudomonas pseudomallei*, J. Hazard. Mater. 149 (2007) 60–66.
[30] C.-J.G. Jou, G.-C. Huang, A pilot study for oil refinery wastewater treatment using a fixed-film bioreactor, Adv. Environ. Res. 7 (2003) 463–469.
[31] Y.F. Tsang, F.L. Hua, H. Chua, S.N. Sin, Y.J. Wang, Optimization of biological treatment of paper mill effluent in a sequencing batch reactor, Biochem. Eng. J. 34 (2007) 193–199.
[32] Ö. Çınar, S. Yaşar, M. Kertmen, K. Demiröz, N.Ö. Yigit, Mehmet Kitis, Effect of cycle time on biodegradation of azo dye in sequencing batch reactor, Process Saf. Environ. Prot. 86 (2008) 455–460.
[33] B. Marrot, A. Barrios-Martinez, P. Moulin, N. Roche, Biodegradation of high phenol concentration by activated sludge in an immersed membrane bioreactor, Biochem. Eng. J. 30 (2006) 174–183.
[34] M.C. Tomei, M.C. Annesini, S. Bussoletti, 4-Nitrophenol biodegradation in a sequencing batch reactor: kinetic study and effect of filling time, Water Res. 38 (2004) 375–384.
[35] E. Sahinkaya, F.B. Dilek, Modeling chlorophenols degradation in sequencing batch reactors with instantaneous feed-effect of 2,4-DCP presence on 4-CP degradation kinetics, Biodegradation 18 (2007) 427–437.
[36] F.J. Ludzack, P.K. Noran, Tolerance of high salinities by conventional wastewater treatment process, J. Water Pollut. Control Fed. 37 (1965) 1404–1416.
[37] P. Oren, A. Gurevich, Y. Malkit, Henis, Microbial degradation of pollutants at high salt concentrations, Biodegradation 3 (1992) 387–398.
[38] G. Moussavi, K. Naddafi, A. Mesdaghinia, M.A. Deshusses, The removal of H_2S from process air by diffusion into activated sludge, Environ. Technol. 28 (2007) 987–993.
[39] M. Figueroa, A. Mosquera-Corral, J.L. Campos, R. Méndez, Treatment of saline wastewater in SBR aerobic granular reactors, Water Sci. Technol. 58 (2008) 479–485.
[40] H.L. Jiang, J.H. Tay, Y. Liu, S.T.L. Tay, Ca^{2+} augmentation for enhancement of aerobically grown microbial granules in sludge blanket reactors, Biotechnol. Lett. 25 (2003) 95–99.
[41] Y. Liu, J.-H. Tay, State of the art of biogranulation technology for wastewater treatment, Biotechnol. Adv. 22 (2004) 533–563.