

## Treatment of composite chemical wastewater by aerobic GAC-biofilm sequencing batch reactor (SBGR)

N. Chandrasekhara Rao, S. Venkata Mohan<sup>\*</sup>, P. Muralikrishna, P.N. Sarma

*Bioengineering and Environmental Center, Indian Institute of Chemical Technology, Tarnaka, Hyderabad 500007, India*

Received 17 August 2004; received in revised form 11 November 2004; accepted 24 March 2005

Available online 12 July 2005

### Abstract

The performance of granular activated carbon (GAC)-biofilm configured sequencing batch reactor (SBGR) in aerobic environment was investigated for the treatment of composite chemical wastewater [low BOD/COD ratio ( $\sim 0.3$ ), high sulfate content (1.75 g/l) and high TDS concentration (11 g/l)]. Composite wastewater was a combined mixture of effluents from about 100 chemical based industries. Reactor was operated under anoxic–aerobic–anoxic microenvironment conditions with a total cycle period of 24 h (fill: 15 min; reaction (aeration with recirculation): 23 h; settle: 30 min; decant: 15 min) and the performance of the system was studied at organic loading rates (OLR) of 1.7 kg COD/cum-day, 3.5 kg COD/cum-day and 5.5 kg COD/cum-day. The reactor showed efficient performance with respect to substrate degradation rate and sustained its performance at higher operating OLR (5.5 kg COD/cum-day) and at low BOD/COD ratio. Substrate utilization was found to increase with increase in the operating OLR. Maximum non-cumulative substrate utilization of 1.837 kg COD/cum-h, 2.99 kg COD/cum-h and 3.821 kg COD/cum-h was observed after 15 h of the cycle operation for operating OLRs of 1.7 kg COD/cum-day, 3.5 kg COD/cum-day and 5.5 kg COD/cum-day, respectively. Sulfate removal efficiency of  $11 \pm 2\%$  was recorded in the SBGR due to the induced anoxic conditions prevailing during the sequence phase operation of the reactor and the existing internal anoxic zones in the biofilm. Effective performance of the reactor may be attributed to sorption capacity of GAC as carrier material facilitating low toxicant concentration in the mixed liquor. The existing high flow rates around the GAC particle results in good mass transfer of the substrate from the bulk liquid. The long retention of biofilm on GAC increases the potential for the treatment of recalcitrant industrial wastewater. GAC configured biofilm configuration coupled with sequencing batch mode operation appears to be promising for the effective treatment of complex industrial wastewater containing poorly degradable compounds.

© 2005 Elsevier B.V. All rights reserved.

**Keywords:** Sequencing batch reactor; Composite chemical wastewater; GAC-biofilm; Suspended growth; Reactor configuration; Sulfates; BOD/COD ratio

### 1. Introduction

Treatment of wastewater generating from chemical processes is considered to be complex and difficult due to the presence of recalcitrant organic compounds, solvents and inorganic salts [1–5]. Conventional biological treatment processes are seldom capable of achieving required degree of performance because of the complex nature of the wastewater and prevailing shock loads. Degradation of industrial wastewater involves a complex suite of interaction between

the residency species and it is essential that microflora should persist in the system to degrade the pollutants even in adverse conditions due to the complex characteristics and transition shock loads [6]. Sequencing batch reactor technology (SBR), a periodic discontinuous process offers robust microflora capable to persist and metabolize at extremely adverse and diverse conditions. Periodic exposure of the microorganisms to defined process conditions is effectively achieved in SBR operation in which exposure time, frequency of exposure and amplitude of the respective concentration can be set independent of any inflow condition [6,7]. Also the periodic discontinuous process imposes regular substrate and oxygen gradients on the organisms that overwhelm natural

<sup>\*</sup> Corresponding author. Tel.: +91 40 27193159; fax: +91 40 27193159.  
E-mail address: vmohan\_s@yahoo.com (S.V. Mohan).

variation in waste strength and composition [8]. SBR has been successfully applied for the treatment of domestic wastewater, medium to low strength wastewater, landfill leachates, simulated dye wastewater, recalcitrant compounds, industrial wastewater and contaminated soils [6–18]. Reactor configuration is one of the important factors, which governs the performance of any biological system. Earlier we have studied the performance of suspended growth configured sequencing batch reactor (SBSR) for treating complex chemical wastewater [17]. The study demonstrated effective performance of SBSR over the corresponding suspended growth continuous system (activated sludge process (ASP)) with respect to substrate degradation rate and sulfate removal efficiency. However, the system resulted in drastic reduction of performance at organic loading rate (OLR) of 3.5 kg COD/cum-day.

It is evident that the biofilm configured systems are well suited for the treatment of wastewater containing poorly degradable compounds [19,20]. Immobilization of microflora on granular activated carbon (GAC) particles as biofilm results in high biomass hold up, which enables the process to be operated significantly at higher liquid throughputs and OLR. GAC as adsorptive medium/carrier materials acts as buffer to reduce the concentration of toxic chemicals during process operation thereby providing advantage for the treatment low biodegradable industrial wastewater containing recalcitrant compounds [21,22]. Another important advantage of using GAC as a biofilm carrier particle is the presence of high surface area and porosity (macropores), which is ideal for the initial and rapid colonization of microflora and also provides shelter niches from the resulting shear forces [23–26]. The low specific gravity of GAC facilitates fluidization even at low upflow velocity [23,25] and the sorption capacity of the GAC protects the attached biofilm from shock loads [27,28]. GAC configured systems with continuous mode operation were reported for treatment of various types of wastewater. The application GAC system was reported for the treatment of model wastewater containing organic compounds such as phenol, benzene, TCE and 2-CP, which are typically found in industrial wastewater [18].

Present communication reports experimental data pertaining to the aerobic GAC-biofilm reactor (SBGR) operated in sequencing batch mode for the treatment complex chemical wastewater. The performance of the reactor was evaluated by varying OLRs.

## 2. Material and methods

### 2.1. Composite chemical wastewater

Composite/combined chemical wastewater was used as feed. The composite wastewater was a combined mixture of effluents from about 100 chemical based industries producing a variety of chemicals, drugs, pharmaceuticals, pesticides and various chemical intermediates. The wastewater was collected from equalization tank of the existing common effluent

Table 1  
Characteristics of complex chemical wastewater used as feed

Parameters	Concentrations
pH	7.83 ± 0.24
TDS (g/l)	11 ± 0.98
Suspended solids (mg/l)	900 ± 181
Oil and grease (mg/l)	14 ± 0.42
COD (mg/l)	6000 ± 342
BOD <sub>5</sub> (mg/l)	2600 ± 108
Chlorides (mg/l)	5000 ± 96
Sulfates (mg/l)	1750 ± 47
Phosphates (mg/l)	360 ± 24
Total nitrogen (TKN) (mg/l)	125 ± 11

treatment plant specifically designed and operated for the treatment of chemical based wastewater. After collection, the wastewater was transferred immediately to the laboratory and stored at 4 °C. The detailed characteristics (in average values) of the wastewater were presented in Table 1. The complexity of the selected composite chemical wastewater could be assessed from its characteristics by the presence of a low BOD/COD ratio (~0.3), high sulfate content (1.75 g/l) and high TDS concentration (11 g/l).

### 2.2. Granular activated carbon

GAC (Extra Pure, LOBA Chemicals, Mumbai) of size ~1.5 mm was used as suspended carrier medium for the aerobic biofilm formation (bulk density: 40 g/100 ml; residue on ignition (600 °C): 5%; loss of drying (120 °C): 10%). GAC was fed to the mixed liquor of the reactor at a rate of 40 g/l of the reactor volume. During the reactor operation, the GAC was neither replaced nor regenerated.

### 2.3. Reactor configuration

GAC-biofilm configuration operated in sequencing batch mode in aerobic condition was studied for the treatment of composite chemical wastewater. The reactor was fabricated in the laboratory using perplex glass column with a total working volume of 1.7 l capacity. The reactor had height/internal diameter (*H*/*i.d.*) ratio of ~3 (*H*: 0.22 m and *i.d.*: 0.07 m). Schematic detail of the reactor along with the experimental setup is depicted in Fig. 1. The reactor outlet used for wastewater withdrawal was provided at a height of 0.045 m from bottom of the reactor. This arrangement prevents loss of GAC and biomass in the reactor after the settling phase. About 0.39 l of mixed liquor was present in the reactor after the withdrawal phase was completed resulting in a total liquid volume of 1.34 l during the reaction phase. Upflow velocity of 0.083 m h<sup>-1</sup> was maintained during the reactor operation by recirculation and air sparging in the upflow mode. This velocity was found to be sufficient to keep carrier GAC in suspension during reaction phase of the reactor operation. Feeding, recirculation and decant operations were done with the help of peristaltic pumps (Watson Marlow 101 U/R) employing preprogrammed timers (ETTS, Germany).

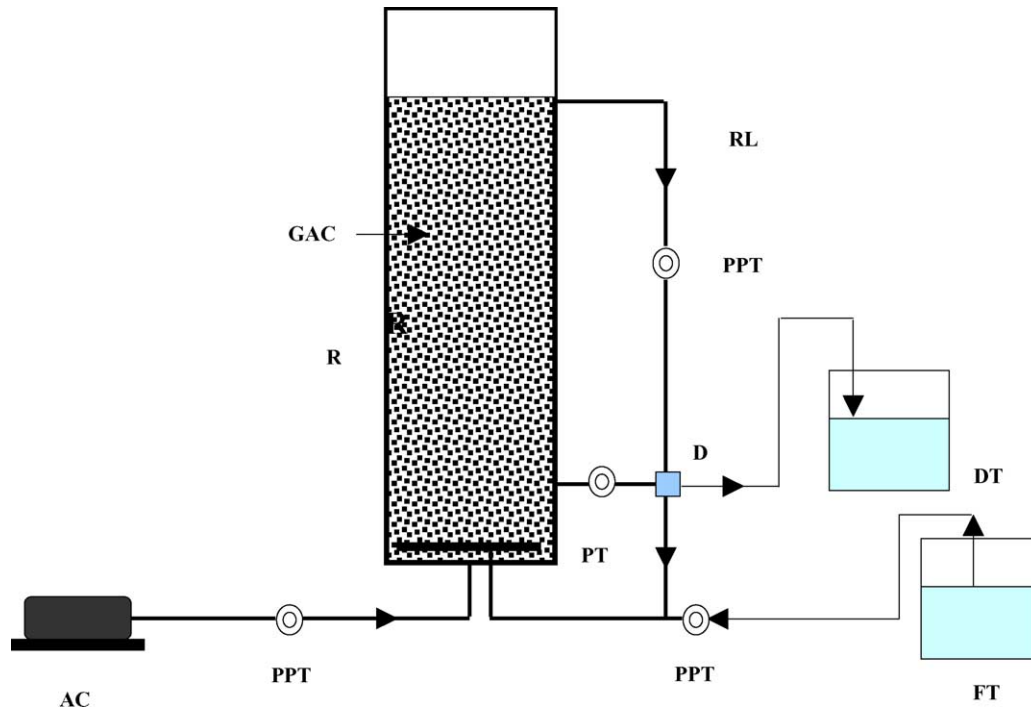


Fig. 1. Schematic representation of SBGR along with experimental setup (AC: air compressor; DT: decant tank; FT: feed tank; RL: recirculation line; PPT: peristaltic pump connected to preprogrammed timer; D: flow distribution; R: reactor; GAC: granular activated carbon).

#### 2.4. Start up

The reactor was inoculated with aerobic biomass acquired from activated sludge unit treating composite chemical effluents for past one year. The mixed liquor from the aeration tank of ASP was acquired (VSS of 3 g/l) and inoculated at a ratio of 1:5 (v/v) with reactor volume. Subsequently, GAC was loaded to the mixed liquor of the reactor (40 g/l of the wastewater treated) and the reactor was operated with designed synthetic feed (g/l) (glucose: 1 g/l; sodium acetate: 1g/l;  $\text{Na}_2\text{HPO}_4$ : 0.3 g/l, pH 7.0) to support biomass formation on GAC. After the formation of biomass on GAC (0.0302 g VSS/g GAC or 1.08 g COD/g GAC), the reactor was fed with wastewater at an OLR of 1.7 kg COD/cum-day and subsequently after stable performance was achieved, the reactor was operated at higher OLRs (3.5 kg COD/cum-day; 5.5 kg COD/cum-day). The startup procedure adopted and inoculation used for both the reactors was similar.

#### 2.5. Reactor operation

The reactor was operated in sequencing batch mode under anoxic–aerobic–anoxic microenvironment conditions with a total cycle period of 24 h consisting of 15 min of fill phase, 23 h of react (aerobic) phase integrated with recirculation, 30 min of settle phase and 15 min of decant phase at a constant temperature of  $27 \pm 2^\circ\text{C}$ . The sequencing phases (feed, aeration, recycling and decant) during the reactor cycle operation were controlled by pre-programmed timers. The entire

reactor volume was recirculated along with aeration during the react phase operation. At the beginning of each cycle, i.e., immediately after withdrawal of treated wastewater of the earlier sequence, a pre-defined feed volume was pumped into the reactor. Aeration was done by supplying air using diffused aerators connected through a sparger arrangement. During the react phase, aqueous phase DO was maintained in the range of 3.0–4.0 mg/l. The influent pH was adjusted to  $7.1 \pm 0.2$  before feeding wastewater. Recirculation at a rate of 4l/day was maintained throughout the investigation to achieve a homogeneous distribution of substrate as well as uniform distribution of GAC and suspended biomass along the reactor depth. Also, the recirculation facilitates linear velocity, which restricts the existence of a concentration gradient during the reaction phase.

The performance of reactor was evaluated by estimating substrate (COD) removal efficiency ( $\xi_{\text{COD}}$ ) calculated by using Eq. (1).  $C_{\text{SO}}$  represents the initial COD concentration (mg/l) in the feed and  $C_{\text{S}}$  denotes COD concentration (mg/l) in the reactor outlet:

$$\xi_{\text{COD}} = \frac{C_{\text{SO}} - C_{\text{S}}}{C_{\text{SO}}} \quad (1)$$

Substrate degradation rate (non-cumulative) ( $\text{SDR}_{\text{T}}$ : kg COD/cum-h) was calculated to study the rate of substrate (COD) removal for a unit time during the sequence phase operation using the following equation, where,  $\text{SDR}_{\text{X}}$  and  $\text{SDR}_{\text{Y}}$  represents, the substrate degradation rate (kg COD/cum-day) at time  $X$  and  $Y$ , respectively, and  $t_{\text{X}}$  and  $t_{\text{Y}}$

denotes time (h) at X and Y, respectively,

$$\text{SDR}_T = \frac{(\text{SDR}_X - \text{SDR}_Y)24}{t_X - t_Y} \quad (2)$$

### 2.6. Kinetics of substrate degradation

Reactor performance was studied by linearly fitting the empirical relationship represented by Eq. (3) and the first order kinetic model represented by Eq. (4) [29,30].  $R_S$  represents substrate degradation rate (kg COD/cum-day),  $C_{SR}$  was the substrate concentration value in the reactor (mg/l) and  $k_1$  represents an empirical kinetic coefficient embodies intrinsic consumption kinetic constant as well as internal and external mass transfer constants. In Eq. (3), the empirical parameters  $a_1$  and  $a_2$  are the maximum value of  $E_1$  and the time required to attain 50% of the maximum value, respectively,

$$\xi = \frac{a_1 t}{a_2 + t} \quad (3)$$

$$R_S = K_1(C_S - C_{SR}) \quad (4)$$

### 2.7. Analytical protocols

The performance of the reactor was assessed by monitoring COD removal efficiency throughout the reactor operation. In addition, pH, ORP, sulfates, BOD<sub>5</sub>, OCR and DO were also determined during the sequence phase operation. The analytical procedures for monitoring the above parameters (COD—closed refluxing titrimetric method (5220 C); BOD<sub>5</sub>—5-day BOD test (5210 B); pH—electrometric method (4500-H<sup>+</sup>B); ORP—electrometric method (2580 B); sulfates—turbidimetric method (4500-SO<sub>4</sub><sup>2-</sup>E); DO—membrane electrode method (4500-0G)) were employed as outlined in the Standard Methods [31]. Oxygen consumption rate (OCR) was determined using DO probe (YSI 5100) by continuously monitoring the DO in the reaction phase when the air supply was turned (APHA, 1998, Method-2710 B). During this phase the DO is linear and OCR is evaluated as

$$\text{OCR} = \frac{\text{DO}_1 - \text{DO}_2}{t_2 - t_1} \quad (5)$$

Where, OCR in mg O<sub>2</sub> min<sup>-1</sup> and DO<sub>1</sub> and DO<sub>2</sub> are the DO concentrations at time  $t_1$  and  $t_2$ , respectively, in minutes.

All the analytical determinations were made in duplicate and the average was taken. The virgin and biofilm immobilized GAC was carefully dehydrating at 30 °C in hot air oven for 24 h without disturbing the actual morphology of the biofilm and was subjected to scanning electron microgram (SEM) to observe surface morphological details. Biofilm size was measured using SEM.

## 3. Results and discussion

### 3.1. Reactor performance

SBGR was initially operated at 1.7 kg COD/cum-day of OLR and the performance of the reactor with respect to COD removal efficiency was assessed during the cycle operation (Fig. 2). The reactor showed a COD removal efficiency of 78% accounting for a substrate degradation rate of 1.33 kg COD/cum-day at steady state condition. Subsequently after achieving stable performance, the reactor was operated at higher OLR to understand the performance (3.5 kg COD/cum-day; 5.5 kg COD/cum-day), respectively, keeping all other operating conditions the same. At 3.5 kg COD/cum-day, the reactor showed about 49% of COD removal efficiency with an SDR of 1.694 kg COD/cum-day, while in the case of 5.5 kg COD/cum-day OLR, the reactor yielded 39% of COD removal efficiency (SDR of 2.128 kg COD/cum-day). It is evident from the results that the SBGR reactor showed consistently good performance at higher OLR. Fig. 3 shows the performance of the reactor with respect to BOD removal efficiency. The BOD profile during the sequence operation showed comparably the same pattern as the COD profile. BOD removal efficiency of 86.04% was observed at operating OLR of 1.7 kg COD/cum-day after the reactor attained steady state. The reactor attained stable conditions within 3 days and remained more or less constant thereafter. BOD removal efficiencies of 63.63 and 66.48% were observed at operating OLRs of 3.5 kg COD/cum-day and 5.5 kg COD/cum-day, respectively, at steady state conditions. With continued operation, the reactor showed enhanced performance with respect to COD and BOD removal and after attaining stable conditions the performance remained more or less constant thereafter.

The performance of the corresponding suspended growth configuration (SBSR) at 1.7 kg COD/cum-day of OLR

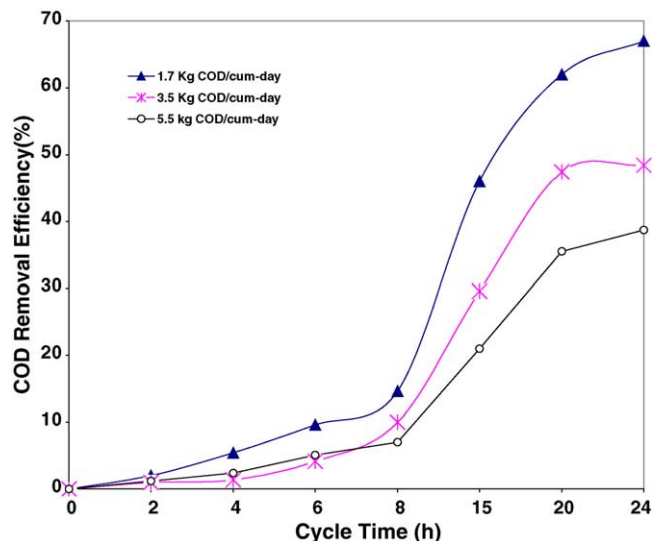


Fig. 2. COD removal efficiency in SBGR.



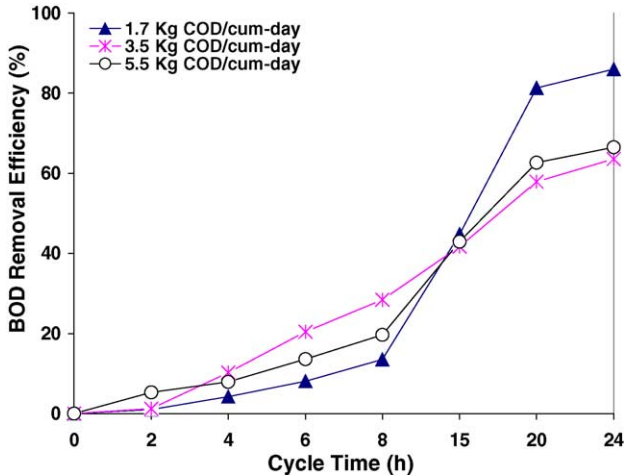


Fig. 3. BOD removal efficiency in SBGR.

recorded 47.1% COD removal efficiency accounting for SDR of 0.80 kg COD/cum-day. Detailed discussion regarding the performance of the SBSR at different OLRs studied was presented elsewhere [17]. At 3.5 kg COD/cum-day of OLR, only 25.3% of COD removal efficiency (0.875 kg COD/cum-day of SDR) was observed. With increase in OLR a significant decrease in the substrate removal efficiency was reported and this observation correlated well with the reduction in mixed liquor VSS concentration [from 1800 mg/l (1.7 kg COD/cum-day) to 900 mg/l (3.5 kg COD/cum-day)]. Comparatively, GAC configured system showed effective performance over the corresponding suspended growth system studied at similar operating conditions treating composite chemical wastewater in our laboratory [17]. The SBGR system sustained its performance even at higher OLRs (up to 5.5 kg COD/cum-day) without process inhibition. However, the corresponding suspended growth system resulted in process failure at OLR of 3.5 kg COD/cum-day.

### 3.2. Non-cumulative SDR<sub>T</sub>

The non-cumulative substrate degradation rate profiles for all the three OLRs studied are depicted in Fig. 4. The profile for all the studied cases showed a consistent trend of increase in the substrate removal rate with the function of cycle period. Rapid substrate removal rate was observed between 8 and 20 h of the cycle period. For 1.7 kg COD/cum-day of OLR, maximum substrate removal rate (1.84 kg COD/cum-h) was observed after 15 h of the cycle operation, while in the case of 3.5 kg COD/cum-day and 5.5 kg COD/cum-day, maximum substrate utilization of 2.99 kg COD/cum-h and 3.82 kg COD/cum-h respectively were observed after 20 h of the cycle operation. Slow substrate utilization observed during initial phase of cycle operation may be attributed to the presence of high concentration gradient of the substrate in the reactor volume. With increase in the cycle period the substrate in the aqueous phase adsorbed on to the GAC resulting in the reduction of actual substrate concentration in the reactor volume leading to rapid substrate removal.

### 3.3. Kinetics of substrate degradation

The reactor performance with respect to substrate degradation was analyzed by linearly fitting the empirical relationship represented by Eq. (4) and the first order kinetic model represented by Eq. (5) [29,30]. The  $R_S$  for all studied conditions estimated by the first order model Eq. (5) is shown in Table 2. For comparison, the table also includes the respective figures of SBSR, which was not discussed earlier with kinetic aspect. The parameter  $k_1$  obtained from the first order model Eq. (5) and the value of parameters  $a_1$  and  $a_2$  obtained from the empirical model Eq. (4) are also shown in Table 2 as a function of OLR and reactor configuration. Fig. 5a and b presents the variation profiles of parameters  $a_2$  and  $k_1$  as a function of OLR and reactor configuration. The results indicated

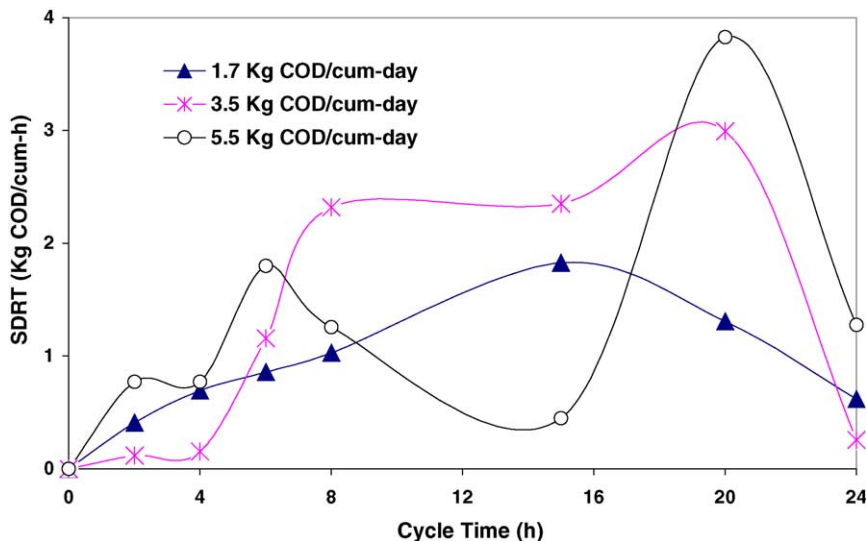


Fig. 4. Substrate degradation rate (non-cumulative) during sequence phase operation.

Table 2

Value of parameters of the empirical model (Eq. (4)) and  $k_1$  and  $C_{SR}$  from the first order model (Eq. (5))

Reactor	OLR (kg COD/cum-day)	$k_1$ ( $\text{h}^{-1}$ )	$t$ (h)	$a_1$ (dimensionless)	$R_S$ (kg COD/cum-day)	$a_2$ (h)	$C_{SR}$ (mg COD/l)
SBGR	1.7	2.03	12.4	0.67	1.14	11.4	1005
	3.5	0.94	15.5	0.48	1.69	14.5	1520
	5.5	0.63	17.4	0.39	2.13	16.4	2260
SBSR	1.7	0.62	13.3	0.38	0.65	12.3	790
	3.5	0.26	3.18	0.20	0.71	9.4	1110

that the overall substrate removal rate increased with the increase in OLR. However, in SBGR system, substantial improvement in the  $R_S$  values was noticed with increase in OLR, while in the case of SBSR, a marginal increase in  $R_S$  value was observed. Stabilization tendency was observed in the case of SBGR system after approaching OLR of 3.5 kg COD/cum-day. It is also evident from the data that SBGR showed superior performance over the corresponding SBSR system.

### 3.4. BOD/COD variation

An attempt was made to study the variation of BOD/COD ratio during the sequence phase operation to understand the influence of the BOD/COD ratio on the process performance (Fig. 6). The BOD/COD ratio with respect to SBSR reactor is also presented in the graph for comparison. The ratio showed a gradual reduction during the course of cycle operation for all the studied cases. It is evident from the profiles that the GAC configured system was observed to be more robust in sustaining its performance at low BOD/COD ratio compared to corresponding suspended growth system. A steep decline in the ratio was observed after 8 h of the cycle operation for all the studied variations. The decline in BOD/COD ratio was observed with an increase in OLR. Process inhibition with respect to substrate removal was not evident in SBGR at the

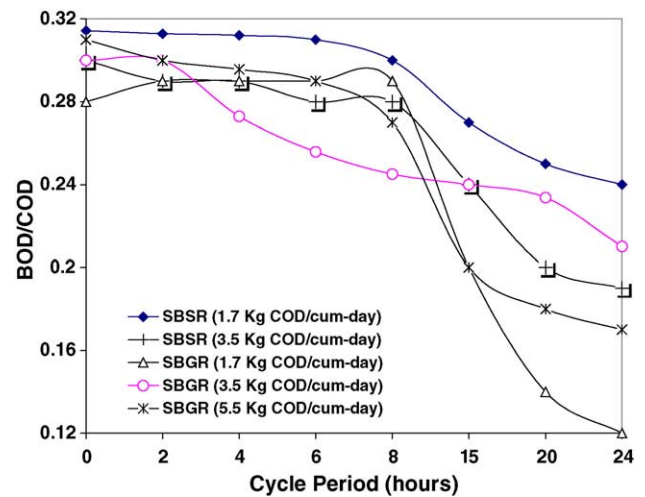


Fig. 6. Variation of BOD/COD ratio during sequence phase operation.

studied higher OLRs. Comparatively poor performance of the SBSR at higher OLRs can be attributed to the presence of high substrate gradients of composite chemical wastewater in the reactor inhibiting the native biomass [loss in mixed liquor biomass (VSS) concentration]. Presence of GAC as supporting material in suspension facilitates low substrate concentration in the bulk liquid of the reactor volume due to sorption phenomena, which reduces biomass exposure to the

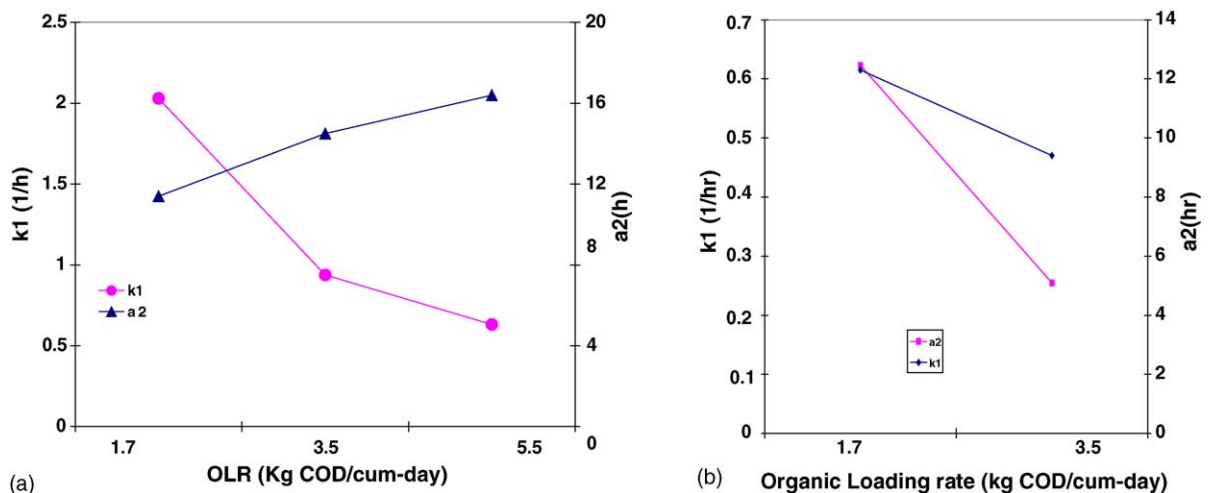


Fig. 5. Variation of parameters of the empirical model (Eq. (4)) and the first order model (Eq. (5)) as a function of OLR and reactor configuration (a) SBGR and (b) SBSR.

Table 3  
Variation of sulfate removal

Reactor	OLR (kg COD/cum-day)	COD/SO <sub>4</sub> <sup>-</sup>	Total sulfate removal (mg/l)
SBGR	1.7	3.34 ± 0.12	69.19 ± 0.49
	3.5	3.23 ± 0.07	114.48 ± 1.12
	5.5	3.42 ± 0.10	164.39 ± 1.46
SBSR	1.7	3.34 ± 0.06	47.07 ± 0.67
	3.5	3.23 ± 0.12	91.23 ± 0.98

toxicants. In addition, the adsorbed toxicant may eventually undergo biodegradation with the acclimatized microbial population [32]. The high flow rate around the particle creates effective mass transfer of dissolved organic matter from the bulk liquid on to the particle surface [26]. The surface texture of the GAC initiates the initial colonization of the microorganisms on the surface and the colonized biofilm on the surface metabolizes the adsorbed pollutants from the bulk fluid or as a result of desorption from the surface of the GAC [33,34].

3.5. Sulfate removal

Conventional aerobic system cannot reduce sulfates, as it needs either anaerobic or anoxic environment to bring about the reduction. In general, the COD/sulfate ratio of 3.3 is normally considered to be highly inhibitory for any anaerobic process [35]. In this study, sulfate reduction in the range of 9–13% was achieved at all the OLRs studied (Table 3 and Fig. 7). About 13.23% of sulfate removal efficiency was observed accounting for 69.19 mg/l of sulfate removal at the OLR of 1.7 kg COD/cum-day. In the case of higher OLRs of 3.5 kg COD/cum-day and 5.5 kg COD/cum-day, sulfate removal of 114.5 mg/l and 164.33 mg/l was observed accounting for 10.6 and 9.7% of sulfate removal efficiency,

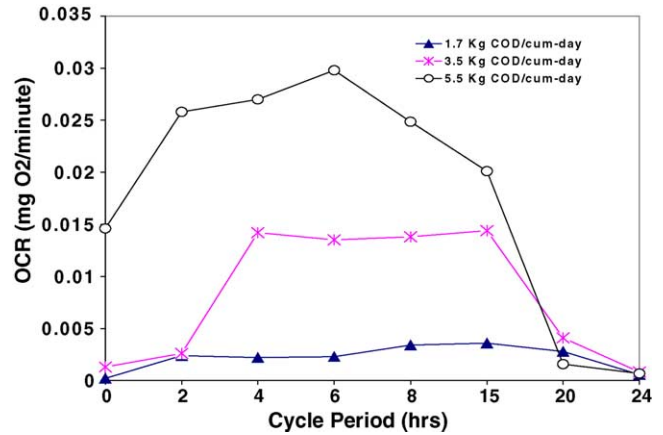


Fig. 8. Variation of OCR during sequence phase operation at 3.5 kg COD/cum-day OLR.

respectively. In case of corresponding suspended growth configured system about 8% of sulfate removal efficiency was reported (by keeping the COD/sulfate ratio constant at 3.3) [17]. Venkata Mohan et al. [17] attributed the transformation in the SBR operation to the presence of prevailing anoxic microenvironment during the sequence phase operation of the SBR and to the induced anoxic zone in the internal layers of the biofilm. A total of 60 min of anoxic microenvironment was included during fill, settle and decant phases of the cycle operation, which facilitates a suitable environment for sulfate reduction. The biofilm size also had significant influence on the extent and presence of anoxic zone and the internal biofilm normally had anoxic environment [10,17]. Biofilm floc size of above 200 μm was reported to have anoxic microniche in the internal part of the thick flocs [10]. The GAC particle size itself was about 1.5 mm in diameter, which facilitate profuse anoxic environment in the internal clusters of GAC-biomass leading to sulfate transformation. Extension of anoxic phase

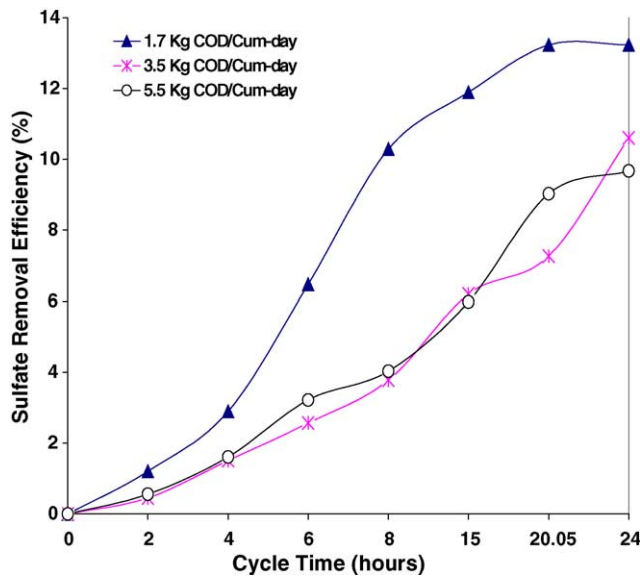


Fig. 7. Sulfate removal efficiency during sequence operation.

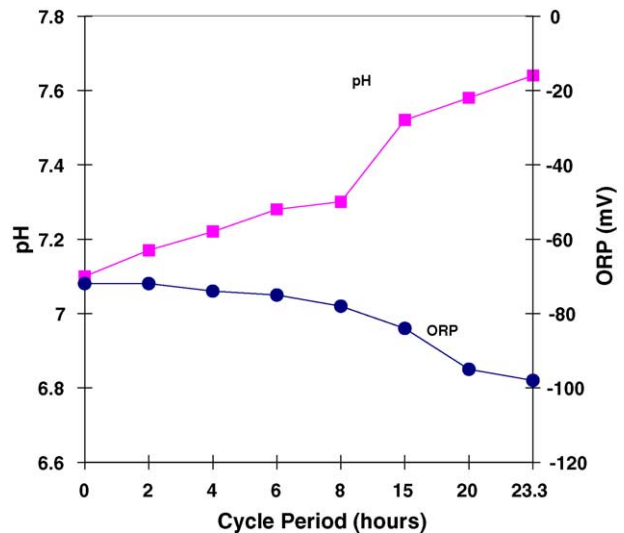


Fig. 9. Variation of pH and ORP during sequence phase operation at 3.5 kg COD/cum-day.

period in total cycle period may further enhance the sulfate removal efficiency. Detailed studies in this direction are being conducted in our laboratory.

### 3.6. Process monitoring

Oxygen consumption/transfer capacity is often one of the important factors that limit the capacity of aerobic biological systems and indicates the ongoing biochemical process. Oxygen consumption rate was monitored to assess the ability of biomass to degrade complex substrate in aerobic environments. OCR was relatively low during the initial phase of

cycle operation and after 4 h of operation the rate increased rapidly and attained maximum (Fig. 8). After 15 h of cycle operation, OCR gradually dropped up to be 20 h and remained more or less constant till the end of the cycle. The consumption rate of oxygen was found to dependent on the OLR. Higher loading rates showed higher oxygen supplementation for aerobic metabolism of the substrates.

The variation of pH and ORP during sequence phase was also monitored and is shown in Fig. 9. The influent feed was adjusted to  $7.1 \pm 0.2$  prior to feeding. The aqueous phase pH was found to increase gradually with time and approached 7.6 at the end of the reaction phase. ORP (mV) profile visualized a mirror image to pH and with increase of sequence time the ORP approached zero (0 mV). For all the experimental variations studied the pH and ORP profiles remained more or less same.

Scanning electron microgram images of virgin GAC and biofilm immobilized GAC (acquired during the reactor operation of reactor at 3.5 kg COD/cum-day of OLR) are shown in Fig. 10. From the microgram, the morphology of the GAC-biofilm was found to be heterogeneous in nature with uneven dense surface texture formed on the carbon surface compared to virgin GAC.

## 4. Conclusions

Studies revealed the efficiency of GAC-biofilm configured system over the corresponding suspended growth system in treating composite chemical wastewater. The reactor showed to sustain its performance at higher organic loading rates and at even low BOD/COD ratio without system inhibition. Sulfate removal efficiency of  $11 \pm 2\%$  was observed due to prevailing anoxic microenvironment during the sequence phase operation of the reactor and the existing internal anoxic zones in the biofilm. GAC as carrier material provided low toxicant concentration in the bulk fluid due to sorption mechanism and thereby reduces the biomass exposure to the toxicant. Operation of reactor in sequencing batch mode provided effective process performance due to enforced short-term unsteady state conditions coupled with periodic exposure of the microorganisms to defined process conditions which in turn facilitate control of the physiological state of microorganisms. GAC-biofilm configured system coupled with sequencing batch mode operation holds promise for the treatment of composite industrial wastewater over the suspended growth system.

## Acknowledgments

One of the authors (Mr. N. Chandrashekar Rao) is thankful to CSIR for providing him Senior Research Fellowship and Dr. S. Venkata Mohan gratefully acknowledges Alexander von Humboldt (AvH) Foundation for giving the fellowship and Prof. Dr.-Ing. P.A. Wilderer for exposing to sequencing batch reactor (SBR) technology.

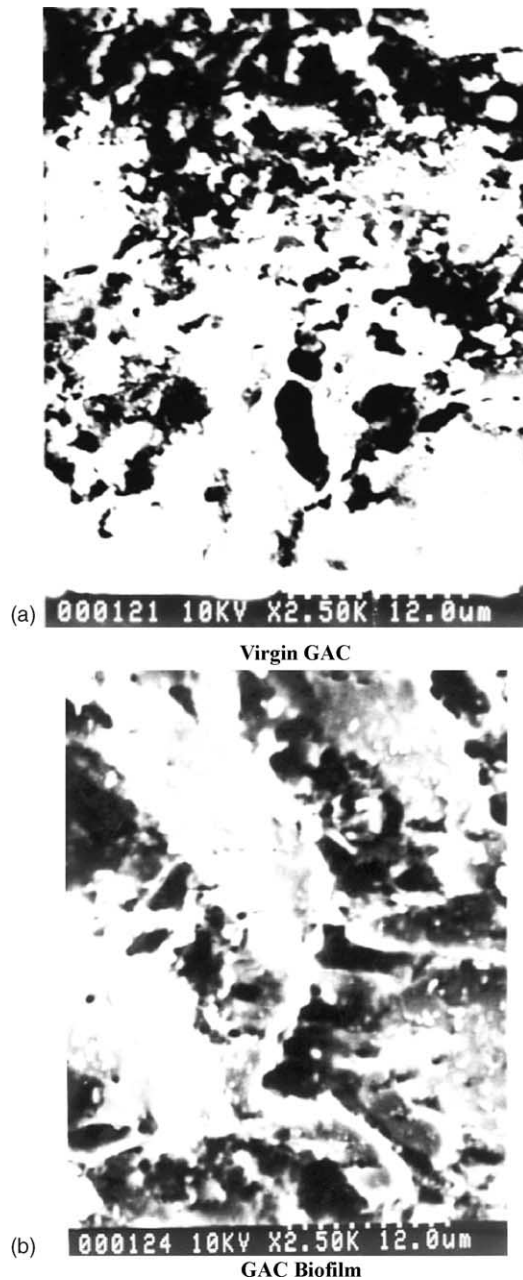


Fig. 10. Scanning electron micrograph (SEM) images of GAC (a) virgin GAC and (b) biofilm immobilized GAC.



## References

- [1] S. Venkata Mohan, R.S. Prakasham, B. Satyavathi, J. Annapurna, S.V. Ramakrishna, *Water Sci. Technol.* 43 (2001) 271.
- [2] S. Venkata Mohan, P.N. Sarma, *Pharm. Biol. World* 11 (2002) 93.
- [3] I.A. Alaton, S. Dogruel, E. Baykal, G. Gerone, *J. Environ. Manage.* 73 (2004) 155.
- [4] C.L. Lai, S.H. Lin, *Chemosphere* 54 (2004) 235.
- [5] D. Rajkumar, K. Palanivelu, *J. Hazard. Mater.* B113 (2004) 123.
- [6] P.A. Wilderer, R.L. Irvine, M.C. Goronszy, *Sequencing Batch Reactor Technology*, Scientific and Technical Report, IWA Publishing, 2001.
- [7] P.A. Wilderer, in: M.R. Lodisch, A. Bose (Eds.), *Harnessing Biotechnology for the 21st Century*, American Chemical Society, 1992.
- [8] C.R. Woolard, *Water Sci. Technol.* 35 (1997) 199.
- [9] J. Dollerer, P.A. Wilderer, *Water Sci. Technol.* 34 (1996) 437.
- [10] L. Pochana, J. Kellen, P. Lant, *Water Sci. Technol.* 39 (1999) 235.
- [11] P. Rajaguru, K. Kalaiselvi, M. Palanivel, V. Subburam, *Appl. Microbiol. Biotech.* 54 (2000) 268.
- [12] L. Fu, X. Wen, Q. Lu, Y. Quain, *Proc. Biochem.* 36 (2001) 1111.
- [13] C. Juneson, O.P. Ward, A. Sing, *Proc. Biochem.* 37 (2001) 305.
- [14] G. Buitron, G. Soto, G. Vite, J. Morena, *Water. Sci. Technol.* 43 (2001) 283.
- [15] S. Venkata Mohan, Y.V. Nancharaiyah, C. Flankentof, P. Wattiau, S. Wuertz, P.A. Wilderer, M. Hausnes, *Proceedings of VAAM Conference*, Gottingen, 2002.
- [16] S. Venkata Mohan, K. Sirisha, N. Chandrasekhar Rao, P.N. Sarma, S.J. Reddy, *J. Hazard. Mater.* B116 (2004) 39.
- [17] S. Venkata Mohan, N. Chandrashekar Rao, K. Krishna Prasad, B.T.V. Madhavi, P.N. Sarma, *Process. Biochem.* 40 (2005) 1501.
- [18] F.R. Kolb, P.A. Wilderer, *Water Sci. Technol.* 35 (1997) 169–176.
- [19] E.J. Bouwer, Transformation of xenobiotics in biofilms, in: W.G. Charcklis, P.A. Wilderer (Eds.), *Structure and Function of Biofilms*, John Wiley, New York, 1989, p. 251.
- [20] P.M. Makinen, T.J. Theno, J.F. Ferghson, J.E. Ongerth, J.A. Puhakka, *Environ. Sci. Technol.* 27 (1993) 1434.
- [21] M.T. Suidan, I.N. Najm, J.T. Pfeffer, Y.T. Wang, *J. Environ. Eng.* 114 (1988) 1359.
- [22] S.I. Safferman, P.L. Bishop, *J. Hazard. Mater.* B54 (1997) 241.
- [23] AWWA Committee Report, *Assessment of Microbial Activity on GAC*, J. Am. Water Works Assoc., 1981, p. 447.
- [24] W.G. Characklis, M.G. Trulear, J.D. Bryers, N. Zelter, *Water Res.* 16 (1982) 1207.
- [25] M.T. Suidan, G.F. Nakhla, Anaerobic fluidized-bed treatment of hazardous waste, in: *Proceeding on Reducing Risks from the Environment through Biotechnology*, Seattle, 1987.
- [26] B.E. Rittmann, P.L. McCarty, *Environmental Biotechnology: Principles and Applications*, McGraw-Hill International Edition, Boston, 2001.
- [27] P.F. Fox, M.T. Suidan, J.T. Bandy, *Water Res.* 24 (1990) 827.
- [28] K.A. Khan, M.T. Suidan, W.H. Cross, *J. Environ. Eng. Division (ASCE)* 108 (1982) 269.
- [29] A. LeDuy, J.E. Zajic, *Biotechnol. Bioeng.* 15 (1973) 805.
- [30] J.A.D. Rodrigues, S.M. Ratusznei, E.F.M. Camargo, M. Zaiat, *Adv. Environ. Res.* 7 (2003) 405.
- [31] *Standard Methods for the Examination of Water and Wastewater*, 20th ed., APHA, WFC, AWWA, Washington DC, 1998.
- [32] J.F. Malin, F.G. Pohland, *Design of Anaerobic Processes for the Treatment of Industrial and Municipal Wastes*, Technomic Publishing Co. Inc., Lancaster, 1992.
- [33] F.R. Kolb, P.A. Wilderer, *Water Sci. Technol.* 35 (1997) 169.
- [34] Y. Liu, J. Tay, *Water Res.* 36 (2002) 1653.
- [35] F. Omil, P. Lens, P. Hulshoff, G. Lettinga, *Process. Biochem.* 31 (1996) 699.