Journal of Hazardous Materials 190 (2011) 260–267

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Kinetic analysis of phenol, thiocyanate and ammonia-nitrogen removals in an anaerobic–anoxic–aerobic moving bed bioreactor system

Biju Prava Sahariah [a], Saswati Chakraborty [b,*]

[a] Centre for the Environment, Indian Institute of Technology Guwahati, Assam 781039, India
[b] Department of Civil Engineering, Indian Institute of Technology Guwahati, Assam 781039, India

ARTICLE INFO

Article history:
Received 28 October 2010
Received in revised form 10 March 2011
Accepted 11 March 2011
Available online 21 March 2011

Keywords:
Bhatia model
Moving bed biofilm reactor
Modified Stover–Kincannon model
Thiocyanate
Hydraulic retention time

ABSTRACT

A simulated wastewater containing phenol (2500 mg/L), thiocyanate and ammonia-nitrogen (500 mg/L) was treated in an anaerobic (R1)–anoxic (R2)–aerobic (R3) moving bed biofilm reactor system at different hydraulic retention time (HRT) intervals (total HRT 3–8 days, R1: 1.5–4 days; R2: 0.75–2 days and R3: 0.75–2 days) and feed thiocyanate (SCN^-) concentrations (110–600 mg/L) to determine substrate removal kinetics. In R1, phenol and COD reduction and specific methanogenic activity were inhibited due to the increase of SCN^- in feed. Bhatia et al. model having inbuilt provision of process inhibition described the kinetics of COD and phenol utilization with maximum utilization rates of 0.398 day^{-1} and 0.486 day^{-1}, respectively. In R2 and R3 modified Stover–Kincannon model was suitable to describe substrate utilization. In R2 respective maximum SCN^-, phenol, COD and NO_3^--N utilization rates were 0.23, 5.28, 37.7 and 11.82 g/L day, respectively. In aerobic reactor R3, COD, SCN^- and NH_4^+-N removal rates were, respectively, 10.53, 1.89, and 2.17 g/L day. The minimum total HRT of three-stage system was recommended as 4 days.

1. Introduction

High concentration of phenol is generated in several wastewaters like petrochemicals and chemical industries. Sometimes along with phenol, ammonia-nitrogen, thiocyanate (SCN^-), etc. are present in wastewaters like synthetic fuel processing and coal gasification wastewater. A number of investigations have been made on the treatment of phenol, thiocyanate and ammonia-nitrogen containing wastewater using sequential anaerobic–anoxic–aerobic, anoxic–aerobic system with suspended growth reactors, fixed-bed biofilm reactors, fluidized bed reactors, membrane based reactors [1–5]. Moving bed biofilm reactor (MBBR) is proved to be very suitable for the removal of nitrogen and treatment of various industrial effluents generated from poultry processing, pulp and paper industry, refinery and slaughterhouse and also landfill leachate [6–9]. The MBBR system is developed as a combination of conventional activated sludge process and fluidized bed system. It is a completely mixed and continuously operated biofilm reactor, where biomass is grown on small carrier elements like sponge and polyurethane foam having density less than water [9]. The biofilm containing carriers move in the reactor due to the effect of aeration (for aerobic system), mechanical stirrer or simply due to the movement of water and gas. Despite the advantages of MBBR system, study on removals of phenol, thiocyanate and ammonia-nitrogen in MBBR system is very less. Present investigation was carried out in an anaerobic–anoxic–aerobic three-stage MBBR system with hydraulic retention time (HRT) and feed thiocyanate as variable parameters. HRT being an operational parameter has profound influence on the performance of any treatment plant. Thiocyanate is known as an inhibitor of biodegradation of both phenol and ammonia [10,11]. Proper understanding of substrate removal kinetics is necessary for the prediction of performance and functioning of any biological reactor system. Literatures on biodegradation kinetics of phenol, thiocyanate and ammonia as individual pollutant are though plenty, very few addressed kinetics aspect in the presence of three pollutants [12,13]. No kinetic study in MBBR system with these multi-substrates had been previously reported to the authors' best knowledge. In the present study emphasis was given to determine the kinetics of substrate utilization in multi-substrate medium in three-stage MBBR system. Mathematical model was also used to predict effluent substrate concentrations.

2. Materials and methods

2.1. Experimental set-up

A schematic representation of the experimental assembly is shown in Fig. 1. It consisted of three PVC (polyvinyl chloride)

* Corresponding author. Tel.: +91 361 2582412; fax: +91 361 2690762.
E-mail addresses: chakraborty_saswati@hotmail.com, saswati@iitg.ernet.in (S. Chakraborty).

0304-3894/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2011.03.038

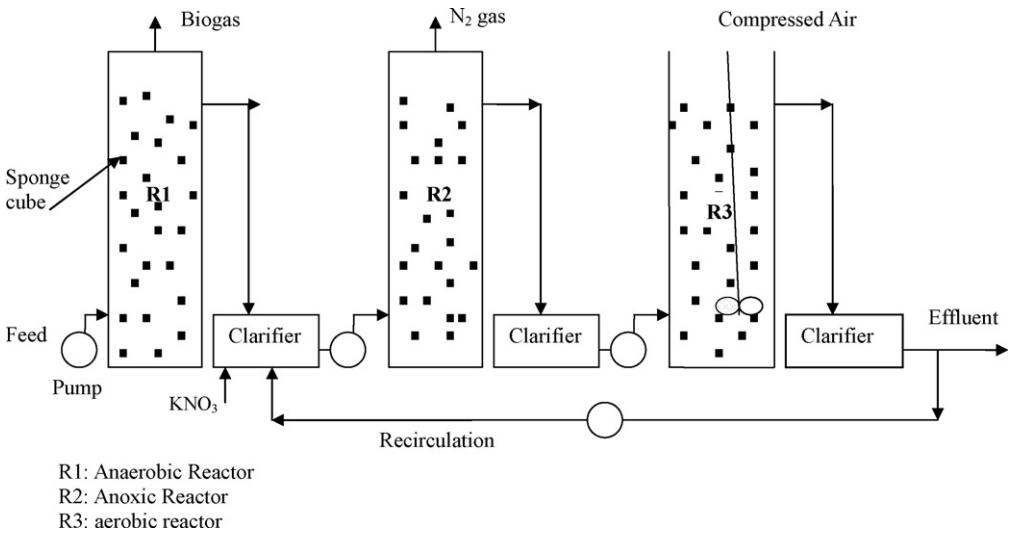

Fig. 1. Schematic representation of continuous three stage moving bed biofilm reactor (MBBR) system.

reactors, each of diameter 15 cm and height 118 cm in series, maintained under anaerobic (R1), anoxic (R2) and aerobic (R3) environments. Working volume (liquid, sponge and biomass) of each reactor was 15 L. In each 15 L reactor 120 g of sponge cubes (dimensions: 1 cm × 1 cm × 1 cm) with porosity 0.81, density 0.051 g/cm^3 and specific surface area 600 m^2/m^3 were added. Total volume of sponge cube in each reactor was 2360 cm^3, which was 15.7% of working volume of each reactor.

All reactors were operated in up flow mode. Each reactor was connected with a clarifier of volume 500 mL. Mixed liquor from each reactor was allowed to flow to the clarifier for settling of biomass. From the clarifier clear supernatant was pumped to the next reactor (R1 to R2 and R2 to R3). The final nitrified effluent from R3 was partially recycled to R2. In this recycle, 1000 mg/L of NO_3^--N (as KNO_3) was added daily, to supply adequate nitrate in anoxic reactor in order to maintain the anoxic condition in R2. In R1 and R2, mixing was achieved only by the upflow motion of the influent. In R3, compressed air (0.15 L/min) was supplied for aeration to provide dissolved oxygen of 4.5–4.8 mg/L.

Total system HRT was 3–8 days (HRT of R1: 1.5–4 days; R2: 0.75–2 days and R3: 0.75–2 days). Dissolved oxygen concentrations (mg/L) in the bioreactors were: 0 (R1 and R2) and 4.5–4.8 (R3). The reactor system was maintained at a constant temperature (30 ± 3 °C) using a temperature controlled blower. Plastic pipes were connected to R1 and R2 which were maintained in a water seal for the collection of biogas by water displacement method.

2.2. Synthetic feed

The study was conducted with synthetic feed containing varying thiocyanate (SCN^-, used as KSCN) along with phenol and NH_4^+-N. NO_3^--N was added in recycle (7201 mg KNO_3/L). Feed pH was maintained at 7.5 ± 0.2 by using phosphate buffer (KH_2PO_4 72.3 g/L and K_2HPO_4 104.5 mg/L). Yeast extract of 10 mg/L and trace metal solution of 1 mL/L feed were added as nutrients. The composition of stock trace metal solution was: $MgSO_4{\cdot}7H_2O$: 10,000 mg/L, $CaCl_2{\cdot}2H_2O$: 10,000 mg/L, $FeCl_3{\cdot}6H_2O$: 5000 mg/L, $CuCl_2$: 1000 mg/L, $ZnCl_2$: 1000 mg/L, $NiCl_2{\cdot}6H_2O$: 500 mg/L, $CoCl_2$: 500 mg/L. The feed thiocyanate concentration was varied at four levels (110–600 mg/L) and all other constituents were constant during the study. Feed COD was in the range of 7500–7980 mg/L during the study.

2.3. Acclimatization of sludge

Seed sludge (total solids of 40 g/L and volatile solids of 15 g/L) collected from one anaerobic biogas plant located at IIT Guwahati was used as inoculum for anaerobic and anoxic reactors. Sewage collected from IIT Guwahati sewage treatment plant (total solids 7.0 g/L and volatile solids of 4.5 g/L) was used as inoculums for the aerobic reactor. Inoculums (20% of reactor volume) and 120 g of sponge were added in each reactor. Acclimatization was carried out in a batch mode in three separate reactors maintained under anaerobic, anoxic and aerobic environments.

Initially for thirty days, R1 was operated with dextrose (500 mg/L day) and ammonia-nitrogen (10 mg NH_4^+-N/L) to develop biomass. Then, phenol 10 mg/L and SCN^- 5 mg/L were added in feed. Phenol, SCN^- and NH_4^+-N were increased gradually in R1 feed to 2500, 110 and 500 mg/L respectively in 217 days. With each feed R1 was operated for 3–5 days before going for next increment. Up to feed phenol concentration of 200 mg/L, dextrose of 500 mg/L day was also added in the feed and then its concentration was decreased gradually and after 90 days it was stopped. In three-stage continuous system influent of anoxic reactor was expected to be diluted by recycled effluent from aerobic reactor. Reactor R2 was acclimatized similarly like R1 up to concentrations of phenol 1250, SCN^- 55, NH_4^+-N 250 mg/L respectively and acclimatization period was 140 days. Nitrate was added in anoxic reactor as potassium nitrate (KNO_3) at phenol: NO_3^--N ratio of 3 [14]. Aerobic reactor (R3) was acclimatized up to phenol SCN^-, NH_4^+-N concentrations of 500, 25, and 250 mg/L respectively in 70 days.

2.4. Operating conditions

Present study was carried out with feed SCN^- and HRT as variable parameters. Four experimental runs (runs 1–4) were conducted at varying feed SCN^- of 110, 200, 400 and 600 mg/L at constant total HRT of 4 days (R1: 2 days; R2 1 day and R3 1 day). Feed phenol and NH_4^+-N were constant throughout the study at 2500 and 500 mg/L respectively with COD 7680–7980 mg/L. Run fifth to eighth were conducted at varying total HRT of 3–8 days at constant feed SCN^- of 600 mg/L, phenol 2500, NH_4^+-N 500 and COD 7980 mg/L. During each run three-stage system was operated for almost 30 days until steady state data was achieved.

2.5. Analytical methods

Samples of reactor effluents were collected and centrifuged prior analysis according to Standard Methods [15]. Thiocyanate was measured by colorimetric method using ferric nitrate in acidic pH. Phenol was estimated using 4-aminoantipyrene at 500 nm and NH_4^+-N was measured by Phenate method. Chemical Oxygen Demand (COD) was estimated by closed reflux titrimetric method. Nitrate-nitrogen concentration was determined by measuring absorbance at 220 and 275 nm in UV-spectrophotometer. Nitrite was measured using colorimetric method; sulfate was measured using turbidity method and pH was monitored using digital pH meter. Specific methanogenic activity (SMA) was carried out with sludge from R1 in a procedure similar to Isa et al. [16]. A known amount of sludge with VSS of 1–2 g/L was taken from R1 and poured into serum bottles. Feed was added to each of serum bottle identical to synthetic feed used in the study with varying thiocyanate concentration of 110, 200, 400 and 600 mg/L. Each test was carried out for three times. Supernatant was decanted, sludge was washed and fresh feed was given after the completion of each cycle. Data of third feeding was considered as data for actual specific methanogenic activity of the R1 sludge.

2.6. Substrate removal kinetics

2.6.1. Modified Stover–Kincannon model

In Modified Stover–Kincannon model substrate utilization rate is expressed as organic loading rate [17,18]. At steady state it is expressed as

$$\frac{ds}{dt} = \frac{\left(\frac{R_{max} Q S_0}{V}\right)}{\left(K_B + \frac{QS_0}{V}\right)} \quad (1)$$

Substituting ds/dt as $Q(S_0 - S_e)/V$ and reversing the expression

$$\frac{V}{Q(S_0 - S_e)} = \frac{\left(K_B + \frac{QS_0}{V}\right)}{\left(R_{max} + \frac{QS_0}{V}\right)}$$

or,

$$\frac{HRT}{S_0 - S_e} = \frac{K_B}{R_{max}}\left(\frac{V}{QS_0}\right) + \frac{1}{R_{max}} \quad (2)$$

where V is volume of liquid in the reactor (L), Q is flow rate (L/day), HRT (=V/Q, day), S_0 and S_e are influent and effluent substrate concentrations at steady state (mg/L), K_B is saturation value constant (g/L day) and R_{max} is maximum substrate utilization rate (g/L day). From the straight line plot of HRT/$(S_0 - S_e)$ vs $V/(QS_0)$, R_{max} and K_B can be determined from intercept and slope.

2.6.2. Inhibition kinetics due to toxicity

The linearized form of Bhatia et al. [19] model considering the process inhibition due to toxicity is given in Eq. (3).

$$\frac{HRT \times S_e}{S_0 - S_e} = \frac{1}{R_{max}} + \left(\frac{K_i}{R_{max}}\right) I_S \quad (3)$$

where K_i is the inhibition coefficient (L/mg) and I_S is the inhibitor concentration in effluent (mg/L).

3. Results and discussion

3.1. Anaerobic reactor (R1)

Steady state performance of R1 at varied influent thiocyanate concentrations and HRT is presented in Table 1. R1 showed little removal of thiocyanate (4–12%) and accounted for decrease in phenol and COD reduction with increase in feed SCN^- concentrations. Phenol degradation rate in R1 decreased from 0.4 to 0.16 g/L day with increase in feed SCN^- concentration (Fig. 2). In the present study feed COD was 7500–7980 mg/L. At feed SCN^- of 110 mg/L, COD reduction efficiency in R1 was 35% and it decreased by 88% at feed SCN^- of 600 mg/L. Fig. 2 shows that COD reduction rate decreased from 1.25 to 0.147 g/L day with increase in feed SCN^- concentration from 110 to 600 mg/L. Present result shows that thiocyanate plays inhibitory effect on phenol and COD degradation in anaerobic environment. In R1, HRT was varied from 0.75 to 4 days with constant feed of SCN^- 600, phenol 2500, NH_4^+-N 500 and COD 7980 mg/L. Fig. 2 shows that phenol and COD removal rates increased with increase in R1 HRT from 0.06 to 0.214 g phenol/L day and 0.19–0.98 g COD/L day.

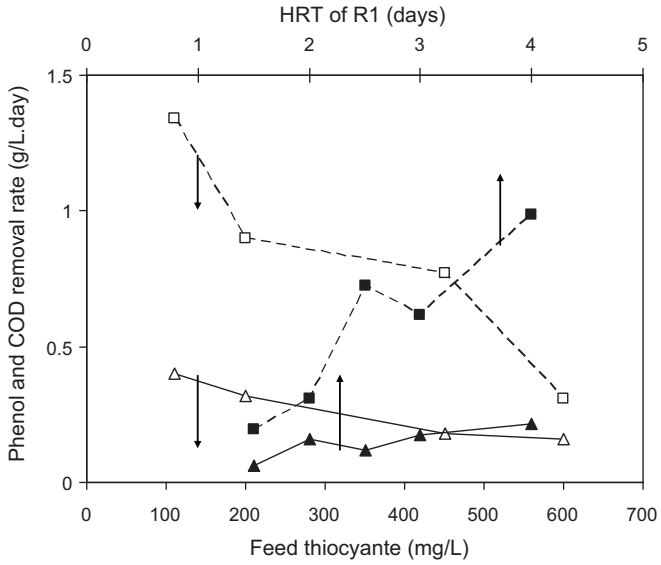

Fig. 2. Effect of feed thiocyanate and reactor HRT on phenol and COD removal rates.

In R1, feed pH decreased from 7.5 to 6.8–6.9. Specific methanogenic activity of anaerobic reactor is shown in Table 1. Specific methanogenic activity in R1 decreased with increase in feed SCN^- concentrations. Activity of 41.95 and 14.78 mL CH_4/g VSS day with activity of 0.1019–0.0359 g CH_4-COD/gVSS day was recorded respectively with feed thiocyanate of 110 and 200 mg/L. No methanogenic activity was detected when thiocyanate in feed was 450 and 600 mg/L. SMA of the R1 sludge with all synthetic feed excluding thiocyanate was observed as 228.13 mL CH_4/gVSS day and activity of 0.554 g CH_4-COD/gVSS day which is close to literature value of phenol degrading anaerobic granules [20]. This results show that SCN^- inhibits methanogenic activity in anaerobic reactor. Similar observation is reported by Hung and Pavlostathis [21] in anaerobic reactor at SCN^- concentration of 145 mg/L.

In R1 when phenol and COD reduction kinetics was plotted using modified Stover–Kincannon model, no correlation was obtained. Table 1 suggests that phenol and COD reduction in R1 were inhibited due to the presence of SCN^- in feed. Bhatia et al. [19] model (Eq. (3)) was used and the plots of (HRT × S_e)/$(S_0 - S_e)$ vs effluent SCN^- for COD and phenol are shown in Fig. 3. The maximum rate of substrate utilization (R_{max}) and inhibition coefficient (K_i) for COD was 0.398 day^{-1} and 0.0056 L/mg, respectively. For phenol these values were 0.486 day^{-1} and 0.01 L/mg, respectively. During the treatment of distillery spent wash in an anaerobic hybrid reactor maximum rate of COD utilization was observed as 1.945 day^{-1} [22], which was much higher than present value of 0.398 day^{-1}. Effluent COD and phenol was calculated using Bhatia et al. model (Eq. (3)) and

Table 1
Average performance of anaerobic reactor (R1) at varying feed SCN^- concentrations and reactor HRT.

HRT of R1 (day)	SCN^-			Phenol		COD			NH_4^+-N	SMA (g CH_4-COD/gVSS day)	pH
	Inf	Eff	Rem	Eff	Rem	Inf	Eff	Rem	Eff		Eff
2	110	105	4.54	1701	31.9	7680	5000	34.9	500	0.1019	6.8
2	200	190	5.0	1858	25.7	7700	5900	23.4	505	0.0359	6.9
2	450	415.3	7.7	2137	14.5	7850	6309	19.6	503	ND	6.8
2	600	572	4.7	2184	12.6	7980	7366	7.7	500	ND	6.7
1.5	600	575	4.1	2410	3.6	7980	7685	3.7	505	ND	6.5
2.5	600	560	6.6	2200	12.0	7980	6165	22.7	500	ND	6.6
3	600	550	8.3	1982	20.7	7980	6130	23.2	505	ND	6.8
4	600	525	12.5	1644	34.2	7980	4036	49.4	505	ND	6.7

Inf: Influent (mg/L), Eff: Effluent (mg/L, except pH), Rem: Removal (%). Feed: Phenol 2500 mg/L, SCN^- 110–600 mg/L, NH_4^+-N 500 mg/L and pH 7.5. ND: Not detected.

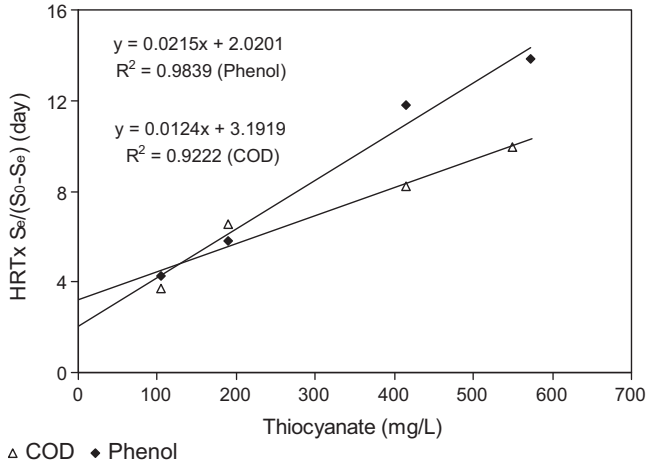

Fig. 3. Estimation of R and K_i of phenol and COD utilization using Bhatia et al. model.

plotted (supplementary figure S1) as predicted and experimental effluents vs HRT. Figure S1 shows that Bhatia et al. model predicted experimental effluent COD and phenol with good agreement (error of ±4–40% and ±4–31%, respectively).

3.2. Anoxic reactor (R2)

Anoxic reactor (R2) received effluent from R1 and recycled effluent from R3. Influent concentration of R2 was calculated using the following equation:

$$\text{Influent concentration to R2} = \frac{Q(\text{effluent concentrations of R1}) + RQ(\text{effluent concentrations of R3})}{Q + RQ} \quad (4)$$

where Q is the feed flow rate to R1, and R is the recycle ratio. In the present work recycle ratio of 1 was used. Steady state performance of R2 is shown in Table 2. In R2, SCN^- loading was varying from 0.054 to 0.288 g/L day. SCN^- degradation rate increased up to loading of 0.24 g/L day and remained constant beyond this loading. Maximum SCN^- degradation rate in R2 was 0.17 g/L day. Table 2 shows that almost 47–63% sulfate was generated in R2. Very few literatures reported about fate and biodegradation of thiocyanate in anoxic environment. Kim et al. [23] reported no SCN^- removal in anoxic reactor. However, SCN^- removal in anoxic reactor by sulfur oxidizing autotrophic bacteria, *Thialkalivibrio thiocyanodenitrificans* was reported, where SCN^- was used as electron donor with nitrate/nitrite as electron acceptors and end products were sulfate and ammonia (Eq. (5)) [24,25]. Probably in the present investigation SCN^- degradation followed similarly like Eq. (5).

$$5SCN^- + 8NO_3^- + H_2O + 8H^+ + 5HCO_3^- \rightarrow 5SO_4^{2-} + 5NH_3 + 10CO_2 + 4N_2 \quad (5)$$

With increase in feed SCN^- concentration, phenol and COD in R1 effluent and correspondingly in R2 influent increased. The maximum phenol and COD degradation rates were 1.2 and 2.65 g/L day, respectively, at influent loadings of 1.6 and 3.4 g/L day. Phenol removal rate of 0.25 g/L day was observed, at influent phenol loading of 267 mg/L in a suspended growth anoxic reactor without any removal of thiocyanate [23]. Phenol removal rate of 0.37 g/L day was observed in a suspended growth anoxic reactor at influent phenol loading of 0.45 g/L day in the presence of thiocyanate, cyanide and ammonia [5].

Previous literatures reported that in anoxic reactor, when nitrate is inadequate as compared to organic carbon, the reactor behaves like an anaerobic reactor after nitrate exhausted [26,27]. In the present study, NO_3^--N concentration in recycle (effluent of R3) was inadequate, so additional nitrate was supplied externally in R3 recycle in order to maintain strict anoxic condition in R2. In R2, denitrification was incomplete throughout the study, indicating existing of complete anoxic condition in R2. Table 2 shows that nitrite (NO_2^--N) was also completely utilized in R2. In R2, influent pH was 7.5–7.7 and this increased to 8.1–8.2, which was probably due to denitrification. The minimum COD/NO_3^--N ratio required to achieve complete denitrification in anoxic reactor was reported as 3.18–5.3 in literatures [14,26]. This ratio was 3.03-4.88 in the present study (Table 2).

In R2 HRT/$(S_0 - S_e)$ vs $\{V/(QS_0)\}$ are plotted for COD, phenol, SCN^- using Eq. (2) according to modified Stove–Kincannon model. The values of R_{max} and K_B for COD, phenol, and SCN^- are given in Table 3. In supplementary Figure S2 experimental and predicted effluent values are presented. Experimental and predicted values matched well for phenol and SCN^- (error of ±0.8–8% and ±2–18%, respectively). For COD error was ±6–34%. Kuscu and Sponza [18] observed maximum COD utilization rate of 29.49 g/L day in anaerobic migrating blanket reactor using modified Stover–Kincannon model during the treatment of synthetic wastewater containing p-nitrophenol and glucose. Sandhya and Swaminathan [28] reported maximum substrate utilization rate of 31.69 g/L day for textile wastewater in hybrid column upflow anaerobic fixed bed reactor. In anaerobic moving bed biofilm reactor and anaerobic filter substrate utilization rates of 89.30 and 86.21 g/L day were observed during the treatment of milk permeate and papermill wastewater respectively [29,30]. In the present study maximum COD utilization rate of 15.08 g/L day in R2 was lower than the literature values, which was probably due to the presence of inhibitory compounds.

3.3. Aerobic reactor (R3)

Average steady state performance of aerobic reactor R3 is shown in Table 4. Fig. 4 shows that both COD and SCN^- removal rates in R3 increased almost linearly with increase in loadings of COD and SCN^-. Maximum SCN^- removal rate in R3 was 0.20 g/L day at loading of 0.23 g/L day. SCN^- degradation rates of 0.2 and 5.0 g/L day respectively in aerobic suspended growth and fluidized bed reac-

Table 2
Average performance of anoxic reactor (R2) at varying feed SCN^- concentrations and HRT.

HRT of R2 (day)	Feed SCN^- (mg/L)	SCN^-			Phenol			COD			NH_4^+-N			NO_3^--N			NO_2^--N			COD: NO_3^--N_{rem} [c]	SO_4^{2-}	
		Inf[a]	Eff	Rem	Inf	Eff	Rem	Inf	Eff	Rem	Inf	Eff	Rem	Inf[b]	Eff	Rem	Inf	Eff			Inf	Eff
1	110	54	30	44	850	344	59	2682	950	65	275	260	92	617.5	47.0	92	2	0		3.03	95	140
1	200	96	45	53	929	410	56	3107	947	70	279	267	92	577.5	45.0	92	3.5	0		4.03	136	225
1	450	208	61	71	1069	450	58	3326	915	72	277	270	78	624	133.0	78	29	0		4.65	353	625
1	600	288	122	57	1092	468	57	3966	1317	67	299	360	79	622	129.0	79	50	0		4.88	355	541
0.75	600	300	177	41	1206	502	74	3853	1931	50	451	481	77	600	140.0	77	22	0		3.98	388	600
1.25	600	302	90	70	1109	450	55	3220	1455	55	369	450	89	615	69.7	89	33	0		3.05	488	747
1.5	600	277	86	69	991	385	69	3185	1150	64	307	325	66	615	210.0	66	90	0		4.11	448	756
2	600	288	40	86	822	307	53	2115	914	57	297	330	75	583	144.0	75	100	0		2.23	448	758

Inf: Influent (mg/L), Eff: Effluent (mg/L), Rem: Removal (%).
[a] Influent to R2 was calculated using Eq. (2).
[b] In R2 influent 500 mg/L of NO_3^--N was added externally.
[c] $\frac{COD}{N_{rem}} = \frac{influentCOD - effluentCOD}{influentNO_3^-\text{-}N - effluentNO_3^-\text{-}N}$.

Table 3
Kinetic constants for pollutants removal in anoxic reactor (R2) according to modified Stover–Kincannon model.

Parameter	R_{max} (g/L day)	K_B (g/L day)	R^2
COD	15.08	27.23	0.98
Phenol	5.283	8.052	0.99
Thiocyanate	0.232	0.126	0.87
NO_3^--N	11.82	6.780	0.93

tor were observed [31,32]. However, these published investigations were carried out using only SCN^- in wastewater without other carbon source. In a suspended growth aerobic reactor maximum SCN^- degradation rate was reported as 0.019 g/L day at influent SCN^- of 210 mg/L in the presence of phenol and NH_4^+-N [33]. Banerjee [10] observed maximum SCN^- degradation rate of 0.2 g/L day in a rotating biological contactor in the presence of phenol, which is close to SCN^- degradation rate observed in the present investigation. Maximum COD removal rate in R3 was 2.1 g COD/L day at COD loading of 2.57 g/L day. Maximum COD removal rate of 0.76 g/L day (removal of 58%) was reported in an aerobic suspended growth reactor at influent COD of 1012 mg/L along with phenol, ammonia and SCN^- [33]. Influent phenol loading in R3 was 0.37 to 0.61 g/L day. Phenol removal in R3 was more than 99% (effluent 1–2 mg/L) and it seemed that SCN^- concentration up to 122 mg/L did not inhibit phenol degradation.

Besides, influent NH_4^+-N from R2, some amount of NH_4^+-N was also generated in R3 from degradation of SCN^- (0.24 g NH_4^+-N from 1 g of SCN^- removed). Table 4 shows that NH_4^+-N removal efficiencies in R3 was 32–80%. However, a balance was made on amount of NH_4^+-N removed in R3 and amount of NH_4^+-N oxidized to NO_2^--N and NO_3^--N. This is shown as unaccounted nitrogen in Table 4, which suggests that unaccounted nitrogen fraction in R3 was 2–32%. Nitrification rate in R3 was calculated based on the generation of NO_3^--N and NO_2^--N and reactor HRT. Nitrification rate in R3 was 0.14–0.22 g/L day and decreased with increase in feed SCN^- concentration. Maximum ammonia removal rate of 0.28 g/L day was observed in a fluidized bed aerobic reactor using wastewater containing phenol, SCN^- and CN^- and NH_4^+-N and COD of 2500 mg/L [1]. Vázquez et al. [33] observed maximum nitrification rate of 0.18 g/L day with nitrification efficiency of 65% in an aerobic suspended growth reactor from influent NH_4^+-N of 1095 mg/L along with phenol of 280 mg/L in aerobic suspended growth reactor.

Modified Stover–Kincannon model (Eq. (2)) was used to determine substrate removal kinetics in R3. Values of R_{max} and K_B for COD, NH_4^+-N and SCN^- are given in Table 5. High correlation coefficient (0.94–0.99) suggests validity of this model. In supplementary

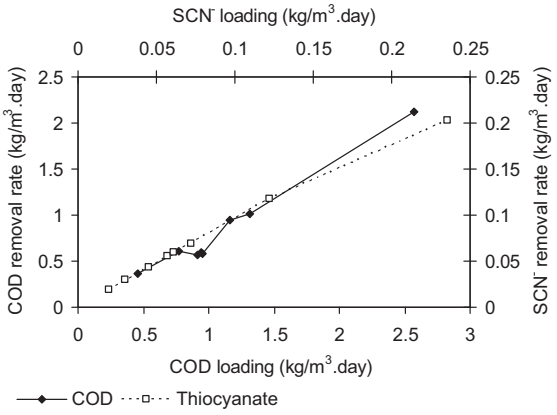

Fig. 4. Effect of COD and thiocyanate loadings on removal rates in R3.

Table 4
Average performance of aerobic reactor (R3) at varying feed SCN^- concentration and HRT.

HRT of R3 (day)	Feed SCN^- (mg/L)	SCN^-			Phenol			COD			NH_4^+-N			NO_3^--N			NO_2^--N		Unaccounted nitrogen (%)	SO_4^{2-}	
		Inf	Eff	Rem	Inf	Eff	Rem	Inf	Eff	Rem	Inf[a]	Eff	Rem	Inf	Eff	Rem	Eff		Inf	Eff
1	110	30	0.8	97.3	344	1.1	99.9	950	364	61.6	267	51	81.0	47	235	4	11		140	190
1	200	45	1.6	96.4	410	1.4	99.7	947	354	62.6	277	54	80.4	45	155	7	47		200	272
1	450	61	1.4	97.7	450	1.0	99.8	915	342	62.6	284	55	80.6	133	247.5	58	25		625	705
1	600	122	3.8	96.9	468	1.5	99.7	1318	310	76.5	388	98	74.7	129	245	100	25		541	710
0.75	600	177	25.0	85.8	502	2.1	99.6	1931	340	82.4	518	353	31.9	140	200	44	37		600	776
1.25	600	90	4.0	95.5	450	1.2	99.7	1455	275	81.1	471	141	70.0	69.7	230	66	31		747	977
1.5	600	86	3.5	95.9	385	1.0	99.8	1150	240	79.1	345	110	68.1	210	230	180	15		757	905
2	600	40	3.3	91.8	307	1.0	99.7	914	195	78.6	338	96	71.6	144	200	200	8		758	895

Inf: Influent (mg/L), Eff: Effluent (mg/L), Rem: Removal (%).
[a] Influent NH_4^+-N of R3 = (effluent NH_4^+-N of R2 + 0.24 × (SCN^- removed in R3)).

Table 5
Kinetic constants for pollutants removal in aerobic reactor (R3) according to modified Stover–Kincannon model.

Parameter	R_{max} (g/L day)	K_B (g/L day)	R^2
COD	10.537	13.39	0.94
Phenol	333	334.6	0.99
Thiocyanate	1.896	2.046	0.99
NH_4^+-N	2.168	3.17	0.95

Figure S3 experimental and predicted effluent values are presented. Comparing Tables 3 and 5 values it can be seen that maximum COD utilization rate in R3 (10.54 g/L day) was less than R2. Maximum phenol removal rate in R3 was much higher than R1 and R2 (333 g/L day). Maximum SCN^- utilization rate was eight times higher in R3 (1.89 g/L day) as compared to R2. Maximum NH_4^+-N removal rate as predicted by the model was 2.16 g/L day. The maximum loading rates of R3 for COD, SCN^- and NH_4^+-N were 2.57, 0.23 and 0.69 g/L day, respectively. Compared with the maximum loading rate obtained in this study, the predicted substrate removal rates (R_{max}) were much higher for COD, SCN^- and NH_4^+-N, suggesting R3 has higher potential in coping with this wastewater.

3.4. Overall performance of three-stage MBBR

The feed and final effluent of R3 was considered to estimate overall performance of three-stage MBBR system. The overall performance of the three-stage MBBR at varying feed SCN^- concentrations is shown in Fig. 5 in terms of COD, SCN^-, NH_4^+-N and phenol removals. It can be seen that phenol and SCN^- removals were complete and independent of feed SCN^- concentration. COD removal was around 95–96% with effluent COD 275–364 mg/L (from influent 7500 to 7980 mg/L) irrespective of influent SCN^- concentration. NH_4^+-N removal in three-stage system was constant at 89% up to feed SCN^- of 400 mg/L and decreased to 80% when feed SCN^- was 600 mg/L. Total nitrogen (TN) in influent and effluent of three-stage MBBR system was estimated from summation of SCN^-N, NH_4^+-N, NO_3^--N and NO_2^--N. Feed TN were 1527, 1548, 1596 and 1644 mg/L at feed SCN^- of 110, 200, 450 and 600 mg/L respectively (considering influent NO_3^--N of 1000 mg/L added in the recycle of R3). Fig. 5 shows that TN removal was 81-86% up to feed SCN^- of 200 mg/L and decreased little to 77% when feed SCN^- was 450 mg/L and above. Fig. 6 shows that phenol removal was above 99% irrespective of total HRT of three-stage system. Removals of SCN^- and NH_4^+-N were above 99% and 72–80% respectively up to total HRT of 4 days and decreased to 96% and 29% at HRT of 3 days, respectively. COD removal was 98% at total HRT of 8 days and decreased to 96% when HRT was decreased to 3–4 days. Fig. 6 shows that total HRT did not show any significant effect on TN removal.

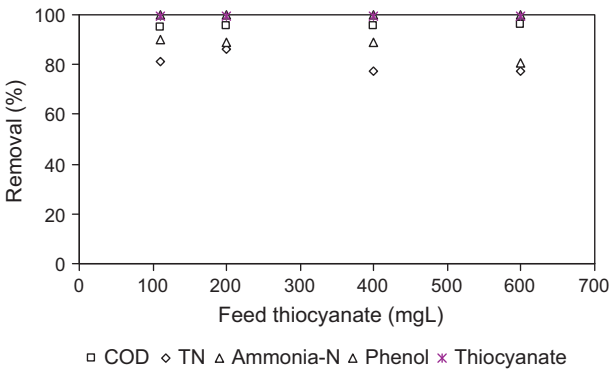

Fig. 5. Effect of feed thiocyanate on pollutant removal in three-stage system.

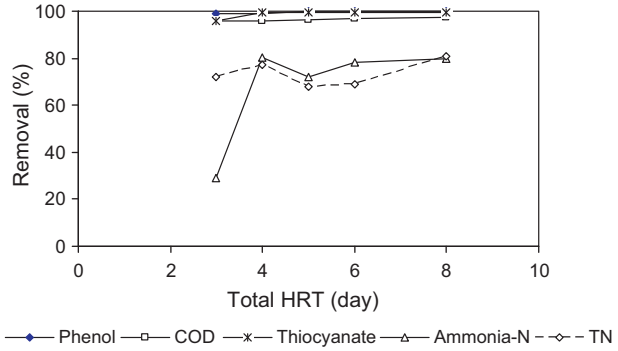

Fig. 6. Effect of total HRT on performance of three-stage system.

Present result shows that the inhibitory effect of feed SCN^- above 400 mg/L on phenol and COD removals in anaerobic reactor was very profound. However, the response of feed SCN^- up to 600 mg/L on the overall performance of the three-stage MBBR system was quite insignificant, as anoxic reactor was highly efficient and helped to improve the overall performance of the three-stage system. The minimum HRT of the three-stage MBBR system should be maintained at 4 days or above to handle feed of phenol 2500, COD 7980, SCN^- 600 mg/L and NH_4^+-N 500 mg/L.

4. Summary and conclusions

Based on the observations of this study following conclusions can be drawn:

1. The three-stage anaerobic (R1)–anoxic (R2)–aerobic (R3) MBBR system can be effectively used for removals of high concentration phenol, SCN^-, NH_4^+-N and COD of 2500, 600, 500 and 7980 mg/L, respectively. Total performance of the system remained constant in terms of phenol, SCN^-, COD and total nitrogen removal within total HRT of 3–8 days. The minimum total HRT of the system should be 4 days and below this NH_4^+-N removal efficiency deteriorated significantly.
2. In R1, removal of phenol, COD reduction and specific methanogenic activity (SMA) were strongly inhibited at feed SCN^- of 450 mg/L and above. According to Bhatia et al. model the maximum rates of COD and phenol utilization in R1 were 0.398 day^{-1} and 0.486 day^{-1} respectively.
3. In R2 simultaneous removals of phenol, COD, SCN^- and denitrification were achieved. The maximum substrate utilization rates according to modified Stover–Kincannon model were 37.7, 5.3, 0.23 and 11.8 g/L day for COD, phenol, SCN^- and NO_3^--N respectively.
4. Aerobic reactor completely removed residual phenol and SCN^-. Nitrification was affected at higher NH_4^+-N influent and lower HRT. Modified Stover–Kincannon model estimated maximum substrate removal rates of 10.5, 1.9 and 2.1 g/L day for COD, SCN^- and NH_4^+-N respectively.

Acknowledgments

Dr. Saswati Chakraborty would like to thank Ministry of Environment & Forest (MoEF), Govt. of India (No. 19-18/2003-RE) for financial support to this work. Ms Biju Prava Sahariah is grateful to Ministry of Environment & Forest (MoEF) for financial support provided as Junior Research Fellowship in this project.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.03.038.

References

[1] Y.S. Jeong, J.S. Chung, Simultaneous removal of COD, thiocyanate, cyanide and nitrogen from coal process wastewater using fluidized biofilm process, Process Biochem. 41 (2006) 1141–1147.
[2] W. Zhu, X. Huang, D. Lee, Enhanced treatment of coke plant wastewater using an anaerobic–anoxic–oxic membrane bioreactor system, Sep. Purif. Technol. 66 (2009) 279–286.
[3] Y.M. Li, G.W. Gu, J.F. Zhao, H.Q. Yu, Y.L. Qiu, Y.Z. Peng, Treatment of coke-plant wastewater by biofilm systems for removal of organic compounds and nitrogen, Chemosphere 52 (2003) 997–1005.
[4] M. Zhang, J.H. Tay, Y. Qian, X.S. Gu, Coke plant wastewater treatment by fixed biofilm system for COD and NH_3-N removal, Water Res. 32 (1998) 519–527.
[5] S. Chakraborty, H. Veeramani, Effect of HRT and recycle ratio on removal of cyanide, phenol, thiocyanate and ammonia in an anaerobic–anoxic–aerobic continuous system, Process Biochem. 41 (2006) 96–105.
[6] B. Rusten, J.G. Siljudalen, A. Wien, D. Eidem, Biological pre-treatment of poultry processing wastewater, Water Sci. Technol. 38 (1998) 19–28.
[7] J.J. Sigrun, A.R. Jukka, H. ∅degaard, Aerobic moving bed biofilm reactor treating thermomechanical pulping white water under thermophilic condition, Water Res. 36 (2002) 1067–1075.
[8] C.H. Johnson, M.W. Page, L. Blaha, Full scale moving bed biofilm reactor results from refinery and slaughterhouse treatment facilities, Water Sci. Technol. 41 (2000) 401–407.
[9] S. Chen, D. Sun, J. Chung, Simultaneous removal of COD and ammonium from landfill leachate using an anaerobic–aerobic moving bed biofilm reactor system, Waste Manage. 28 (2008) 339–346.
[10] G. Banerjee, Phenol and thiocyanate based wastewater treatment in RBC reactor, J. Environ. Eng. 122 (1996) 941–948.
[11] Y.M. Kim, P. Donghee, D.S. Lee, J.M. Park, Inhibitory effects of toxic compounds on nitrification process for cokes wastewater treatment, J. Hazard. Mater. 152 (2008) 915–921.
[12] A. Banerjee, A.K. Ghoshal, Phenol degradation by *Bacillus cereus*: pathway and kinetic modeling, Bioresour. Technol. 101 (2010) 5501–5507.
[13] M. Lay-Son, C. Drakides, New approach to optimize operational conditions for the biological treatment of a high-strength thiocyanate and ammonium waste: pH as key factor, Water Res. 42 (2008) 774–780.
[14] J. Zhu, J. Lin, B. Zhang, X. Yan, Z. Peng, Simultaneous removal of phenol and nitrate in an anaerobic bioreactor, J. Environ. Eng. 132 (2006) 1073–1077.
[15] APHA, AWWA, WPCF, Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, Washington, DC, 1998.
[16] M.H. Isa, I.H. Farooqi, R.H. Siddiqi, Methanogenic activity test for study of anaerobic processes, Indian J. Environ. Health 35 (1993) 1–8.
[17] J.H. Ahn, C.F. Forster, Kinetic analyses of the operation of mesophilic and thermophilic anaerobic filters treating a simulated starch wastewater, Process Biochem. 36 (2000) 19–23.
[18] Ö.S. Kuscu, D.T. Sponza, Kinetics of *para*-nitrophenol and chemical oxygen demand removal from synthetic wastewater in an anaerobic migrating blanket reactor, J. Hazard. Mater. 161 (2009) 787–799.
[19] D. Bhatia, W.R. Vieth, K. Vekatasubramanian, Steady state and transit behaviour in microbial methanification: II. Mathematical modelling and verification, Biotechnol. Bioeng. 27 (1985) 1192–1198.
[20] H.H.P. Fang, T. Chen, Y. Li, H. Chui, Degradation of phenol wastewater in upflow anaerobic sludge blanket reactor, Water Res. 30 (1996) 1353–1360.
[21] C. Hung, S.G. Pavlostathis, Fate and transformation of thiocyanate and cyanate under methanogenic condition, Appl. Microbiol. Biotechnol. 49 (1998) 112–116.
[22] S.K. Kumar, S.K. Gupta, G. Singh, Biodegradation of distillery spent wash in anaerobic hybrid reactor, Water Res. 41 (2007) 721–730.
[23] Y.M. Kim, D. Park, C. Jeon, D.S. Lee, J.M. Park, Effect of HRT on the biological pre-denitrification process for the simultaneous removal of toxic pollutants from cokes wastewater, Bioresour. Technol. 99 (2008) 8824–8832.
[24] V. Andreoni, A. Ferrari, A. Pagani, C. Sorlini, V. Tandoi, V. Treccani, Thiocyanate degradation by denitrifying mixed cultures of bacteria, Ann. Microbiol. 38 (1988) 193–200.
[25] D.Y. Sorokin, T.P. Tourova, A.N. Antipov, G. Muyzer, J.G. Kuenen, Anaerobic growth of the haloalkaliphilic denitrifying sulphur-oxidizing bacterium *Thialkalivibrio thiocyanodenitrificans* sp. nov. with thiocyanate, Microbiology 150 (2004) 2435–2442.
[26] S. Sarfaraz, S. Thomas, U.K. Tiwari, L. Iyengar, Anoxic treatment of phenolic wastewater in sequential batch reactor, Water Res. 38 (2004) 965–971.
[27] K. Karim, S.K. Gupta, Continuous biotransformation and removal of nitrophenols under denitrifying conditions, Water Res. 37 (2003) 2953–2959.
[28] S. Sandhya, K. Swaminathan, Kinetic analysis of treatment of textile wastewater in hybrid column upflow anaerobic fixed bed reactor, Chem. Eng. J. 122 (2006) 87–92.

[29] T. Yilmaz, A. Yuceer, M. Basibuyuk, A comparison of the performance of mesophilic and thermophilic anaerobic filters treating papermill wastewater, Bioresour. Technol. 99 (2008) 156–163.
[30] S. Wang, N.C. Rao, R. Qiu, R. Moletta, Performance and kinetic evaluation of anaerobic moving bed biofilm reactor for treating milk permeate from dairy industry, Bioresour. Technol. 100 (2009) 5641–5647.
[31] C. Hung, S.G. Pavlostathis, Aerobic biodegradation of thiocyanate, Water Res. 31 (1997) 2761–2770.
[32] Y.S. Jeong, J.S. Chung, Biodegradation of thiocyanate in biofilm reactor using fluidized-carriers, Process Biochem. 41 (2006) 701–707.
[33] I. Vázquez, J. Rodriguez, E. Maranon, L. Castrillon, Y. Fernandez, Simultaneous removal of phenol, ammonium and thiocyanate from coke wastewater by aerobic biodegradation, J. Hazard. Mater. B137 (2006) 1773–1780.