

57 (2016) 14396–14402 July



Treatment of coke oven wastewater in an anaerobic–anoxic–aerobic moving bed bioreactor system

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Received 20 February 2015; Accepted 15 June 2015

ABSTRACT

In this work, sequential moving bed bioreactor (MBBR) system with mixed heterogeneous biomass was selected for the treatment of coke oven wastewater (CW). The reactors were arranged in anaerobic (R1)-anoxic (R2)-aerobic (R3) sequence. CW was collected from an industrial site which contains phenol, ammonia, sulfate, iron, oil, and grease. Few heavy metals (cadmium, lead, and cobalt) were also detected in CW at low concentrations. Raw CW was pretreated by primary settling process to remove high solid concentrations. Thereafter, CW was spiked with synthetic pollutants to make the picture of model industrial wastewater. Phenol (1,350 mg/L), ammonia-N (500 mg/L), thiocyanate (800 mg/L), pyridine (50 mg/L), m-, o-, and p-cresols (50 mg/L each) were added as synthetic pollutants in CW. The system was operated at 6 d hydraulic retention time. R1 showed only less phenol (2-5%) and chemical oxygen demand (COD) (~2%) removal. However, R2 and R3 removed significant amount of thiocyanate (>85%), cresols (~88%), and pyridine (>48%) along with the residual phenol (R2: 88%; R3: 98%) and COD (R2: 58%; R3: 79%). Also, denitrification efficiency of R2 was ~94% throughout the study. Ammonia-N removal by R3 was 64-71% comprising 75–77% of total nitrogen removal. Hence, three stage sequential MBBR could be successfully used to treat high strength CW to achieve the discharge limit of effluent.

Keywords: Moving bed bioreactor; Coke oven wastewater; Phenol; Thiocyanate; Nitrification–denitrification

1. Introduction

Moving bed bioreactor (MBBR) is a continuous flow biofilm reactor with a high density of biomass without backwashing or sludge return. The biomass grows on small carrier elements such as sponge having density less than water. It is less prone to clogging and biomass washout, but it retains the other benefits of attached growth system. For instance it has less space requirement due to its compactness with high biomass hold up in biofilm. This biofilm works as buffer to reduce the intensity of toxic chemicals [1]. Hence, nowadays MBBR becomes an efficient treatment technology for many industrial wastewaters such as dairy wastewater, refinery and slaughterhouse, coke industry wastewater, landfill leachate, etc. [2–4]. The wastewater from coal gasification, synthetic fuel processing, and coal carbonization process mostly contain phenol, thiocyanate (SCN⁻), and ammonia

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nitrogen (NH_4^+-N) as major pollutants along with numerous other pollutants such as sulfides, fluoride, nitrate, heavy metals, etc. [2,5]. Presence of these multiple sets of pollutant demands highly efficient treatment process to meet its discharge limit. Design data on the application of anaerobic-anoxic-aerobic MBBR system for treatment of complex wastewater is very limited. This process is a preferential choice for simultaneous removal of organic matters and ammonia from wastewater [6,7]. In this process, the anaerobic unit is mainly used as a pretreatment. The partially treated organic compounds from anaerobic unit are oxidized by nitrate in anoxic unit, while nitrate is reduced to N₂ and discarded from the system. Phenolics and other refractory compounds with the inhibitory effect on nitrification are expected to get removed in the upstream reactors. Finally, the residual pollutants such as chemical oxygen demand (COD) and ammonia further get oxidized in the aerobic unit. Kuscu and Sponza [8] used sequential anaerobic migrating blanket reactor (AMBR) and completely stirred tank reactor system for treatment of nitrobenzene and observed that most of the COD removed in the AMBR itself. Several reactor configurations in anaerobic- anoxic-aerobic mode were used such as suspended growth, fluidized bed, membrane system, biofilm process, etc. [9,10]. However, only few studies have been reported for the performance of anaerobicanoxic-aerobic MBBR system to treat wastewater containing multiple pollutants. Also, though many times industrial wastewater treatment is performed in biological treatment system, the present study describes the attempts of treatment of CW from coal rich northeast region of India in a sequential MBBR system. In the present work, a continuous moving bed bioreactor (CMBR) system was used in anaerobicanoxic-aerobic mode to treat CW containing phenol, cresols, SCN⁻, pyridine, and NH₄⁺-N.

2. Materials and methods

2.1. Experimental setup

Chemicals and reagents used in the study were of analytical grade and procured from Merck and CDH. In this study, three polyvinyl chloride (PVC) columns of each 15 cm diameter and 118 cm height were used as reactors with working volume of each 15 L. Sponge cube of (dimension 1 cm^3 ; specific surface area $600 \text{ m}^2/\text{m}^3$) 120 g was added in each reactor for bacteria immobilization. The total volume of sponge cube in each reactor was 2,350 cm³, which was 15.67% working volume of each reactor. All reactors were operated in up-flow mode. Anaerobic (R1) and anoxic

(R2) reactors were kept closed at both upper and lower ends, and mixing was achieved only by the up-flow motion of the influent and the gas generated, whereas in the aerobic reactor (R3) compressed air was supplied continuously for aeration. Dissolved oxygen (DO) concentration in the effluents of R1, R2, and R3, were observed as 0, 0.30 ± 0.10 and 3.5 ± 0.50 mg/L, respectively. One multichannel peristaltic pump was used to deliver influents to all the reactors continuously. Hence, the system was labeled as CMBR. The reactors were maintained at a temperature controlled room (30 ± 2 °C).

2.2. Acclimatization of culture

Initial seed sludge (volatile solids of 15 g/L) was collected from the anaerobic biogas plant located at IIT Guwahati for seeding of R1 and R2. Sewage from IIT Guwahati sewage treatment plant (volatile solids of 4.5 g/L) was used as inoculums for R3. Acclimatization of culture was conducted separately in anaerobic, anoxic, and aerobic environments in batch mode. The mixed heterogeneous biomass was grown on sponge cube of R1, R2, and R3 and acclimatized with the gradual increase in influent concentration of pollutants. For acclimatization initially, R1 was fed for 15 d with dextrose (1,000 mg/L), NH_4^+ -N (5 mg/L), phosphate buffer (1 ml/L) and trace metal solution 1 ml/L, and yeast extract 50 mg/L as nutrients. Feed pH was maintained at 7.5 ± 0.2 using phosphate buffer (KH₂PO₄ 72.3 g/L and K₂HPO₄ 104.5 g/L) and NaHCO₃. Feed solution was purged with nitrogen gas to remove DO before feeding to R1. Phenol, SCN⁻, and NH₄⁺-N concentrations in feed solution were increased in a stepwise manner, and dextrose concentration was decreased gradually. In feed of R1, the phenol, SCN⁻, and NH₄⁺-N was increased up to 1,500, 800 and 500 mg/L, respectively, in 170 d with zero dextrose. Similarly, R2 was acclimatized with phenol (700 mg/L), NH_4^+ -N (250 mg/L), SCN^{-} (400 mg/L) and $NO_{3}^{-}-N$ (500 mg/L) in 113 d in batch mode. Thereafter, R2 was operated with same feed concentration in till 170th d. R3 was acclimatized with NH_4^+ -N (initially 5 mg/L) of 250 mg/L in 83 d and the same condition was maintained up to 170th d. From 170th d onwards reactors were connected in series to operate in continuous mode. Afterward, the potential of CMBR treating synthetic wastewater with different ratio of mixed substrate (phenol/ thiocyanate/ammonia) was evaluated for three and half year [10]. Thereafter, to conduct real CW experiment, the system was stepwise acclimatized with pyridine and cresols (m-, o- and p-) up to 50 mg/L each for 25 d along with existing influent constituents.

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2.3. Experimental design

In the present study, wastewater collected from Barnyhat industrial site, Guwahati, India was considered for performance evaluation of CMBR system. R1, being the first stage reactor received a fresh influent. Effluent from R1 was mixed with effluent of R3 (recycle ratio, R = 1) with the addition of 500 mg/L NO₃⁻-N and fed to R2. Influent concentration of R2 was calculated using Eq. (1).

2.4. Analytical methods

Feed samples and effluents from reactors were collected and centrifuged at 7,500 rpm (REMI) for five minutes prior to analysis of SCN⁻ (colorimetric method using ferric nitrate in acidic pH at 460 nm), NH_4^+ -N (Phenate method), COD (closed reflux titrimetric method), NO_3^- -N (ultraviolet screening method measuring absorbance at 220 and 275 nm in UV–vis spectrophotometer), NO_2^- -N (colorimetric method),

Influent concentration to
$$R2 = \frac{Q \text{ (Effluent concentrations of R1)} + RQ \text{ (Effluent concentrations of R3)}}{(Q + RQ)}$$
 (1)

where Q is the influent flow rate (L/d) to R1. Effluent of R2 was directly fed to R3 after necessary pH adjustment with 1 N HCl or 1 N NaOH. Hydraulic retention time (HRT) of each reactor was constant (R1: 3, R2: 1.5, R3: 1.5, and total 6 d). Loading rates and removal rates in each reactor were calculated using Eqs. (2) and (3), respectively [6].

Loading rate
$$(g/L d) = \frac{S_0}{(HRT \times 1,000)}$$
 (2)

Removal rate
$$(g/L d) = \frac{(S_0 - S_e)}{(HRT \times 1,000)}$$
 (3)

where S_0 and S_e are influent and effluent concentration (mg/L), respectively. The actual raw wastewater contains very low concentrations of phenol, ammonia, and some species of heavy metals with no thiocyanate when compared to the synthetic wastewater used in this study (Table 1). As the pH of the raw wastewater was 6.9, it was adjusted up to pH 7.5 using dilute NaHCO₃ solution. Also, COD of real wastewater was very low (185 mg/L). Hence, addition of raw CW may not provide the adequate substrate to microbes in R1 and R2. Therefore, phenol (~1,350 mg/L), ammonia-N (500 mg/L), thiocyanate (800 mg/L), pyridine (50 mg/L), and (m-, o- and p-) cresols (50 mg/L, each)were added to make the picture of real coal gasification/synthetic fuel processing/coke oven wastewater. The real wastewater had very high settleable suspended solids of 28,000 mg/L, and this was reduced up to 880 mg/L by 20 min of settling to avoid the clogging of reactors. Feed was prepared daily with real wastewater and kept in closed plastic tank. Feed temperature was maintained near room temperature $(30 \pm 2^{\circ}C).$

lead, chromium, and cobalt (atomic absorption spectroscopy), iron (spectrophotometer), chlorine (titration), solids (weighing methods), sulfate (ion chromatography), and sulfide (iodometric method) as per standard methods, APHA, 2005 [11]. Phenol, cresols, and pyridine were estimated using HPLC (ProSTAR, Varian) equipped with a UV–vis detector and C18 column (particle size: $5 \,\mu$ m, length: 15 cm and diameter: 4.6 mm) at room temperature with a mobile phase of acetonitrile (80%): water (20%) at a flow rate of 0.8 ml/min. An aliquot of 20 μ l sample was injected to analyze pyridine (253 nm) and phenols (280 nm) using a UV–vis detector at a particular wavelength [12]. DO concentration was measured using a digital DO meter (Orion 3 star–QY-14478, Thermo Scientific, Singapore).

3. Result and discussions

3.1. Phenolics removal

Phenolics (phenol, o-, m-, and p-cresol) are the main organic constituents of coal gasification process and coke oven wastewaters, which are alone responsible for 80% of the total COD. Therefore, 0.8 g/L dloading rate of phenolics was considered in this study. Kim et al. [13] reported other possible organics including polynuclear aromatic hydrocarbons (PAHs), and heterocyclic compounds containing nitrogen, oxygen, and sulfur. Fig. 1 shows the phenolics removal efficiency (%) of CMBR. Initially, removal of phenolics by R1, R2, and R3, were 13.33, 88.47 and 98.67%, respectively, in total phenolics removal (99.93%) by CMBR. However, it decreased with time and after 10 d of operation phenolics removal in R1 decreased up to 5.33%, whereas no significant change observed in R2, R3, and total phenolics removal throughout the study. In this study, R1 received various pollutants such as

Parameter	Concentration in wastewater	Parameter	Concentration in wastewater (mg/L)
pН	6.9	Sulfide	3
Conductivity	1.005 mS/cm	Phosphate	3
DO	0.65 mg/L	Total solids ^b	28,000 880 ^b
Phenol	3 mg/L 1,500 mg/L ^b	Volatile solids	180
COD	185 mg/L 5,840 mg/L ^b	Chloride	410
BOD ₅ , 20°C	12 mg/L	Iron	15
Ammonia-N	15 mg/L 500 mg/L ^b	Fluoride	22
Thiocyanate	800 mg/L^{b}	Lead	1
Nitrate-N	2 mg/L 500 mg/L ^b	Cadmium	1.3
Turbidity	>200 NTU ^a 25 NTU ^b	Cobalt	0.02
Sulfate	130 mg/L	Oil and grease	58

 Table 1

 Characteristics of the raw wastewater collected from coke oven industry

^aNTU = Nephelo turbidity unit.

^bInfluent concentration to MBBR system after raw CW was spiked with additional pollutants.



Fig. 1. Phenolics removal profile by CMBR system from actual coke oven wastewater.

pyridine, fluoride, iron, and few heavy metals which are having inhibitory effects on anaerobic biomass. Hence, these pollutants might have inhibited the efficiency of anaerobes in R1, which decreases the pollutant removal performance.

Ochoea-Herrera et al. [14] reported that 18–43 mg/L of fluoride concentration causes 50% of metabolic inhibition of propionate–buterate degrading biomass as well as mesophilic and thermophilic methanogens. Ramakrishnan and Gupta [15] reported 96% phenolics removal using hybrid up-flow anaerobic sludge blanket reactor for synthetic coal wastewater treatment containing cresols with 0.0075 g/L d phenolic loading rate. Zheng and Li [16] achieved almost 100% phenol

removal from influent phenol concentration of 1,200–1,700 mg/L, while treating coke oven wastewater in an anaerobic–anoxic–aerobic system in the presence of high concentration of ammonia-N. In the present study, the efficiency of CMBR system is comparable with the recent reported literatures.

3.2. COD removal by CMBR

In this study, influent COD of R1 was maintained at 5,840 mg/L with loading rate of 1.946 g/L d. Whereas, the loading rate of R2 and R3 was 1.8-1.9 g COD/L d and 0.80-0.83 g COD/L d, respectively. COD is mostly comprised by phenolics (experimentally observed: ~2.38 mg COD/mg phenolics) and thiocyanate (1.1 mg COD/mg SCN⁻). COD removal of R1, R2, and R3 was 3.4, 57.75, and 80.16%, respectively, for synthetic wastewater. But, COD removal efficiency of R1 and R2 decreased up to 1.6 and 56.13%, respectively, for model CW. After 5 d of operation with model CW, R1 showed stable COD removal of 2.3% (removal rate 0.047 g COD/L d), which might be due to other materials such as fluoride, sulfide, heavy metals, etc. in model CW. COD removal in R1 was less than the phenolics removal. It might be due to accumulation of intermediates in the reactor. From the fourth day of model CW addition COD removal efficiency of R2 increased to 57-59% and R2 showed COD removal rate of 1.13–1.19 g/L d for both synthetic and real wastewaters.

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After model CW addition COD removal efficiency of R3 slightly decreased to 78% and remained stable. The COD removal rate of R3 was 0.67 g/L d with synthetic wastewater that decreased up to 0.62 g/L d and remained stable with model CW. After 5 d of operation with model CW, R1, R2, and R3 exhibited steady COD removal. The total removal was always stable at >95.5% (Fig. 2). Peng et al. [17] reported COD and ammonia-nitrogen removals of 91 and 96.8%, respectively, from coke effluent in an anaerobic-aerobicaerobic biofilm reactor system at HRT of 2.5 d and no effluent recirculation. Zhao et al. [18] reported COD, phenol, ammonia, and total nitrogen removals of almost 89.8, >99.9, 99.5, and 71.5%, respectively, in a laboratory-scale anaerobic-anoxic-aerobic membrane bioreactor system for treatment of heavily loaded and toxic coke plant wastewater at total HRT of 1.67 d. The COD removal efficiency of the CMBR system in the present study is higher than the reported values.

3.3. Thiocyanate removal by CMBR

Similar to synthetic wastewater study, no thiocyanate removal occurred in R1 after addition of model CW [6]. Synthetic wastewater thiocyanate removal by R2 and R3 was 85.54 and 96.55% with their influent concentrations of 400 and 54 mg/L, respectively. However, thiocyanate removal rate of R2 (0.224 g/L d) was higher than R3 (0.035 g/L d). The SCN⁻ loading rate of both synthetic as well as model wastewater in R2 was 0.267 g/L d.

After addition of model CW day in R2 from fifth to seventh day SCN⁻ removal decreased up to 81% (0.221 g/L d). This might be due to the presence of other toxic materials in the influent. However, R2 regained its removal efficiency up to 84% (0.224 g/L d) from the seventh day onward and remained static



Fig. 2. COD removal profile by CMBR system from actual coke oven wastewater.



Fig. 3. Thiocyanate removal profile by CMBR system from actual coke oven wastewater.

(Fig. 3), which indicates that the anoxic microbes in R2 was able to sustain with the model CW containing other materials such as heavy metals. In R3, thiocyanate removal efficiency from synthetic wastewater was ~96.5%, and it released 2 mg/L of SCN⁻ in effluent. On the other hand, SCN⁻ removal in R3 decreased up to 94.6% for model CW from third to fourth day of operation and released 3 mg/L SCN⁻ in its effluent. However, R3 recovered its removal efficiency up to 96.88%, when upstream reactor R2 regained its efficiency. Marañón et al. [5] reported thiocyanate removal of 97% in a three-step activated sludge process from coke wastewater containing thiocyanate concentration of 198-427 mg/L. In the present study, total SCN⁻ removal efficiency of CMBR was always more than 99.6% for its influent concentration of 800 mg/L (loading rate 0.133 g SCN⁻/L d). Similar results (99%) were obtained by Jeong and Chung [19] for thiocyanate removal while treating real coke wastewater in an anoxic-oxic-anoxic-oxic (AOAO) system at the loading rate of 0.12–0.82 g SCN⁻/L d.



Fig. 4. Pyridine removal profile by CMBR system from actual coke oven wastewater.

3.4. Pyridine removal by CMBR

R2 and R3 of CMBR system played a significant role for pyridine removal, whereas R1 performance was negligible (Fig. 4). Influent pyridine of R2 was about 25-28 mg/L from initial feed concentration of 50 mg/L. Pyridine removal of R2 and R3 was 53.8 and 66.67%, respectively, with total pyridine removal of 92% in synthetic wastewater. For model CW, pyridine removal in R2 decreased up to 26-33% after 5 d. From eighth day onwards, the removal efficiency of R2 gradually increased and remained stable at 48.15%. Li et al. [20] reported complete removal of pyridine in anoxic environment within 12-24 h at initial pyridine concentration of 20-100 mg/L in the absence of any other pollutant. In the present study, pyridine was associated with other pollutants such as phenol, thiocyanate, and NH⁺₄-N. However, pyridine removal efficiency of R3 was continuously decreased up to 57% for model CW. Sun et al. [21] observed simultaneous degradations of pyridine and phenol by an aerobic strain Rhodococcus, using phenol as carbon source and pyridine as the nitrogen source. The total pyridine removal by CMBR system was 88% from 10th d onward till end of the study.

3.5. Denitrification/nitrification in CMBR

Nitrate (NO₃⁻-N) was added externally to nitrified recycle, which was taken from R3 to R2 to make strict anoxic condition in R2. The anoxic microbes utilize NO_x-N ($NO_3^--N + NO_2^--N$) for oxidation of phenolics, thiocyanate, and pyridine. NO_x-N removal efficiency of R2 was 93.58-93.85% for the entire study with model CW. Nitrite-nitrogen (NO_2^--N) was completely reduced in both synthetic and model CW treatment [6]. Influent concentration of ammonia to R3 was ~405 mg/L (received from R2 + NH_4^+ -N generated from SCN⁻ and pyridine degradation). Nitrification in R3 decreased from 71.32 to 64.28% on the fifth day of model CW treatment (Fig. 5). This might be due to the presence of higher concentrations of phenol (710 mg/L) and thiocyanate (75 mg/L) in the influent of R3 [8,13]. In R3 effluent, nearly 165 mg/L of nitrite was found, and that indicates the incomplete nitrification in R3. NO_2^--N concentration of 50 mg/L and above also inhibits the nitrification [22]. Also, influent NH₄⁺-N to R3 were higher (~405 mg/L) than the threshold value of 350 mg/L, responsible for decrease in nitrification as reported by Kim et al. [23]. Toxicity exerted by other pollutants such as heavy metals present in the model CW might also be the reason for lower nitrification efficiency in R3. Total nitrogen removal by the CMBR system was 81-82% in the entire study. In the present



Fig. 5. Nitrogen removal profile by CMBR system with actual coke oven wastewater.

study, R2 was significantly responsible for nitrogen removal (denitrification) from total influent nitrogen, and it was always higher than R3 nitrification.

3.6. Other pollutants removal by CMBR

The effluent concentrations of cadmium, cobalt, and lead were under the detectable limit due their low influent concentration in R1. Hence, R2 as well as R3 was expected to be free from the adverse effect of these heavy metals. In the present study, raw wastewater contained sulfate and sulfide concentrations of 130 and 3 mg/L, respectively. The sulfide concentration in effluent of R1 increased up to 8 mg/L, and it indicated the probability of existence of bacteria with sulfate reduction potential. Viggi et al. [24] also observed the complete removal of heavy metals [As (V), Cd, Cr(VI), Cu, and Zn] by sulfate reducing bacteria in fixed bed reactors. Similarly, 3 mg/L of iron from R1 effluent was undetectable in R2 effluent. Zhang et al. [25] reported enhanced COD removal by anaerobic reactor supplied with iron in a coupled microbial electrolysis cell.

4. Conclusion

In this work, CW collected from coal rich region of northeast India was treated in sequential anaerobic– anoxic–aerobic moving bed biofilm reactor. This CW was mixed with synthetic pollutants of phenol, cresols, SCN⁻, pyridine to make the model CW. The locally available biomass was acclimatized with synthetic pollutant and it was efficient for removal of multiple pollutants. In anaerobic CMBR, phenol and COD removal decreased, whereas performance of anoxic and aerobic CMBR remained unchanged in terms of phenol/COD removal for both model CW and synthetic wastewater. However, SCN⁻ removal of model CW in anoxic CMBR decreased immediately, and it regained its normal removal efficiency (88%) in the next 4–5 d of operation and remained stable. Anoxic and aerobic CMBR was mainly responsible for pyridine removal. For model CW, nitrification in aerobic CMBR decreased from 71.32 to 64.28%, and its high nitrite accumulation up to 165 mg/L indicated the incomplete nitrification. Total phenolics, SCN⁻, COD, pyridine, and total nitrogen removal were 99.93, 99.63, 95.5, 94.5, and 81.4%, respectively, in the entire study. Therefore, the sequential anaerobic-anoxic–aerobic CMBR system can be effectively used to treat high concentrated coke oven wastewater and such.

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