

Anaerobic-Anoxic-Aerobic Sequential Degradation of Synthetic Wastewaters

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Abstract

This study was conducted in a continuous three-stage system of anaerobic (R1)–anoxic (R2)–aerobic (R3) reactors with synthetic wastewater containing phenol (1000 mg/L), chemical oxygen demand (COD) (3000 mg/L), CN^- (30 mg/L), SCN^- (400 mg/L), and $\text{NH}_4^+\text{-N}$ (600 mg/L) as principal pollutants and well-acclimated heterogeneous microbial cultures. The final effluent was partially returned to R2 with a recycle ratio of 1. Anaerobic stage served to detoxify the feed by removing up to 80% of cyanide. Complete SCN^- removal and denitrification could be achieved in the anoxic stage by utilizing phenol as an internal source of carbon. Nitrification efficiency of 93% was obtained in the aerobic reactor. The results demonstrated that the three-stage system can give the desired final treated effluent quality (0 mg/L of phenol, 0.2 mg/L of CN^- , 210 mg/L of COD, and 20 mg/L of $\text{NH}_4^+\text{-N}$) and that the $\text{NO}_3^-\text{-N}$ concentration can be lowered by a higher recycle ratio.

Index Entries: Complex wastewater; acclimation; anaerobic detoxification; nitrification; denitrification; recycle ratio.

Introduction

Process wastewaters from coke-oven and coal-gasification processes are difficult to treat by conventional methods owing to the presence of high concentrations of toxicants such as phenol (1000–1600 mg/L), COD (4000–6000 mg/L), cyanide (CN^- : 40–100 mg/L), thiocyanate (SCN^- : 400–600 mg/L), and ammonia-nitrogen ($\text{NH}_4^+\text{-N}$: 200–4000 mg/L) (1).

Nitrifying bacteria are inhibited by the feed components (2), and both single- and two-stage activated sludge processes have been reported to be inadequate to handle such wastewaters (3). Recent trends show that anaerobic-anoxic-aerobic reactors with biomass growth in suspension or as a film on fluidized media can be used for complex wastewater treatment (4). The anaerobic stage acts as a pretreatment step for partial detoxification by

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Table 1
Patterns of Pollutant Removal Under Sequential Environment^a

1. Anaerobic	
$C_6H_5OH + 4 H_2O \rightarrow 3.5 CH_4 + 2.5 CO_2$	(1)
$HCN + 2 H_2O \rightarrow HCOOH + NH_3$	(2)
$SCN^- + 2 H_2O \rightarrow CO_2 + NH_4^+ + S^{2-}$	(3)
2. Anoxic	
$10 NO_3^- + 2 C_6H_5OH \rightarrow 5 N_2 + 12 CO_2 + 4 H_2O + 4 OH^-$	(4)
$NO_3^- + 0.33 C_6H_5OH \rightarrow 0.166 C_5H_7NO_2 + 1.167 CO_2 + 0.5 OH^-$ $+ 0.416 N_2 + 0.167 H_2O$	(5)
3. Aerobic	
$C_6H_5OH + 7 O_2 \rightarrow 6 CO_2 + 3 H_2O$	(6)
$SCN^- + 2 O_2 + 2 H_2O \rightarrow CO_2 + NH_4^+ + SO_4^{2-}$	(7)
$NH_4^+ + 1.5 O_2 \rightarrow NO_2^- + 2 H^+ + H_2O$	(8)
$NO_2^- + 0.5 O_2 \rightarrow NO_3^-$	(9)

^aAdapted from refs. 9, 14, 15, and 16.

CN⁻ removal (5). The anoxic-aerobic sequence has been suggested for the simultaneous removal of carbon and nitrogen compounds through denitrification-nitrification reactions (6).

A logical sequence of biochemical reactions leading to mineralization of target pollutants under anaerobic (reactions 1–3), anoxic (reactions 4 and 5), and aerobic (reactions 6–9) environments is shown in Table 1. A strict anaerobic environment results in complete conversion of phenol to methane and CO₂, while cyanide is converted stoichiometrically to formic acid and ammonia (0.53 g of NH₄⁺-N per g of CN⁻). Under an anoxic environment, phenol serves as an electron donor with nitrate as electron acceptor in the denitrification reaction. With aerobic conditions, SCN⁻ is oxidized to SO₄²⁻ and NH₄⁺-N is converted to NO₃⁻-N via NO₂⁻-N as an intermediate. OH⁻ and H⁺ ions generated during denitrification or nitrification lead to a proportionate change in pH.

The objective of the present study was to develop stagewise profiles of pollutant removal during sequential exposure to anaerobic-anoxic-aerobic environments.

Materials and Methods

Well-acclimated heterogeneous anaerobic, anoxic, aerobic cultures were developed separately in batch reactors, with synthetic feed containing phenol (1000 mg/L), CN⁻ (30 mg/L), SCN⁻ (400 mg/L), NH₄⁺-N (600 mg/L), COD (3000 mg/L), phosphate buffer, yeast extract, and trace metals at pH 7.8.

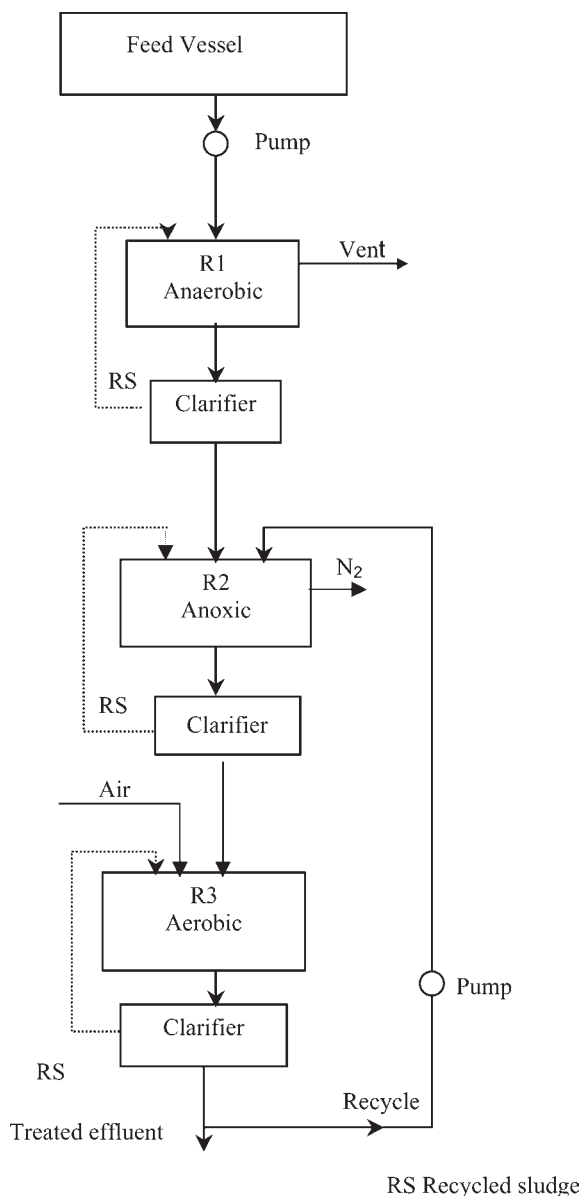


Fig. 1. Schematic of continuous three-stage reactor assembly.

A schematic representation of the experimental assembly is shown in Fig. 1. It consisted of three suspended growth bioreactors (5-L capacity each) in series, maintained under anaerobic (R1), anoxic (R2), and aerobic (R3) environments. Mixing of reactor content was achieved by a variable-speed magnetic stirrer in R1 and R2 and by diffused aeration (airflow of 1–1.5 L/min) in R3. Synthetic feed was added to reactor R1 by a peristaltic pump (model Gibson-minipuls-3). Each reactor was followed by a clarifier (capacity: 500/1000 mL) for biomass separation. The supernatant from the

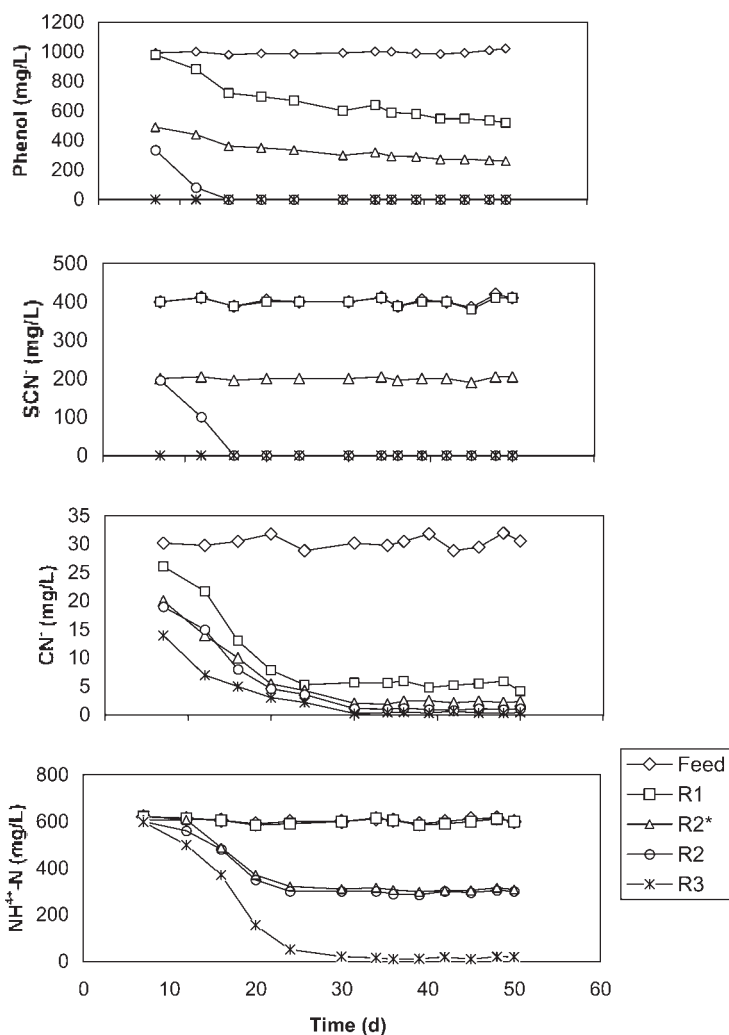


Fig. 2. Profiles for pollutant removal in continuous three-stage system during transient (0–24 d) and steady-state (25–50 d) periods.

clarifier was fed to the next reactor by gravity, and settled sludge was recycled to the respective reactor. Treated effluent from R3 was partially recycled to R2. The study was conducted at a feed rate of 1 L/d and a recycle ratio of 1 to give a total system HRT (hydraulic retention time) of 10 d. Dissolved oxygen (DO) concentrations in the bioreactors were as follows: 0 mg/L (R1), 0.5–0.7 mg/L (R2), and 4.5–4.8 mg/L (R3). The temperature in all the reactors was $26 \pm 0.5^\circ\text{C}$. The study was conducted for 50 d, until steady-state performance was achieved. A set of 8–10 observations was made to establish the performance of the system at steady state.

Samples of reactor effluents were collected on alternate days and centrifuged prior to analysis according to standard methods (7).

Results and Discussion

The three-stage system was operated for a period of 50 d, and the profiles of observed concentrations of pollutants across the reactors is shown in Fig. 2. The profiles depict the concentrations of the individual pollutants in the feed and the streams leaving the three reactors—R1, R2, and R3—as well as the feed to the anoxic reactor (R2) representing the weighted average of the anaerobic reactor (R1) effluent and the recycled effluent of R3. The graphs indicate a transient period of reactor operation up to d 20–25, and subsequently steady state was developed and maintained from d 25–50.

During steady state cyanide and phenol were removed to the extent of 80 and 30%, respectively, in R1, with essentially no change in the concentrations of SCN^- and NH_4^+ -N. Denitrification reaction proceeded efficiently in the anoxic reactor (R2) with the complete utilization of residual phenol and NO_3^- -N recycled from R3 to R2. Thiocyanate was also removed completely in the anoxic stage. Nitrification started in the aerobic reactor (R3) after d 11 and stabilized to >95% efficiency during steady operation.

Table 2 gives the average concentration of different pollutants at the inlet and exit of each reactor based on the set of eight observations made during steady-state operation of the system.

Anaerobic Stage

The anaerobic reactor (R1) gave up to 82% removal of cyanide in the feed (30 mg/L). Phenol removal efficiency in R1 was only 30% for an influent concentration of 1000 mg/L. SCN^- and NH_4^+ -N were not removed in the anaerobic reactor, similar to observations reported by Edeline et al. (8). Average values of MLVSS (mixed liquor volatile suspended solids) and MLSS (mixed liquor suspended solids) in R1 were 3200 and 4000 mg/L for reactor operation with a COD loading rate of 0.5 kg/(m³·d) and an F/M ratio of 0.16 mg of COD/(mg of MLVSS·d).

The absence of biogas generation in the anaerobic reactor throughout the study period indicates that the anaerobic reactor (R1) was probably working in the acidogenic phase, which is also evident from the observed decrease in pH from 7.8 to 7.2. High-feed CN^- concentration (30 mg/L) apparently inhibited methanogenic activity at a CN^- concentration of 10 mg/L, as reported by Fedorak et al. (9). Ng et al. (10) have also observed that the anaerobic reactor worked under the acidogenic phase, while treating nitrobenzene and polycyclic aromatic hydrocarbons containing wastewater. Significant removal of CN^- by the anaerobic reactor reduced the potential toxicity in downstream reactors.

Anoxic Stage

Feed to the anoxic stage represents effluents from R1 mixed with recycled effluent from R3. In R2, NH_4^+ -N removal was negligible throughout the period of reactor operation. However, the removal of phenol and NO_3^- -N was essentially complete in all the runs, which indicates the roles of phenol

Table 2
Observed Steady-State Performance Trends of Anaerobic (R1)–Anoxic (R2)–Aerobic (R3) Reactors

Parameter (mg/L)	Anaerobic (R1)			Anoxic (R2)		Aerobic (R3)		Overall efficiency (%)
	Feed	Outlet	Efficiency (%)	Inlet ^a	Outlet	Inlet	Outlet	
Phenol	987 (12) ^c	676 (40) ^c	32	338 (20) ^c	0 (0) ^c	0	0	100
CN ⁻	30 (1.0)	5.3 (0.6)	82	2.7 (0.2)	1.7 (0.13)	1.7	0.2 (0.13) ^c	88
SCN ⁻	400 (12)	378 (12)	5	199 (2)	0 (0)	0 (0) ^c	0 (0)	100
NH ₄ ⁺ -N	600 (8.0)	590 (9.8)	2	321 (5.5)	281 (6.5)	281	20 (4.2)	93
COD ^b	2490 (72)	1849 (56)	25	950 (36)	260 (23)	260	210 (25)	19
NO ₃ ⁻ -N	0	0	—	131 (5.1)	0 (0)	0 (0)	262 (10.4)	—
NO ₂ ⁻ -N	0	0	—	1 (3)	0 (0)	0 (0)	2.0 (1)	—
SO ₄ ²⁻	0	0	—	310 (19)	610 (18)	610 (15)	610 (16)	—

^aInfluent to R2 expressed as weighted average of R1 and recycled R3 outlet streams.

^bCOD corrected for SCN⁻ interference.

^cNumbers in parentheses indicate SD values.

as an efficient electron donor and carbon source for denitrification. The phenol to NO_3^- -N ratio in R2 was 2.58 (corresponding a C/N ratio of 1.97) and complete denitrification was achieved, which is contradictory to the findings of Bridle et al. (11), who reported a minimum C/N ratio needed for complete denitrification to be >3.5 with phenol as the sole carbon source. As reported by Richards and Shieh (12), TOC/NO_3^- -N ratio with phenol as the carbon source was 1.2–2.2 depending on the system's SRT (solid retention time), which is comparable with the C/N value of the present study.

SCN^- was completely oxidized to sulfate as per stoichiometry (1 mg of SCN^- oxidized to 1.65 mg of SO_4^{2-}) in R2. This is contradictory to the findings of Richards and Shieh (12), in which no SCN^- removal was achieved under anoxic environments. According to Zhang et al. (1), under oxygen-deficient conditions SCN^- degradation was possible (see Eq. 3 Table 1), without generation of SO_4^{2-} . The extent of SCN^- degradation in the present study under anoxic environment could not be determined. The oxygen needed either came from NO_3^- or was present in the anoxic environment (0.5–0.7 mg/L of DO).

COD removal in R2 was 72%, which indicates that most of the COD was removed in the anoxic reactor, and residual COD indicates the generation of some intermediates. In R2, alkalinity generation was in the range of 450–460 mg/L of CaCO_3 , and there was increase in pH, which confirms the progress of denitrification reactions. Theoretical alkalinity generation per milligram of NO_3^- -N is 3.87 g of CaCO_3 , and the present value of alkalinity generation matched this value (450 mg/L of CaCO_3 generation per 130 mg/L of NO_3^- -N removal). In the anoxic reactor (R2), average MLVSS and MLSS concentrations were 1820 and 2100 mg/L, respectively. COD loading rate was 0.4 kg/($\text{m}^3\cdot\text{d}$), and the corresponding loading rates of phenol and NO_3^- -N were 0.135 and 0.052 kg/($\text{m}^3\cdot\text{d}$) respectively.

Aerobic Stage

NH_4^+ -N, being the most difficult and critical pollutant, was removed only under aerobic conditions (R3). With an influent NH_4^+ -N concentration of 300 mg/L, 93% removal efficiency was achieved at 3.5 d of HRT of the aerobic reactor. Throughout the study, the NO_2^- -N concentration in the aerobic reactor was <2 mg/L, which shows negligible inhibition by nitrobacter. In R3, alkalinity was in the range of 20–40 mg/L of CaCO_3 and there was a drop in pH (from 7.6 to 6.2), which indicates the progress of the nitrification reaction.

The aerobic reactor (R3) was started with an MLVSS concentration of 3000 mg/L, and this remained constant during the experimental runs. The actual proportion of nitrifiers in R3 biomass could not be established, but low COD utilization indicates a low concentration of heterotrophs in the microbial cultures. The loading rate of NH_4^+ -N in R3 was 0.112 kg/($\text{m}^3\cdot\text{d}$) (0.038 mg of NH_4^+ -N/[mg of MLVSS $\cdot\text{d}$]) and nitrification efficiency was 93%, comparable with 95% reported by Lee and Park (4) with coke-plant wastewater for a similar loading rate.

The concentrations of total nitrogen ($\text{TN} = \text{SCN}^- - \text{N} + \text{NH}_4^+ - \text{N} + \text{CN}^- - \text{N} + \text{NO}_3^- - \text{N}$) in the feed and final effluent were 713 and 305 mg/L, respectively, with a total nitrogen removal efficiency of 57%. Liu et al. (13) had reported that TN removal efficiency can be represented by $R/(1 + R)$, in which R is the recycle ratio to the anoxic reactor. With $R = 1$, TN removal efficiency becomes 50%, which is close to the present value. The result suggests that to achieve a higher TN removal efficiency, the system should be operated at a higher recycle ratio.

Conclusion

The primary objective of this study was to investigate the feasibility of a three-stage anaerobic-anoxic-aerobic system for handling complex nitrogenous wastewater and to achieve nitrification and denitrification without external carbon addition. The following observations were made: A high concentration of toxic pollutants such as phenol (1000 mg/L), CN^- (30 mg/L), SCN^- (400 mg/L), and $\text{NH}_4^+ - \text{N}$ (600 mg/L) could be efficiently treated by the three-stage system with heterogeneous acclimated cultures at 10 d total HRT. The anaerobic first stage served as a detoxification step for the removal of 80% cyanide and one-third phenol degradation, to reduce the toxicity effect in downstream reactors substantially. Complete phenol and $\text{NO}_3^- - \text{N}$ removal was achieved in the anoxic reactor, with a phenol: $\text{NO}_3^- - \text{N}$ ratio of 2.58 (corresponding C/N ratio was 1.97), sufficient to achieve complete denitrification. SCN^- was also completely oxidized to sulfate in the anoxic reactor. An overall COD removal efficiency of 93% was achieved in the three-stage system, and COD was mainly removed in the anoxic reactor. Complete denitrification was achieved in R2 but the $\text{NO}_3^- - \text{N}$ concentration in the final effluent was high (260 mg/L). The three-stage system can be operated at a higher recycle ratio to reduce the final effluent $\text{NO}_3^- - \text{N}$ concentration.

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