Comparative Study on Response of Thiocyanate Shock Load on Continuous and Fed Batch Anaerobic – Anoxic – Aerobic Sequential Moving Bed Reactors

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Abstract

A comparative study on response of a toxic compound thiocyanate (SCN⁻) was carried out in continuous and fed batch moving bed reactor systems. Both systems had three sequential anaerobic, anoxic and aerobic reactors and operated at same hydraulic retention time. Feed SCN⁻ was first increased from 600 mg/L to 1,000 mg/L for 3 days (shock 1) and then from 600 to 1,200 mg/L for 3 days (shock 2). In anaerobic continuous reactor, increase of effluent COD (chemical oxygen demand) due to shock load was only 2%, whereas in fed batch reactor it was 14%. In anoxic fed batch reactor recovery was partial in terms of SCN⁻, phenol, COD and NO₃⁻–N and NO₂⁻–N removals and in continuous reactor complete recovery was possible. In both systems, inhibition was more significant on aerobic reactors than anaerobic and anoxic reactors. In aerobic reactors ammonia removal efficiency deteriorated and damage was irreversible. Present study showed that fed batch reactors showed higher substrate removal efficiency than continuous reactors during regular operation, but are more susceptible to toxic feed shock load and in nitrifying reactor damage was irreversible.

Keywords: Ammonia-nitrogen, Anaerobic-anoxic-aerobic sequential reactors, Biomass washout, Continuous reactors, Fed batch reactor, Nitrifying bacteria, Phenol, Substrate peak, Thiocyanate shock load

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1. Introduction

Any industrial wastewater treatment plant undergoes different intermittent organic and pollutant loading conditions, when concentrations of its pollutants change abruptly. Therefore, feed shock loading generally refers to sudden increased input of pollutants to the reactor, which results in substrate accumulation and further inhibition. The degree of inhibition depends on overall microbial activity, the extent of shock loading and type of reactor [1]. Suspended growth reactors are expected to be affected the most due to less concentration of biomass in the reactor and higher possibility of biomass washout. Attached growth reactors like anaerobic filters, trickling filter are more robust to handle shock loads, but more prone to clogging. In moving bed reactors (MBR) freely moving carrier media (like sponge) is added in the reactor [2]. Biomass is attached on the media surface and moves in the reactor either due to movement of gas, or by flowing liquid or both. MBR system consists of very high biomass concentration compared to suspended growth process and less prone to clogging, compared to anaerobic/aerobic filters. Besides, type of reactor, the inhibition of shock load on reactor system may depend on reactor operation. Reactor can be operated as continuously fed, where raw wastewater is continuously fed to the reactor and effluent is continuously withdrawn. On the other hand, in the fed batch reactor, which works like a SBR (sequential batch reactor) the reactor is fed intermittently and effluent is withdrawn, only after reaction is complete. Fed batch reactor has several phases like fill, reaction, settle and decant phases. This type of reactor has several advantages over continuous fed system like more compact process, higher substrate removal efficiency, higher flexibility, no need for separate settling tank (space saving), no need for continuous wastewater pumping to the reactor (power saving). Though several advantages of batch reactors are well-known, however its recovery after feed
toxic shock load as compared to continuous reactors is not studied much. Synthetic wastewater was used for this study with high concentrations of phenol, thiocyanate (SCN−) and ammonia (NH4+-N). This type of wastewater is common in coke oven industries, coal gasification process, synthetic fuel processing, petrochemicals etc. [3-5]. To treat these multiple pollutants, a combination of anaerobic, anoxic, aerobic reactors could achieve the desirable results instead of a single reactor [3, 6]. The anaerobic reactor is used for partial phenol and COD removals, anoxic unit for remaining phenol, COD and SCN− removals along with denitrification and aerobic unit for ammonia removal and nitrification. Nitrified effluent is recycled to upstream anoxic reactor [7]. The objective of the present work is to compare responses of thiocyanate shock load on continuous anaerobic-anoxic-aerobic moving bed reactor system with a similar fed batch reactor system.

2. Materials and Methods

2.1. Experimental Set Up

Fig. 1. Schematic of continuous and fed batch reactor system. (1) Anaerobic reactor, (2) Anoxic reactor, (3) Aerobic reactor, (4) Sponge cube, (5) Influent, (6) Peristaltic pump, (7) Clarifier, (8) Biogas collection pipe, (9) Gas outlet, (10) Effluent reservoir, (11) Recirculation to anoxic reactor, (12) Separator with nylon mesh, (13) Compressed air supplier.
Two experimental systems were used for this study: (i) continuous moving bed reactor system and (ii) fed batch moving bed reactor system. Each system consisting of three reactors connected in series, maintained under anaerobic, anoxic and aerobic environments, named R1, R2 and R3, respectively for continuous system and B1, B2 and B3 respectively for fed batch system. Each system consisted of three identical PVC (polyvinyl chloride) reactors, each of diameter 15 cm and height 118 cm. A schematic diagram of figure is shown in Fig. 1. [8].

Working volume (liquid, sponge and biomass) of each reactor (R1, R2 and R3) in continuous system was 15L. Sponge cubes (dimensions: 1cm x 1cm x 1cm) 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 of R1, R2 and R3 was 2940 cm\(^3\), which was 19.6% of working volume of each reactor. Working volume (liquid, sponge and biomass) of each reactor (B1, B2 and B3) in fed batch system was 10L. In each of B1, B2 and B3, total volume of sponge cubes was 1960 cm\(^3\) which was 19.6% of working volume of each reactor. All six reactors were operated in upflow mode.

In R1 and B1, feed was directly added. Effluents of R1 and B1 were mixed with effluents of R3 and B3, respectively (ratio of 1:1) with external addition of 1000 mg/L NO\(_3^-\)-N and then added to R2 and B2. This extra nitrate was added in influent of R2 and B2, to ensure strict anoxic condition in R2 and B2. Feed/influent was continuously added to R1, R2 and R3. In continuous fed system hydraulic retention times were decided based on reactor volume and flow rate. In fed batch system HRT was calculated using Eq. (1).

\[
\text{HRT (day)} = \frac{\text{Reactor volume (L)}}{\left(\text{Volume decanted per cycle in L}\right)\left(\text{No. of cycles per day}\right)} 
\]

(1)

Cycle times, fill times and decant times for B1, B2 and B3 are given in Table 1. Fill times values were decided based on our previous study [9]. Hydraulic retention times of R1 and B1
were of 3 days each, R2 and B2 were of 1.5 days each and R3 and B3 were 1.5 days each. Total HRT of both systems were of 6 days each.

Influent to R2 was calculated using Eq. (2). Effluent of R2 or B2 were directly fed to R3 or B3, respectively after necessary pH adjustment with 1N HCl or 1N NaHCO₃.

Influent concentration to R2 or B2 =

\[
\frac{Q \text{ (Eff. concentrations of R1 or B1)} + RQ \text{ (Eff. concentrations of R3 or B3)}}{Q + RQ}
\]

where, Q was the feed flow rate to R1/B1, and R was the recycle ratio. In R1, B1 and R2, B2, mixing was achieved only by the upflow motion of the influent. In B3 and R3, compressed air (0.15 L/min) was supplied. Dissolved oxygen concentrations (mg/L) in six reactors were: 0 (R1, R2, B1 and B2) and 3.5-4.0 (R3 and B3). The two reactor systems were maintained at a constant temperature (30 ± 3 °C) using a temperature controlled blower.

| cycle variation          | Anaerobic (B1) | Anoxic (B2) | Aerobic (B3) |
|--------------------------|----------------|-------------|--------------|
| Cycle time (h)           | 24             | 24          | 24           |
| Flow during fill period  |                |             |              |
| (L/h)                    | 1.6            | 1.6         | 0.8          |
| Amount withdrawn (L)     | 3.33           | 6.66        | 6.66         |
| Fill period (h)          | 2.08           | 4.16        | 8.33         |
| Decant time (min)        | 15             | 20-30       | 20-30        |
| HRT (day)                | 3.00           | 1.50        | 1.50         |
| Reaction time (h)        | 21.67          | 19.34       | 15.17        |
| Aeration                 | -              | -           | Continuous   |
2.2. Synthetic Feed

The study was conducted with identical synthetic feed containing thiocyanate (SCN−) of 600 mg/L, (used as KSCN) in regular condition that was increased to 1,000 and 1,200 mg/L along with phenol (2,500 mg/L), NH₄⁺–N (500 mg/L). NO₃⁻-N was added in recycle of 1,000 mg/L (as 7,201 mg KNO₃/L) in regular condition and increased to 1200 (shock 1) and 1,400 mg/L (shock 2). Feed pH was maintained at 7.5 ± 0.2 by using phosphate buffer (KH₂PO₄ 72.3 g/L and K₂HPO₄ 104.5 g/L). Yeast extract of 50 mg/L and trace metals solution of 1 mL/L feed were added as nutrients. The composition of trace metal solution was: MgSO₄.7H₂O: 10,000 mg/L, CaCl₂.2H₂O: 10,000 mg/L, FeCl₃.6H₂O: 5,000 mg/L, CuCl₂: 1,000 mg/L, ZnCl₂: 1,000 mg/L, NiCl₂.6H₂O: 500 mg/L, CoCl₂: 500 mg/L [7]. Feed COD was in the range of 7,980-8,900 mg/L during the study.

2.3. Culture Development

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 R1, B1 and R2 and B2. 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 aerobic reactors, R3 and B3. Inoculums (20% of reactor volume) were added in each reactor. Acclimatization was carried out by slowly increasing pollutant concentration in each reactor. After acclimatization R1, R2 and R3 were connected in each series and reactor operation started. Similarly batch reactor operation also started with reactors B1, B2 and B3 with acclimatized biomass.
2.4. Experimental Procedure

Feed phenol, SCN\(^-\) and NH\(_4\)^+-N were constant at 2,500 mg/L, 600 mg/L and 500 mg/L, respectively and COD was 7,980 mg/L in regular condition. Reactor was operated for 12 days with this feed condition and then first shock load (shock 1 from day 13\(^{th}\) to 15\(^{th}\)) was applied by increasing feed SCN\(^-\) to 1,000 mg/L for 3 days and then normal feed (SCN\(^-\) 600 mg/L) was started. In the second shock load (shock 2 from day 26\(^{th}\) to 29\(^{th}\)) feed SCN\(^-\) was increased to 1,200 mg/L and after 3 days regular feed was started. Influent COD increased to 8,300 mg/L and 8,900 mg/L during the shock load study. In order to remove these higher organic carbon, NO\(_3\)^-N was increased in recycle of R3 and B3 to 1,200 mg/L in shock 1 and 1,400 mg/L in shock 2. This NO\(_3\)^-N concentration was continued even after shock 1 and shock 2. After 19 days of second shock load, feed was stopped for four days (47\(^{th}\)-50\(^{th}\)) in both systems to improve reactor performance. Then both systems were operated for another 16 days with regular feed. The performance of reactors was calculated in terms of pollutant removal (%) and steadiness in effluent concentration.

2.5. Analytical Techniques

Samples of reactor effluents were collected and centrifuged prior analysis according to APHA [10]. 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. NO\(_3\)^-N concentration was determined by measuring absorbance at 220 and 275 nm in UV-spectrophotometer. Nitrite was measured using colorimetric method at 543 nm.
3. Results and discussion

3.1. Performances of Anaerobic Reactors R1 and B1

3.1.1. Phenol Removals in R1 and B1

The first SCN⁻ shock load (shock 1) was employed to continuous and fed batch systems from day 13\textsuperscript{th} to 15\textsuperscript{th}, by increasing feed SCN⁻ concentration by 66\% (from 600 to 1,000 mg/L) and then again feed SCN⁻ of 600 mg/L was applied from day 16\textsuperscript{th} onward. Prior to first shock load, phenol removal efficiency of R1 was 20\% (2,000±41 mg/L effluent phenol) [Fig. 2(a)]. B1 showed slightly higher phenol removal efficiency of 25\% (effluent 1,881±12.7 mg/L). R1 and B1 achieved new steady states in terms of phenol removal within next 5-7 days (two-times of reactor HRT) with phenol removal efficiencies of 12\% (R1) and 15.6\% (B1). After application of second shock load, these further went down to around 6\% in both R1 and B1. After stop feeding, phenol removals in R1 and B1 improved to 9\% and 15\%. Effluent phenol increased in R1 from 2,000 to 2,280 mg/L (14\% increase) and in B1 from 1,881 to 2,110 mg/L (12\% increase).
3.1.2. COD Removals in R1 and B1

Before shock load application, effluent COD of R1 was 7,550 mg/L (removal was only 5.3% from feed of 7,980±43.6 mg/L) [Fig. 2(b)]. In B1, COD removal was much higher of 17.5% (effluent COD 6,580±95.2 mg/L). There was initial transient phase of 5 days in R1 and B1 and then in a similar way like phenol, R1 and B1 achieved new steady states in terms of COD removal with effluent COD values of 7,780 mg/L and 7,560 mg/L (removals of 2.5% in R1
and 5.6% in B1). After second shock load, COD removal in both the reactors became same of 2.9% (effluent COD of 7,750 mg/L). After shock load effluent COD increased from 7,550 mg/L to 7,700±65 mg/L (2% increase) in R1 and from 6,580 to 7,620±52 mg/L (15.8% increase) in B1. Overall shock load caused decrease in COD removal from 17% to 4.5% in B1 (73% decrease) and 5.4% to 3.5% in R1 (35% decrease).

In previous literature [8], it was observed that higher thiocyanate was responsible for decrease in phenol and COD removals in anaerobic reactor, suggesting inhibitory effect on phenol degrading biomass. Present study shows that thiocyanate shock load had strong inhibitory effect on phenol and COD removals in both anaerobic reactors and inhibition was more profound in B1 than R1.

3.1.3. Thiocyanate Removal in R1 and B1

Fig. 2(c) shows effluent thiocyanate profile in anaerobic reactors R1 and B1. Before shock load application, SCN⁻ removal was nil in R1 and B1. On day 15ᵗʰ, effluent SCN⁻ concentration increased to 980 mg/L in R1 and B1 and they required almost 3-4 days time to achieve the steady state condition with effluent SCN⁻ of 598±2 mg/L. On day 27-29ᵗʰ, again second SCN⁻ shock load was applied by increasing SCN⁻ concentration 100% (from 600 to 1,200 mg/L) and then from day 30ᵗʰ onward, feed SCN⁻ was again decreased to regular level of 600 mg/L. R1 and B1 required nearly 3 days achieving the pre-shock effluent SCN⁻. Since R1 and B1 did not show any SCN⁻ removal even before shock load application, it is obvious that 3 days time were required to dilute the effluent (same as HRT of reactors).
3.2. Performances of Anoxic Reactors R2 and B2

3.2.1. Thiocyanate Removals in R2 and B2

Fig. 3. Effluent profiles in anoxic reactors after thiocyanate shock load. (a) Thiocyanate, (b) Phenol, (c) COD, (d) Nitrate-nitrogen.

Effluent of anaerobic reactors (R1 and B1) was diluted with effluent of downstream aerobic reactors (R3 and B3) using recycle ratio of one. Fig. 3(a) shows the profiles of SCN⁻ in R2 and B2. Influent SCN⁻ to both R2 and B2 was around 300 mg/L. Before shock load application, R2 achieved around 68% SCN removal with effluent of 95±2.1 mg/L. These were 75% and 75±3.1 mg/L in B2, respectively.
After shock 1, both reactors were unsteady for around 6-7 days (four times of reactor HRT). Maximum influent SCN concentration increased from 300 to 480 mg/L (around 63% increase) in both systems. Then R2 and B2 achieved steady state with respective removals of 65% and 62%. After shock 2, influent SCN concentration increased from 300 to 600 mg/L (100% increase). R2 and B2 required longer time of around 10-11 days to stabilize as compared to the first shock load with steady state removals of 60% and 56%, respectively. When feed was stopped for four days, effluent SCN in both R2 and B2 further approached to 100 mg/L. R2 regained almost the pre–shock SCN removal efficiency of 67-68%, whereas in B2 efficiency decreased from 75% to 68% (effluent increased from 75 to 100 mg/L). It shows that even 100% increase of SCN shock load, recovery was feasible only in R2, not in B2.

Before shock load, influent NH4+-N to R2 and B2 were 320±5 and 302±3 mg/L, respectively with effluents of 350±4 and 330±6 mg/L. From degradation of SCN in R2 and B2, theoretical NH4+-N generation could be 49 mg/L and 54 mg/L (Eq. (3)) [8], suggesting that 19-26 mg/L of NH4+-N were removed in R2 and B2, which could be due to incorporation into biomass.

\[
\text{SCN}^- + 1.6\text{NO}_3^- + 0.2\text{H}_2\text{O} + 1.6\text{H}^+ + \text{HCO}_3^- \rightarrow \text{SO}_4^{2-} + \text{NH}_4^+ + 2\text{CO}_2 + 0.8\text{N}_2
\] (3)

After shock 1, influent NH4+-N in R2 remained same but effluent NH4+-N increased to 370 mg/L on day 21st. In B2 both influent and effluent NH4+-N increased to 342 and 380 mg/L, respectively. After shock 1, NH4+-N removal in both R2 and B2 decreased. After shock 2, influent NH4+-N further increased to 395 and 425 mg/L, respectively in R2 and B2. Due to shock load, SCN removal in R2 and B2 decreased, suggesting less generation of NH4+-N from SCN degradation, though influent NH4+-N increased. This could be due to higher
effluent NH$_4^+$-N concentration in downstream reactor R3 and B3, which was recycled back to R2 and B2.

3.2.2. Phenol Removals in R2 and B2

Phenol removals in R2 reactor was around 65% (effluent phenol of 350±0.3 mg/L) from influent of 1,000 mg/L during regular operation. In B2, influent phenol was lower (941±3.4 mg/L) and almost 91% phenol removal was achieved. The reason was higher phenol removal in upstream batch reactor B1 than R1. Effluent phenol profiles in B2 and R2 are shown in Fig. 3(b). Average influent phenol increased to 1,107±55.4 mg/L in B2 and 1,125±30 mg/L in R2 after first shock load. After 5-6 days unsteady condition, reactors achieved steady state with higher influent phenol concentration of 1,056 and 1,100 mg/L for B2 and R2, respectively. However, both R2 and B2 regained almost pre-shock removal efficiencies of 69% and 89%, suggesting temporary effect of the first shock load on anoxic reactors. After the second shock load, influent phenol further increased to 1,230-1,300 mg/L in R2 and B2 (15-25% increase). R2 achieved 65% efficiency within 12 days and this improved further to 69% (higher than pre-shock) (effluent phenol 357±11 mg/L). Phenol removal in R2 actually increased after shock load from 65% to 69%. The reason was higher supply of phenol due to upset of upstream reactor R1. B2 also showed 87% removal efficiency after shock 2 (effluent phenol 146±25 mg/L). This suggests that both anoxic reactors, R2 and B2 showed excellent recoveries of 100% and 96%, respectively after SCN$^-$ shock load.
3.2.3. COD and Oxidized Nitrogen Removals in R2 and B2

Profiles of effluent COD in R2 and B2 are shown in Fig. 3(c). In B2 influent COD was 3197 mg/L and it removed 78% of influent COD with effluent of 690±30 mg/L. In R2 influent COD was higher than fed batch system (3905 mg/L) due to lower COD removal efficiency of R1 than B1. R2 had 72% COD removal efficiency in regular operation (effluent COD 1,171±72 mg/L) Influent COD increased to 4,265-4,295 mg/L immediately after first shock load, due to lower COD removal in R1 and B1 after shock 1. After 7 days, both reactors achieved steady state. However, there was permanent shift of influent (from 3,197 to 3,900 mg/L) and effluent COD values (from 680 to 950 mg/L) in B2 and removal was 76%. In R2 also influent and effluent COD increased slightly from 3,900 to 4,000 mg/L and from 1,100 to 1,300 mg/L, with removal decreased from 72% to 67%.

After shock 2, influent COD increased to 4,600 mg/L on day 30th (18% increase of influent COD). R2 and B2 required almost 12 days to achieve the steady state. After stop feeding, effluent COD values decreased to 950 and 1150 mg/L, respectively. In R2, effluent COD values and removals remained same (77%) during pre-shock and post shock 2, suggesting complete recovery. However, there was permanent increase in influent COD by 23% (from 3,100 to 3,900 mg/L) and effluent COD by 39% (from 680 to 950 mg/L) in B2, though removal almost remained same (78% to 76%).

In R2 and B2, COD removal occurred concurrently with denitrification. Fig. 3(d) shows profiles of NO\textsubscript{X^-}-N (NO\textsubscript{3^-}-N + NO\textsubscript{2^-}-N) in R2 and B2 before and after shock load. Influent NO\textsubscript{X^-}-N to R2 and B2 were 650-667±9.1 mg/L before shock load and both reactors showed almost 87% denitrification efficiency. In order to cope with higher influent COD in R2 and
B2, influent NO$_3^-$-N in recycle of R3 and B3 were increased from 1,000 to 1,200 mg/L after shock 1 and then from 1,200 to 1,400 mg/L after shock 2. Influent NO$_x^-$-N in R2 and B2 increased to 670-684 mg/L after shock 1. After shock 2, it further increased to 700 in R2 and 780 mg/L in B2. Denitrification efficiency increased with higher influent NO$_x^-$-N concentration to 89% in B2 and 93% in R2, indicating denitrification was unaffected by thiocyanate shock load.

In anoxic reactors, the effect of shock load was secondary in nature, since these reactors did not receive the primary shock load unlike R1 and B1. In both reactors denitrification remained unaffected due to shock load. In R2, inhibitory effect of shock load was negligible in terms of thiocyanate, phenol and COD degradations, whereas in B2 removals of phenol and COD slightly decreased due to shock load effect. Thiocyanate removal in B2 was affected more than COD and phenol removals.

### 3.3. Performances of Aerobic Reactors R3 and B3

#### 3.3.1. Phenol and COD Removals

Fig. 4(a) shows the effluent phenol profiles in R3 and B3. Prior to shock 1, influent phenol concentrations were 350 and 80 mg/L in R3 and B3, respectively and both reactors showed 99% removals with effluent phenol 1±0.5 mg/L. In R3, influent phenol increased to 450 and then to 900 mg/L on day 16$^{th}$ and day 30$^{th}$, respectively after shock 1 and 2. However, effluent phenol concentration remained unaffected in R3, except days 30$^{th}$ -34$^{th}$, when it slightly increased to 10-25 mg/L and the finally came down to 3±1.5 mg/L. In B3, after shock 1, effluent increased slightly to 3 mg/L from 1 mg/L. After shock 2, B3 reactor was unstable for almost 10 days and then achieved steady state with effluent phenol of 70 mg/L. Four days of
stop feeding improved performance of B3 and effluent phenol decreased to 15 mg/L, still much higher than pre-shock condition of 1 mg/L. In R3 after shock 2, effluent phenol was 3 mg/L, much lower than B3. In R3, phenol removal remained same (99%) before and after shock, suggesting almost complete recovery. In B2, phenol removal decreased from 99% to 89%.

COD profiles were similar to phenol in R3 and B3 [Fig. 4(b)]. Before shock load COD removal in R3 was around 78% with effluent of 245±7.4 mg/L from 1100 mg/L influent. In B3 influent was lower of 680 mg/L with effluent of 235±6 mg/L (removal 65%). After shock 1, effluent COD increased to 280 mg/L in R3 and within next 6 days it achieved the steady state with pre-shock effluent COD of 245 mg/L. After shock 2, R3 required 8 days to achieve a new steady state with effluent COD of 280 mg/L and after stop feeding it decreased to 265 mg/L (removal of 77%). In B3, after first shock load, effluent COD increased to 300 mg/L from 235 mg/L, as pre-shock condition. After second shock load B3 had fluctuating effluent COD for almost 12 days and after stop feeding, it achieved steady state with effluent COD of 250-260 mg/L (removal 72%). In R3, after shock 2, effluent COD increased by 8% and in B3, it was 10%.
3.3.2. Thiocyanate Removal

Reactors R3 and B3 showed almost 98-99% SCN⁻ removals with effluent of 0.5-1±0.9 mg/L form influents of 95 and 75 mg/L, respectively [Fig. 3(c)]. Shock 1, was responsible for higher influent SCN⁻ of 165 mg/L in R3 and 198 mg/L in B3. Both reactors were able to maintain effluent SCN⁻ of 2 mg/L with removal of 98%, irrespective of influent SCN⁻ concentration. After shock 2, effluent SCN⁻ in R3 was 2 mg/L (98% removal). B3 was more
unstable than R3 with effluent concentration increased to 40 mg/L (71% removal) after 10 days of operation. After stop feeding, effluent SCN⁻ in B3 was 25 mg/L. In R3, effluent SCN⁻ concentration increased from 1 to 2 mg/L (efficiency dropped from 99.7% to 99.1%), in B3 it increased from 1 to 25 mg/L (efficiency decreased from 98.7% to 75%).

3.3.3. Ammonia-nitrogen Removal

Before application of shock load, influent NH₄⁺-N to R3 was 350±14 mg/L and another 22 mg/L was generated from SCN⁻ degradation (total 372 mg/L). Effluent NH₄⁺-N was 135±4.3 mg/L with removal of 63%. In B3, influent NH₄⁺-N was 330±0.22 mg/L in addition to another 17 mg/L (total 347 mg/L) from SCN⁻ degradation (Eq. (4)) [9]. Effluent NH₄⁺-N was 100 mg/L with 71% removal.

\[
\text{SCN}^- + 2\text{O}_2 + 2\text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \text{NH}_4^+ + \text{CO}_2
\]

After application of shock 1, influent NH₄⁺-N increased in both the reactors to 394-407 mg/L (almost 7.5% increase of influent NH₄⁺-N) [Fig. 4(d)]. R3 achieved steady state in next 5 days with removal of 64% and effluent NH₄⁺-N of 140 mg/L. In B3, removal decreased to 56% (from 71%) with effluent NH₄⁺-N of 180 mg/L (influent 407 mg/L). Due to shock 1, removal of NH₄⁺-N decreased form 71% to 55% in B3 and remained same of 64% in R3.

After shock 2, influent NH₄⁺-N to R3 increased to 510 mg/L on day 30th and reactor was unstable for next 8 days and then achieved a new steady state with removal of 40% and effluent of 270 mg/L. After stop feeding from day 47th-50th, it further improved to 45% and effluent NH₄⁺-N of 230 mg/L. In B3, immediately after the second shock load, influent NH₄⁺-N increased to 490 mg/L. Reactor required another 9 days to get steady state with much lower
removal efficiency of 24% with effluent of 360 mg/L from 474 mg/L. Even after stop feeding of 4 days, effluent decreased slightly to 345 mg/L with removal of 26%. Shock 2 was responsible for decrease in NH₄⁺-N removal from 71% to 26% in B3 and from 64% to 45% in R3.

This result suggests that thiocyanate shock load was responsible for significant decrease of ammonia removal in both R3 and B3 and inhibition was higher in B3 than R3. Similar observation was reported by previous researchers on drop in ammonia removal due to thiocyanate shock load in continuous reactors [11, 12]. Previous literatures reported inhibition on ammonia removal when influent phenol above 200 mg/L and ammonia above 350 mg/L [13]. In this study, influent phenol was 80 mg/L in B3 and 350 mg/L in R3, and influent ammonia concentrations were 372 and 347 mg/L in R3 and B3, respectively. Almost 71% and 64% of steady ammonia removals were achieved before shock load in B3 and R3. During shock load application, influent phenol increased to 450-900 mg/L in R3 and 380-890 mg/L in B3. Influent ammonia also increased to 400-500 mg/L in both reactors. These high phenol and ammonia probably caused irreversible damage in both reactors and inhibition was more in B3 than R3.

Present study shows that effect of shock load and further recovery of bioreactor depends on mode of reactor operation and also on type of biomass. Heterotrophic biomass in anoxic reactor seems to be more robust than anaerobic bacteria and autotrophic biomass in aerobic reactor. Also, continuous fed reactor is more efficient to handle shock load than fed batch reactor. Kaballo et al. [14] observed that batch biofilm reactor performed better than continuous fed reactor during shock load of toxic compound p-chlorophenol due to more uniform biomass distribution in batch reactor as compared to continuous reactor. In the
present investigation, no tracer study was carried out, however reactor geometry suggests that all reactors in present study were of long and tubular type like plug flow reactor, with negligible/less axial dispersion. This plug flow type geometry causes slow dispersion of pollutants during shock load [15, 16]. During regular operation, substrate was added for a short period of time in fed batch system, thus biomass was exposed to higher substrate gradient. In continuous fed system, the substrate gradient was less due to continuous addition of feed. Biomass was acclimatized to high concentration of substrate and higher substrate gradient helped to achieve better effluent quality in fed batch system [17]. During shock load study the toxic substance like thiocyanate of very high concentration was added. In fed batch anaerobic and aerobic reactors, sharp peak of pollutants occurred and biomass was not acclimatized with these high pollutants concentration and efficiency dropped. In continuous reactors, peaks of substrates were less and inhibitory effect was also smaller and recovery was higher.

4. Conclusion

A comparative study was carried out to investigate the effect of thiocyanate (SCN⁻) shock load on performances of anaerobic-anoxic-aerobic fed batch (B1-B2-B3) and continuous (R1-R2-R3) moving bed reactors. Feed SCN⁻ concentration was increased in two levels from 600 to 1,000 and then from 600 to 1,200 mg/L. Phenol and COD removals were inhibited in both B1 and R1 and effect was more profound in B1. In R2 complete recovery was possible in terms of phenol, COD and SCN⁻ removals, where as in B2 recovery was partial. Denitrification was unaffected by thiocyanate shock load in both R2 and B2. Thiocyanate shock load showed maximum impact on aerobic reactors R3 and B3. Recovery was possible
for phenol, SCN⁻ and COD removals in R3 and not in B3. Effluent ammonia-nitrogen was also higher in B3 than R3. During regular reactor operation, higher substrate gradient helped to achieve better effluent quality in fed batch system than continuous fed system. However, during shock load, in fed batch system peak of substrates were much higher, than continuous system. Biomass was not acclimatized with such high peaks of toxic pollutants and efficiency deteriorated more in fed batch system than continuous fed system.

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