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Treatment of carbofuran-bearing synthetic wastewater using UASB process

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2Department of Civil and Environmental Engineering, The University of the West Indies, St. Augustine, Trinidad (WI)

In the present study, fate of carbofuran in anaerobic environments and the adverse effects of carbofuran on conventional anaerobic systems were evaluated. Carbofuran degradation studies were carried out in batch reactors with varying carbofuran concentrations of 0 to 270.73 mg/L corresponding to a sludge-loading rate (SLR) of $2.12 \times 10^{-6}$ to $3.83 \times 10^{-3}$ g of carbofuran/g of volatile suspended solids (VSS)/d. Carbofuran concentration was reduced to undetectable levels at the end of 8 and 13 days in the batch reactors operated with a SLR of $2.12 \times 10^{-6}$ and $3.33 \times 10^{-5}$ g of carbofuran/g of VSS/d, respectively. Performances of two anaerobic reactors i.e. upflow anaerobic sludge blanket (UASB) and modified UASB (with tube settlers) were evaluated in the presence and absence of carbofuran using synthetic wastewater. In the absence of carbofuran, the soluble chemical oxygen demand (COD) removal efficiency in the conventional UASB reactor at 8 h and 6 h hydraulic retention time (HRT) was nearly 88% and 76%, respectively, whereas in modified UASB reactor it was increased to 90% at 8 h HRT and 78% at 6 h HRT. When 28 mg/L (SLR of $1.19 \times 10^{-2}$ g of carbofuran/g of VSS/d) of carbofuran was introduced in the reactors, the COD removal efficiency was reduced to 41% and 44% in conventional and modified UASB reactors respectively. However, the reactor could maintain around 80% COD removal efficiency at a carbofuran concentration of 7.84 mg/L (SLR of $3.64 \times 10^{-3}$ g of carbofuran/g of VSS/d). The reactor efficiency was also measured in terms of specific acetoclastic methanogenic activity (SMA). The toxic effect of carbofuran was reversible to a certain extent. Carbofuran removal efficiency in the conventional UASB reactor at carbofuran concentrations of 7, 13 and 28 mg/L were $40 \pm 3\%$, $27 \pm 3\%$, and $11 \pm 3\%$, respectively. In modified UASB reactor, carbofuran removal efficiency was almost uniform at 7 and 13 mg/L but it was reduced nearly by 56% at 28 mg/L. The major metabolite of carbofuran i.e. 3-keto carbofuran was found in all the reactors.

Keywords: UASB; tube settlers; Carbofuran; insecticide; wastewater.

Introduction

Carbofuran (2, 3-dihydro-2, 2-dimethylbenzofuran-7-methylcarbamate) is an insecticide of the organophosphorus subgroup. Due to its widespread use and high water solubility, carbofuran has been detected in groundwater, surface and rain water, in soils, air, food and wildlife.[1–3] Base-catalyzed hydrolysis to carbofuran phenol is the major degradation pathway of carbofuran in both water and sediment.[11–7] The rate of aqueous hydrolysis of carbofuran increases dramatically with increasing pH.[5] Several technologies like ozonation, ultra violet (UV) radiation, advanced oxidation processes[8] and bioremediation are available for the removal of carbofuran from water and contaminated soils. Biological methods are gaining much more attention due to their sustainability. Many anaerobic pure bacterial isolates have been found to be successful in dechlorination and degradation of many recalcitrant and toxic organic substances like heptachlor,[9] chlorophenols,[10] chlorobenzene[11] and pentachloroethylene.[12] Earlier anaerobic biotechnology was used mainly for the digestion of sludge produced by other treatment processes. The popularity of biogas technology for large-scale application has been limited essentially due to the slow rate and process instability of anaerobic digestion and consequently greater costs and space requirements. Introduction of the Up-flow anaerobic filter, Up-flow anaerobic sludge blanket reactor, Anaerobic fluidized bed reactor and Up-flow anaerobic hybrid reactors have brought down the hydraulic retention time (HRT) of anaerobic processes. UASB reactors are very popular in recent days and in India, a full-scale anaerobic treatment plant for industrial wastewater has been installed.[13]
Also, many modifications were employed in the UASB reactors i.e. UASB with tube settlers to increase the settling of biomass in the reactor. However, there is no information available on the potential of UASB as well modified UASB (UASB with tube settlers) to respond to the presence of toxic compounds like carbofuran in the wastewater. This investigation is, thus, focused to evaluate the performance of the UASB and modified UASB reactors for the treatment of carbofuran-bearing synthetic wastewater.

Materials and methods

Chemicals

Standard carbofuran (99% purity) was purchased from Accustandard, USA and primary metabolites of carbofuran viz., Carbofuran phenol-3-keto (99% purity), Carbofuran-3-keto (99% purity) were purchased from Supelco, USA and Carbofuran-3-hydroxy (98.8% purity) was purchased from Sigma-Aldrich, USA. Commercial grade carbofuran was purchased from EID parry India Ltd, Chennai, India. All glassware used were supplied by Borosil, India and was cleaned with distilled water and dried at 110°C for 5 h prior to use. Batch experiments were carried out in triplicate to ensure the reproducibility of results and the average value is reported in all the cases.

Anaerobic sludge

The seed anaerobic sludge collected from Central Leather Research Institute (CLRI), Chennai, India was used for the primary start up of the reactors. It was ensured that the seed sludge was not exposed to carbofuran. The characteristics of the seed sludge are given in Table 1.

Analytical procedure

Analysis of carbofuran

Ten millilitres of effluent were collected from the reactor and centrifuged at 2000 × g for 20 min. (Remi instruments Ltd., India). After centrifugation, the supernatant was transferred to a separating funnel and then was extracted with 10 mL of ethyl acetate and hexane (1:1). The water layer was decanted carefully and the supernatant was extracted with 5 mL of ethyl acetate and hexane (1:1) twice more. Finally, extracted samples were filtered through anhydrous sodium sulfate to remove the moisture content. The extracted samples were analyzed using Gas Chromatograph (Perkin Elmer Clarus 500) with nitrogen phosphorous detector (NPD) equipped with an autosampler, an on column, split/splitless capillary injection system, with a Perkin Elmer Elite (PEE)-5 (cross bond 5% diphenyl—95% dimethyl Polysiloxane) capillary column (30 m × 0.53 mm × 0.5 μm film thickness). The operating conditions were as follows: The column was held initially at a temperature of 120°C for 5 min, then at 5°C min−1 to 140°C for 2 min, followed by 5°C min−1 to 210°C for 2 min, 7°C min−1 to 240°C and held for 2 min. The temperature of injector and detector were maintained at 220°C and 280°C, respectively. Helium was used as a carrier gas at a flow rate of 7 mL/min. Under these conditions, the retention time for carbofuran, Carbofuran-3-keto, Carbofuran-3-hydroxyl and Carbofuran phenol-3-keto were 7.31, 6.17, 9.42 and 11.34 min, respectively (Fig. 1).

Volatile fatty acids (VFA), total alkalinity (TA), TSS and VSS

Direct titration method prescribed by DeLailo and Albertson[14] was used to determine volatile fatty acids (VFA) and total alkalinity (TA). Total Suspended Solids (TSS) and Volatile Suspended Solids (VSS) of the samples were determined as per the Standard Methods[15] by gravimetry.

Specific aceticlastic methanogenic activity (SMA)

In the present study, biological activity of the sludge was measured as specific aceticlastic methanogenic activity (SMA). The methanogenic activity test is one of the most important tests for assessing the performance of methanogens in a mixed anaerobic bacterial system. A typical experiment set up for SMA is shown in Figure 2. The sludge sample was first diluted to get a VSS concentration of approximately 5 g/L with a mineral solution consisting of (g L−1)KH2PO4:2.5, K2HPO4:1, NH4Cl:1, MgCl2:0.1. Yeast Extract: 0.2, Na2S·7H2O: 0.1. To each of a series of 500 mL flasks, 350 mL of sludge diluted with mineral solution was added. The samples were subsequently acclimated for 24–48 h at 30°C without the addition of substrate. Thereafter, increasing amounts of sodium acetate as substrate was added to get sludge loading in the range of 0.3 to 1.0 g acetate/g of VSS. The pH of sludge samples was adjusted to 6.7 ± 0.1 with 1 N HCl or 1 N NaOH. The flasks were, then, flushed with nitrogen gas for a minimum of 2 min and incubated at 30°C for 24 h in a constant temperature water bath. The gas produced was bubbled through saturated KOH solution to remove CO2 and the volume

<table>
<thead>
<tr>
<th>S. no</th>
<th>Parameter</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PH</td>
<td>6.5 ± 0.2</td>
</tr>
<tr>
<td>2</td>
<td>Total Solids (TS), g/L</td>
<td>105 ± 5</td>
</tr>
<tr>
<td>3</td>
<td>Volatile Solids (VS), g/L</td>
<td>48 ± 4</td>
</tr>
<tr>
<td>4</td>
<td>Total Suspended Solids (TSS), g/L</td>
<td>45 ± 5</td>
</tr>
<tr>
<td>5</td>
<td>Volatile Suspended Solids (VSS), g/L</td>
<td>22 ± 3</td>
</tr>
<tr>
<td>6</td>
<td>VSS/TSS</td>
<td>0.5 ± 0.05</td>
</tr>
<tr>
<td>7</td>
<td>Volatile Fatty Acid (VFA) g/L as CH3COOH</td>
<td>8.0 ± 0.5</td>
</tr>
<tr>
<td>8</td>
<td>VFA/Alkalinity</td>
<td>1.5 ± 0.1</td>
</tr>
</tbody>
</table>
of methane produced was measured by the liquid displacement method. Gas production was noted up to 24–30 h, after which the VSS concentration of the sludge sample was determined. The maximum specific methane production rate in mL CH₄/g of VSS/d was calculated. Considering the theoretical COD of CH₄ (Equal to 4 g of COD/g of CH₄) the maximum specific methane production rate was expressed in terms of g CH₄–COD/g of VSS/d and was reported as the Specific Methanogenic Activity (SMA) of the sludge.

**Carbofuran degradation experiments**

**Batch studies**

Five hundred millilitre glass bottles were used for the batch studies and the mouth of the bottles were closed with air tight septums. Seven such reactors were operated in triplicate with varying carbofuran concentrations of 0, 0.5, 7.84, 28.06, 62.48, 159.08, 217.14 and 270.73 mg/L with a uniform feeding and operating condition. The feed conditions and the working volume of the reactors are given in Table 2. The initial VSS concentration in all the reactors was maintained at 8.4 g/L and dextrose concentration of 1 g/L was supplied to the biomass as external carbon source. The pH of the system was adjusted to 9.9 ± 0.1 in all the reactors using NaHCO₃ and the reactors were kept in an incubator at 35 ± 2°C and operated for 28 days. At regular time intervals, 20 mL of the samples were withdrawn from the reactors and analyzed for COD removal, biomass concentration and residual carbofuran and its known metabolites concentrations.

**Continuous mode experiments**

The bench scale UASB reactor was fabricated with transparent Perspex sheet. The reactor was divided into two zones based on its functionality, namely, digestion zone and the settler zone. The working volume of the digestion zone

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Feed composition</th>
<th>Working volume (Total volume) in mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-0</td>
<td>Nutrient (S-1) + Dextrose (S-2)</td>
<td>300 (500)</td>
</tr>
<tr>
<td>R-1</td>
<td>Nutrient (S-1) + Dextrose (S-2) + Carbofuran (S-3)</td>
<td>300 (500)</td>
</tr>
<tr>
<td>R-2</td>
<td>Nutrient (S-1) + Dextrose (S-2) + Carbofuran (S-3)</td>
<td>300 (500)</td>
</tr>
<tr>
<td>R-3</td>
<td>Nutrient (S-1) + Dextrose (S-2) + Carbofuran (S-3)</td>
<td>300 (500)</td>
</tr>
<tr>
<td>R-4</td>
<td>Nutrient (S-1) + Dextrose (S-2) + Carbofuran (S-3)</td>
<td>300 (500)</td>
</tr>
<tr>
<td>R-5</td>
<td>Nutrient (S-1) + Dextrose (S-2) + Carbofuran (S-3)</td>
<td>300 (500)</td>
</tr>
<tr>
<td>R-6</td>
<td>Nutrient (S-1) + Dextrose (S-2) + Carbofuran (S-3)</td>
<td>300 (500)</td>
</tr>
<tr>
<td>R-7</td>
<td>Nutrient (S-1) + Dextrose (S-2) + Carbofuran (S-3)</td>
<td>400 (500)</td>
</tr>
</tbody>
</table>
Fig. 3. (a) Schematic diagram of Conventional upflow anaerobic sludge blanket (UASB) Reactor, (b) Schematic diagram of modified UASB reactor.
and the total reactor volume were 9 and 23.6 L, respectively. Four sampling ports were provided in the digestion zone at 150 mm intervals. The schematic of the UASB reactor is given in Figure 3(a). For a uniform distribution of the influent into the reactor, a distribution system made up of polyvinyl chloride (PVC) tube of 15 mm internal diameter and 2–3 mm diameter openings drilled at close intervals at the bottom side of the tube was used. The synthetic wastewater (characteristics are given in Table 3) was supplied to the reactor at a constant upflow velocity by a peristaltic pump (Miclins, India Ltd). The gas–liquid–solid separator (GLSS) system, one of the important components of a UASB reactor, consisted of a deflector beam below a funnel. A hollow perspex disk, with external diameter of 150 mm (same as internal diameter of the main reactor) and internal diameter of 125 mm, tapered outside was fitted inside the main reactor, at a depth of 640 mm from the top of the reactor. The funnel placed above the deflector beam was having hollow cylindrical portion with internal diameter of 125 mm. The GLSS arrangement is shown in Figure 3(a). The lower-most portion of the funnel was at a height of 20 mm above the deflector beam and the upper portion was connected to the gas collection system through a pipe.

### Modified UASB reactor with tube settlers

The schematic diagram of the modified UASB reactors is shown in Figure 3(b), which was developed by modifying the gas–liquid–solid separator (GLSS) of the conventional UASB reactor with the aim of minimizing the escape of suspended biosolids in the reactor effluent. Tube settlers were incorporated in the settling zone (600 mm height) of the UASB reactor to replace the conventional GLSS. An assembly of PVC tubes (39 nos of 25 mm internal diameter tubes) at 55° inclination, supported on polyethylene mesh with proper opening size, acted as the GLSS. The fine bioflocs were lifted up due to the adhering/entrapped gas bubbles and rose along with treated liquid. These particles entered into the tube settlers through the polyethylene mesh openings. These biosolids move against the top inside surface of the tubes, the frictional resistance offered by the tube surface to the gas bubble is expected to affect the release of gas from the biosolids making them heavier for their settlement on the tubes. The settled solids, then, slide down to the sludge zone of the reactor through the same mesh opening. The chance of biofilm growth on the inner side of the tube can not be ruled out.

### Results and discussion

#### Treatability of carbofuran

This paper deals with the feasibility of carbofuran degradation by mixed anaerobic microbial flora by batch and continuous UASB reactors. It is reported in the literature that xenobiotic compounds like DDT,[17] Benzene Hexachloride (BHC),[18] Tetrachloroethylene (TCE)[19] and many other toxic compounds degrade faster in an anaerobic environment than in aerobic environment.

The seed sludge (not exposed to carbofuran earlier) used for primary start-up of the reactor was collected from the pilot scale UASB reactor treating the domestic wastewater of the campus of Central Leather Research Institute (CLRI), Chennai, India. This sludge was acclimatized to synthetic wastewater till the sludge became stabilized in terms of COD removal.

The laboratory-acclimatized sludge from the UASB reactor was used to determine its potential to degrade the carbofuran in batch mode prior to UASB being challenged by carbofuran. Eight batch reactors (R-0 to R-7) including a blank (R-0) were started with a working volume of 300 mL and the initial volatile suspended solids concentration (VSS) of 8.4 g/L. Different concentrations of carbofuran i.e., 0.5, 7.84, 28.06, 62.48, 159.08, 217.14 and 270.73 mg/L were added, respectively to reactors R-1 to R-7 and the corresponding sludge-loading rates (SLR) of carbofuran were computed as $2.12 \times 10^{-6}$, $3.33 \times 10^{-5}$, $1.19 \times 10^{-4}$, $2.65 \times 10^{-4}$, $6.76 \times 10^{-4}$, $9.32 \times 10^{-4}$ and $3.83 \times 10^{-3}$ g of carbofuran/g of VSS/d for R-1 to R-7, respectively. Dextrose was used as an external carbon source and the initial COD in all reactors (R-0 to R-7) was maintained at 1280 ± 10 mg/L. The reactors were operated for 28 days at 35 ± 2°C with continuous mixing. Simultaneously, two control reactors were also started with 7 mg/L (BR-1) and 28 mg/L (BR-2) of carbofuran and a COD of 1030 mg/L (dextrose) without any microbes, to account for the abiotic carbofuran degradation in the reactors. The pH of the two reactors was maintained in the range of 9.8 ± 0.04. On alternate days, 20 mL of the representative sample from each of the reactors was analyzed for COD, biomass, alkalinity, pH and residual carbofuran concentration.

The soluble COD removals by the reactors R-0 to R-7 is shown in Figure 4. At the end of 28 days, the soluble
COD removal efficiency in reactor R-0 was around 95% whereas in reactor R-4 it was 71.5%. A further increase in carbofuran concentration in reactors R-5, R-6 and R-7 decreased the COD removal efficiency to 64%, 58% and 43%, respectively.

After 8 days of reaction time, the carbofuran concentration in reactor R-1 was below the detectable limit whereas in reactors R-2 and R-3 it was around 60% and 28%, respectively. The variation of carbofuran concentration in the reactors is presented in Figure 5. At the end of three days, 36%, 29% and 15% of carbofuran was converted into 3-keto carbofuran in reactors R-1, R-2 and R-3, respectively. Later, the concentration of 3-keto carbofuran in the reactors had decreased gradually. At the end of 8 days of incubation, both carbofuran and 3-keto carbofuran were non-detectable in the reactor R-1 whereas in other reactors
significant amount of carbofuran and its metabolites were present. After 7 days of incubation nearly 7% and 16% of the initial carbofuran concentration was converted into 3-keto carbofuran in reactors BR-1 and BR-2, respectively. Thereafter, the concentrations of carbofuran and 3-keto carbofuran were remained the same in both the reactors. The results of COD removal and carbofuran removal in the reactors indicated that the inhibition SLR of carbofuran on anaerobic system was in the range of $1.19 \times 10^{-4}$ g of carbofuran/g of VSS/d (28.06 mg/L).

At regular intervals, withdrawn sludge samples were sonicated, extracted and analyzed for carbofuran and its metabolites. It was found that the carbofuran and its metabolites were below detectable limits. This reveals that biodegradation is responsible for the carbofuran removal from the system and there was no bioaccumulation taking place in the sludge.

**Treatment of synthetic wastewater in UASB reactor**

The guidelines of Hulshoff Pol [20] and Hu et al. [21] were followed for the primary start-up and granular sludge development. The seed sludge was added to both the reactors to get reactor volatile suspended solids concentration of nearly 6 g/L and the reactors were started initially at a hydraulic retention time of 8 h, feeding synthetic wastewater containing sucrose as carbon source with the other essential nutrients. The pH of the reactor was adjusted to 7–7.3 with the addition of bicarbonates. Once the reactors reached pseudo steady state (PSS) condition with respect to COD removal, the hydraulic retention time (HRT) was reduced to 6 h and the operation was continued up to PSS condition. This phase of the study with sucrose synthetic wastewater lasted for 92 days. The summary of operation of events in different phases is given in Table 4. The influent COD was nearly at 500 ± 10 mg/L with an organic loading rate of 1.56 g of COD/L.d at 8 h HRT and 2.09 g COD/L.d at 6 h HRT. After nearly 60 days, PSS condition at 8 h HRT was reached with a corresponding soluble and total COD removal efficiency of 90% and 86%, respectively. The percentage of total COD removal and VFA alkalinity ratio at 8 h and 6 h HRT were shown in Figures 6(a) and 6(b), respectively. The soluble COD removal efficiency in UASB reactor with tube settler was 92.45% whereas in conventional UASB reactor it was 91.25% at 8 h HRT. When the HRT was reduced to 6 h, the soluble COD removal efficiency reduced to 80% and 77% in UASB with tube settler and conventional UASB reactors, respectively. The reason can be attributed to the fact that in modified UASB reactor settling zone was 50% of the total reactor volume. Because of long settling zone the suspended particles that are floculent in nature were removed in a better way. Also, the observed sludge height in the reactors indicated that the accumulation of biomass in UASB reactor with tube settlers was more compared to the conventional UASB reactor.

**Specific methanogenic activity (SMA)**

Sludge samples were collected from all the ports and were analyzed for the SMA to determine the aceticlastic methanogens present inside the digestion zone of the reactor. SMA tests were carried out with acetate as the carbon source. The sludge samples collected from various ports was first acclimatized with a mineral medium. After 48 h, acetate was added in the form of sodium acetate to the system and methane gas production was noted at various time intervals. The experiment was stopped when the production of methane gas was negligible from the reactors. The results of SMA test for the reactors at 8 h and 6 h HRT was shown in Table 5. Methane gas production in both the reactors was very low at 8 h HRT.

**Evaluation of the performance of UASB reactors treating synthetic carbofuran bearing wastewater**

The main objective of the present study was to evaluate the performance of UASB reactors for the treatment of synthetic carbofuran bearing wastewater. Results of the batch treatability study indicated that, carbofuran concentrations up to 8 mg/L did not have significant impact on COD removal. Hence, the UASB reactors operating at a HRT of 6 h were subjected to a carbofuran concentration of 13 mg/L. The influent COD and organic loading rate was estimated as 520 ± 10 mg/L.d and 2.09 g COD/L.d, respectively. The total period of study was divided into three phases. During phase-I, the UASB reactors were operated at 13 mg/L of carbofuran, and in phase-II carbofuran was withdrawn from the feed. Later, in phase-III the reactor was operated at a lower carbofuran concentration of 7.89 mg/L. The total and soluble COD removal efficiency of the UASB reactors was shown in Figures 7(a) and 7(b), respectively. Before introducing carbofuran in the reactors, the COD removal

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**Table 4. Summary of the operating events**

<table>
<thead>
<tr>
<th>Day</th>
<th>Event/condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-60</td>
<td>UASB reactor was operated at an SLR of 1.56 g COD/L.d, HRT of 8 h</td>
</tr>
<tr>
<td>61-152</td>
<td>Operated with OLR of 2.09 g COD/L.d and HRT of 6 h</td>
</tr>
<tr>
<td>153-170</td>
<td>Phase-I, Carbofuran concentration of 13 mg/L was introduced and operated with OLR of 2.09 g COD/L.d and SLR of 3.64 × 10^{-3} g of carbofuran/ g of VSS/d and HRT of 6 h</td>
</tr>
<tr>
<td>171-186</td>
<td>Phase-II No carbofuran was supplied into the reactor</td>
</tr>
<tr>
<td>187-210</td>
<td>Phase-III Operated with carbofuran concentration of 7 mg/L, SLR of 5.53 × 10^{-3} g of carbofuran/g of VSS/d</td>
</tr>
<tr>
<td>210-215</td>
<td>Phase-IV operated with carbofuran concentration of 28 mg/L</td>
</tr>
</tbody>
</table>

UASB; SLR; COD; HRT; OLR.
### Table 5. Specific Methanogenic Activity in UASB reactor with synthetic wastewater

<table>
<thead>
<tr>
<th>Parameters</th>
<th><strong>Conventional UASB</strong></th>
<th></th>
<th><strong>Modified UASB with tube settlers</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(monitored at 30°C)</td>
<td><strong>8 hrs HRT</strong></td>
<td><strong>6 hrs HRT</strong></td>
<td><strong>8 hrs HRT</strong></td>
<td><strong>6 hrs HRT</strong></td>
</tr>
<tr>
<td>Methane Production (m³/kg COD Destroyed/d)</td>
<td>0.159</td>
<td>0.171</td>
<td>0.157</td>
<td>0.159</td>
</tr>
<tr>
<td>SMA (mL CH₄/g VS/d)</td>
<td>138.37</td>
<td>123.38</td>
<td>131.92</td>
<td>113.41</td>
</tr>
<tr>
<td>SMA (g COD/g VS/d)</td>
<td>0.355</td>
<td>0.317</td>
<td>0.339</td>
<td>0.291</td>
</tr>
<tr>
<td>Standard (m³ CH₄/kg COD Destroyed/d) at STP</td>
<td>0.35</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

UASB; HRT; COD; SMA; STP.

![Graph](image)

**Fig. 6.** (a) Total chemical oxygen demand (COD) removal in upflow anaerobic sludge blanket (UASB) reactors operated with synthetic wastewater, (b) VFA- Alkalinity ratio in the upflow anaerobic sludge blanket (UASB) reactor operated with synthetic wastewater.
Treatment of carbofuran-bearing wastewater

The results of the treatability study showed that, carbofuran concentration of 28.06 mg/L (SLR of $2.126 \times 10^{-4}$ g of carbofuran/g of VSS/d) in batch system did not affect the COD removal efficiency, whereas in continuous system the carbofuran concentration of 13 mg/L (SLR of $5.53 \times 10^{-3}$ g of carbofuran/g of VSS/d) significantly decreased the COD removal efficiency. Though the concentration of carbofuran in the continuous reactor was less compared to batch systems, the corresponding sludge loading rate was more. This may be the reason for the decreased COD removal efficiency in the continuous reactors. Also, it can be extended that, the removal of carbofuran was much faster at alkaline pH and hydrolysis is the main degradation pathway for carbofuran degradation. The pH of the reactor systems was maintained in the range of $7.8 \pm 0.2$ while the batch studies were conducted at a pH 9.5–10. Maintaining a higher pH value may not be economical in practical applications. Hence, the rate of alkaline hydrolysis in the continuous reactors may be slow.

At the end of Phase-I, the total COD removal efficiency in both conventional and modified reactors were 62% and 68%, respectively. The phase-II operation was continued for 16 days with synthetic feed without carbofuran. During this period, an increase in COD removal efficiency of $82 \pm 3\%$ was observed. At this PSS, the reactors were again fed with 7.84 mg/L of carbofuran along with the feed. No reduction in the COD removal efficiency was observed despite the presence of the toxicant. In the final phase of the study, the carbofuran concentration was increased to 28 mg/L (SLR

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**Fig. 7.** (a) Chemical oxygen demand (COD) (total) removal efficiency variation, (b) (COD) (soluble) removal efficiency variation, (c) variation of carbofuran and 3-keto carbofuran in conventional UASB reactor, (d) variation of carbofuran and 3-keto carbofuran in modified UASB reactor.
Fig. 8. (a) Volatile fatty acids (VFA) variation in both upflow anaerobic sludge blanket (UASB) reactors, (b) Alkalinity variation in both upflow anaerobic sludge blanket (UASB) reactors.

The removal of carbofuran by the mixed microbial culture was varied from 12% to 27%. At the end of 1 day, the carbofuran removal by both conventional and modified reactors was 27% and 25%, respectively. Later the removal efficiency was gradually reduced and reached around 12% for both conventional and modified reactors by the end of 14 days. The only significant metabolite detected in the effluents from the reactors was 3-keto carbofuran. The concentration of metabolite was varied in the range of 0.25 to 0.91 mg/L for conventional UASB reactor and 0.23 to 1.53 mg/L for modified UASB reactor. After 18 days, carbofuran feeding was stopped and the carbofuran that remained in the reactors was flushed out with tap water purged with nitrogen. Later the reactors were fed with soluble synthetic wastewater without carbofuran. Once the reactors reached 85% COD removal potential, 7.84 mg/L of carbofuran was introduced along with the synthetic wastewater. The variation of carbofuran concentration for the effluent from conventional and modified UASB reactors was shown in Figures 7(c) and 7(d), respectively. Nearly 40 ± 3% of carbofuran was removed by the conventional UASB reactor and 17 ± 3% of this was converted to 3-keto carbofuran and the remaining might have been mineralized. In the modified-UASB reactor, 22 ± 6% of parent carbofuran was converted into 3-keto carbofuran and remaining 25 ± 3% of carbofuran might have mineralized. In the final phase of the study, the carbofuran concentration was increased to 28 mg/L from 7.84 mg/L. This mode of operation was continued for three days. During this period, 11 ± 3% of parent carbofuran was converted into 3-keto carbofuran. The remaining carbofuran was found in the effluent from both the UASB reactors. Simultaneously, control reactors were also operated at carbofuran concentrations of 7 mg/L (CR-1), 13 mg/L (CR-2) and 28 mg/L (CR-3) at pH 7.2 ± 0.1. After 28 days, nearly 4.5%, 6.2% and 7.4% of the carbofuran concentration was converted into 3-keto carbofuran in control reactors CR-1, CR-2 and CR-3, respectively.

The samples were collected from the digestion zone of the UASB reactors and analyzed simultaneously for VFA and alkalinity and the results are shown in Figures 8(a) and 8(b), respectively. During the degradation of carbofuran, 3-keto carbofuran was the only significant metabolite observed. The concentration of metabolite was varied in the range of 0.25 to 0.91 mg/L in conventional and 0.23 to 1.53 mg/L in modified UASB reactor.

Conclusion

The performance of conventional upflow anaerobic sludge blanket (UASB) reactor and UASB with tube settlers (modified UASB) for the treatment of carbofuran-bearing synthetic wastewater was evaluated. The COD removal efficiency of a modified-UASB reactor was higher compared to a conventional UASB reactor at both 8h and 6h. HRT. In batch reactors, carbofuran concentration was reduced to undetectable levels at the end of 8 and 13 days corresponding to a carbofuran concentration of 0.5 mg/L (SLR of 2.12 × 10⁻⁶ g of carbofuran/g of VSS/d) and 7.84 mg/L (SLR of 3.33 × 10⁻⁵ g of carbofuran/g of VSS/d), respectively. The carbofuran concentration of
Treatment of carbofuran-bearing wastewater

7.84 mg/L (SLR of $3.64 \times 10^{-3}$ g of carbofuran/g of VSS/d) in the UASB reactor did not affect the COD removal efficiency but it was reduced considerably at 13 mg/L and 28 mg/L. The carbofuran removal efficiency in conventional UASB reactor at carbofuran concentrations of 7 mg/L, 13 mg/L and 28 mg/L were 40 ± 3%, 27 ± 3%, and 11 ± 3%, respectively, whereas in the modified UASB reactor, carbofuran removal efficiency was almost uniform at 7 mg/L and 13 mg/L but it was reduced nearly by 56% at 28 mg/L. Throughout the study, 3-keto carbofuran was the only significant metabolite observed in all the reactors.

References