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Biodegradation of 1,1,2,2-tetrachloroethane in Upflow Anaerobic Sludge Blanket (UASB) reactor

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ABSTRACT

This study examines the performance of bench-scale Upflow Anaerobic Sludge Blanket (UASB) reactor in treating simulated wastewaters containing 1,1,2,2-tetrachloroethane (TeCA). Reactors R1 (control) and R2 (containing TeCA) were operated at Hydraulic Retention Times (HRTs) of 36, 30, 24, 18 and 12 h. The removal of TeCA decreased from 99.85% to 98.40% as the HRT was lowered down from 36 to 12 h. The maximum TeCA dechlorination rate and the half velocity coefficient were 0.2 d^{-1} and 18.58 mg TeCA/l, respectively. The Organic Loading Rate (OLR) was varied from 1.5 to 3.1 kg/m^3/d to yield various substrate:co-substrate ratios and the overall removal of TeCA throughout this study was more than 99%. The average effluent TeCA concentration at optimum HRT (24 h) and substrate:co-substrate ratio (100:1) was less than 0.1 mg/l. The granules within the reactor were 0.1–3.2 mm in size with a heterogeneous bacterial population.

1. Introduction

With the widespread use of halogenated ethanes as solvents, feedstocks for industrial-scale chemical synthesis, pesticides, pharmaceuticals, fuel additives, refrigerants and propellants, it has been accepted that these compounds constitute a widely recognized class of environmental contaminants (O'Loughlin and Burris, 2004). Amongst the chlorinated ethanes, 1,1,2,2-tetrachloroethane (TeCA) is mainly released as an industrial solvent, chemical intermediate or extractant waste. Due to its uncontrolled synthesis by industrial activity, careless handling during production, transportation, application and discharge, this chlorinated xenobiotic compound remains to be the principal contaminant in industrial wastewaters making its way to groundwater as well as surface water receptors. This environmentally persistent pollutant has been found to be toxic to living organisms. In case of humans, TeCA was found to be responsible for accumulation of fats in the liver resulting in a hepatocyte imbalance between the rate of synthesis and output of triglycerides into the plasma (Barisione et al., 1993). The USEPA has laid down stringent drinking water equivalent level for TeCA as 0.002 mg/l Maximum Contaminant Level (MCL) considering the possible carcinogenic effects (ATSDR, 2008). Consequently, the need for removal of this compound from the wastewater before its discharge into the environment has been strongly felt.

The tetrachloroethanes are proven to be degraded primarily through reductive reactions producing less toxic and comparatively easily degradable metabolites, although these were considered to be non-biodegradable earlier. A few laboratory and field studies have examined the natural attenuation of TeCA in groundwater and soils of industrially polluted sites (Aulenta et al., 2006; Lee et al., 1998). Other reported investigations on the degradation of TeCA focused on laboratory experiments with sludge, sediment and cultures (Chen et al., 1996; Lorah and Voytek, 2004). Such studies have elucidated the biotransformation mechanisms of TeCA in the environment and provided little information on the scope for degradation of this compound within the reactor system. Also, very few studies have been directed towards evaluating the efficiency of anaerobic reactor technology in detoxification of TeCA contaminated industrial wastewaters. An anaerobic fixed-film stationary-bed bioreactor with an adsorbent carrier consisting of activated carbon in polyeurethane foam and microbial consortium developed from a methanogenic community was successful in high-rate degradation of tetrachloroethane, while treating a mixture of 30 chlorinated aliphatic compounds (Boucquey et al., 1995). Navarrete et al. (1999) indicated that the UASB reactor could treat industrial wastewaters containing TeCA up to a high concentration of 130 mg/l or with incidental punctual discharges up to 400 mg/l.

Due to highly settling character of the active granular sludge, UASB reactor allows the loading rates to go far beyond the common loading rates applied so far in other conventional processes resulting to reduced reactor size and required area. Invariably, this would make the investment cost lower accompanied by reduced operating cost due to the absence of aeration. The application of this anaerobic treatment system has proven to be effective for a wide range of industrial effluents containing the priority pollutants, i.e. carbon tetrachloride, chlorinated phenols and cresols,

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nitrophenols, trichloroethylene and tetrachloroethylene (Sponza, 2005; Majumder and Gupta, 2008; Karim and Gupta, 2001; Prakash and Gupta, 2000). Although the literature available on UASB reactor is extensive, very few efforts have been made to utilize this reactor for the biodegradation of wastewaters containing TeCA. Also, no study has been reported by the previous researchers to examine the influence of varied HRT as well as OLR in the biotreatment of TeCA using the UASB reactor. Hence, the present study has aimed to look into the effects of variation of these operational parameters in the biodegradation of TeCA within the UASB reactor.

2. Methods

2.1. Experimental set-up

Two bench-scale UASB reactors (R1 and R2) were fabricated from transparent acrylic plastic sheet having working volume of 12.5 l (inner cross-section – 0.1 m × 0.1 m; length – 1.2 m and wall thickness – 6.0 mm) and were maintained at room temperature (27 ± 4 °C). Each of the two reactors was provided with a hopper bottom of 0.15 m length and square pyramidal gas–liquid–solid separator (GLSS) having the bottom dimension of 80 mm × 80 mm. One of the UASB reactors was used as control (R1) with no exposure to any toxic pollutant; whereas the other reactor (R2) was used for treating wastewater containing TeCA. Synthetic wastewater was pumped into the reactors at the required flow rates through an inlet pipe of 1.25 cm diameter with the help of a peristaltic pump. The outlet pipe was provided at a height of 1.2 m from the bottom and connected to the effluent tank. The reactor was provided with three equidistant sampling ports.

2.2. Start-up of the reactors

Each bench-scale UASB reactor was inoculated with 5 l anaerobic granular seed sludge collected from another bench-scale UASB reactor used earlier to treat chlorinated aromatic compounds. The volatile suspended solid (VSS) and suspended solid (SS) content in the sludge blanket of the reactors were 22 kg VSS/m^3 and 34 kg SS/m^3, respectively. The composition of synthetic wastewater used in the study was: 4.4 g/l $CH_3COONa{\cdot}3H_2O$, 127.4 mg/l NH_4Cl, 37.4 mg/l K_2HPO_4, 150 mg/l $CaCl_2{\cdot}2H_2O$, 40 mg/l $MgSO_4{\cdot}7H_2O$, 250 mg/l $NaHCO_3$ and 1 ml/l trace metal solution. Sodium acetate was used as the single carbon source. The composition of trace metal solution chosen in this study was similar to that used by Prakash and Gupta (2000). The COD:N:P:S ratio of 300:5:1:1 was maintained in the feed. Both the reactors were operated in a continuous mode at HRT of 24 h, OLR of 2 kg COD/m^3/d and Sludge Loading Rate (SLR) of 0.1 kg COD/kg VSS/d.

2.3. Acclimation of reactor R2 with TeCA

Acclimation of UASB reactor R2 was started with the addition of TeCA (98%, S.D. Fine Chem. Ltd., India) to the feed at an initial concentration of 5 mg/l. Subsequently, the concentration of TeCA was increased in stepped manner to 10 mg/l, 20 mg/l and 30 mg/l. The composition of the simulated wastewater and other operational parameters like HRT, OLR and SLR were maintained the same as that during the start-up period.

2.4. Hydraulic retention time study

The reactors R1 and R2 were operated at five different HRTs, i.e. 36, 30, 24, 18 and 12 h to obtain the range of medium- to high-organic loading rates (1.3–4 kg COD/m^3/d) within the reactors. For each HRT, the reactors were operated for about 20–25 d under pseudo-steady state condition. The concentrations of TeCA and sodium acetate in the influent of reactor R2 were 20 mg/l and 2 g/l, respectively. The composition of other chemicals used in the feed was maintained the same as that followed during the start-up phase.

2.5. Substrate:co-substrate ratio study

This study was carried out to evaluate the effect of substrate (sodium acetate) concentration on the efficiency of UASB reactor R2 for the removal of TeCA. Four different substrate concentrations, e.g. 1.5, 2, 2.5 and 3 g/l corresponding to substrate:co-substrate ratios of 75:1, 100:1, 125:1 and 150:1 were maintained during this study. The concentration of TeCA in the reactor was 20 mg/l.

2.6. Analytical methods

Measurements were taken daily for the influent and effluent COD, alkalinity, pH and rate of biogas production. The production of total biogas was measured using the water displacement method. The sludge samples were analyzed biweekly to ascertain SS and VSS. The analytical procedures for all the tests were followed as outlined in the Standard Methods (APHA, 1998).

TeCA, 1,1,2 trichloroethane (1,1,2 TCA) and 1,2 dichloroethane (1,2 DCA) were determined by gas chromatograph (Agilent Model: 6890 No. G1530, USA). The liquid sample was filtered through a 0.45 μm membrane filter and extracted with cyclohexane prior to injection into the column and directly analyzed in gas chromatograph equipped with capillary column (Thermo TR-VI 30 m × 0.32 mm × 1.8 mm). Nitrogen was used as a carrier gas and Electron Capture Detector (ECD) was provided. The injector temperature was 250 °C, while the detector temperature was 280 °C. The initial temperature of the column was 70 °C followed by the first ramp of 10 °C/min up to the temperature of 150 °C for duration of 1 min and thereafter the final ramp of 25 °C/min continued up to the temperature of 280 °C.

Volatile Fatty Acids (VFA) in the effluent were measured according to the method described by Karim and Gupta (2001). Influent and effluent from the UASB reactors were analyzed for chloride by Metrohm Ion Chromatogram (Model-792 Basic IC, Switzerland), equipped with the A SUPP 5-250 column. Oxidation reduction potential (ORP) was measured by ORP meter (Model-108, Orion, USA). The sludge samples for examination in Scanning Electron Microscope (SEM) were prepared by the method mentioned by Prakash and Gupta (2000). The samples so prepared were scanned using SEM (JEOL, 840 A, Japan). The sludge samples were also analyzed in PW 2404, Phillips, X-ray Fluorescence Spectrometer (XRF) for obtaining the mineral contents within the biomass.

2.7. Statistical analysis

One-way analysis of variance (ANOVA) for TeCA and COD removal was carried out using the software Microsoft Excel (Microsoft Corporation, Redmond, USA) for the five sets of HRT data and four sets of data obtained from the substrate:co-substrate ratio study.

3. Results and discussions

3.1. Start-up

The bench-scale UASB reactors namely R1 and R2 contained 5 l anaerobic granular sludge acclimated previously to chlorinated priority pollutants other than chloroethanes. The COD removal efficiency was observed to be 96.16 ± 0.82% at the end of start-up per-