Management of Atrazine Bearing Wastewater Using an Upflow Anaerobic Sludge Blanket Reactor–Adsorption System

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Abstract: In the present investigation, an attempt was made to develop a treatment system for the management of atrazine bearing wastewater. The system consists of an upflow anaerobic sludge blanket (UASB) reactor followed by an adsorption column using waste activated carbon as the adsorbent. The UASB reactor could remove more than 80% of organic matter and 40–50% of atrazine, irrespective of the concentration of organic matter and atrazine tried. Though low concentration of atrazine did not affect the anaerobic system, higher atrazine concentration in the range of 10–15 mg/L had a little effect on the treatment system. The adsorption column could remove atrazine from the UASB effluent effectively. Methanol could desorb the atrazine from the adsorbent. The regenerated adsorbent retained 80% of its original capacity. The regenerant can be utilized as a pesticide.

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CE Database subject headings: Wastewater treatment; Anaerobic processes; Biodegradation; Adsorption.

Introduction

Modern agricultural practices often include the extensive use of a wide range of herbicides and insecticides. Environmental contamination due to the excessive use of pesticides has become a great concern to the public and to environmental regulatory authorities. Among the pesticides produced, atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine), a chlorinated herbicide (a class of pesticide) took the front seat by production as well as usage (Hayes et al. 2002). The sources of atrazine pollution are nonpoint sources such as agricultural runoff and aerial transport and pesticide industrial effluent. Numerous cases were recorded on contamination of surface waters, ground waters, and soils by atrazine (Kearney and Robert 1998). Due to its various toxicity properties, its permissible limit in drinking water has been restricted to 2 μg/L by the World Health Organization (1990), 0.1 μg/L in European countries (Council of European communities 1980), and maximum contaminant level of 3 μg/L by USEPA (U.S. National Library of Medicine 1995). But due to its high rate of use and high persistence in neutral environment (pH near 7.0), as high as 22 mg/L of atrazine was found in ground water (Long 1987; Habecker 1989). By many means, domestic wastewater can be contaminated by atrazine (Ghosh 2002). Gerecke et al. (2002) observed atrazine concentration in the effluent from a wastewater treatment plant more than the permissible limit fixed by the European countries. Removal of atrazine from ground water or surface water by adsorption by activated carbon is considered as the best available technology (Adams and Watson 1996). However, the character of atrazine contaminated domestic wastewater and wastewater from atrazine manufacturing plant, contain not only atrazine but also high dissolved organic matter. Being a nonselective process, adsorption by activated carbon is not suitable, as its adsorptive capacity reduces significantly in presence of dissolved organic matter (DOM) (Baldauf et al. 1986). For such types of wastewater, the biological method seems to be one of the best alternatives.

There are several reports on atrazine biodegradation by pure culture bacteria in aerobic and oxygen deficient conditions (Cook and Hütter 1981; Jessee et al. 1983; Behki and Khan 1986; Cook 1987; Behki et al. 1993; Mandelbaum et al. 1993; Radosevich et al. 1995; Crowford et al. 1998, Shapir et al. 1998, Rousseaux et al. 2001; Saybold et al. 2001). Handling of pure culture bacteria in actual field and preventing the growth of other mixed bacterial culture is not at all practicable. Mandelbaum et al. (1993) observed mineralization of atrazine, only after mixing a number of pure culture bacteria. Many chlorinated aliphatic and aromatic compounds, which were earlier considered as recalcitrant in the aerobic process, were successfully degraded under anaerobic conditions. Kearney et al. (1965) indicated that atrazine disappears more rapidly under anaerobic compared to aerobic conditions. The literature shows that the aromatic structure of lignin, benzoate, and other aromatic acids were metabolized to gaseous products in mixed cultures, under methanogenic conditions (Young and Häggblom 1990). Nevertheless, the degradation rate of such compounds by anaerobic mixed microbial culture is slow, as the energy required for bacterial growth is not sufficiently provided by such toxic compounds. In such cases, the addition of easily biodegradable organic compounds serves as a primary source of carbon and energy, stimulates the growth of anaerobic bacteria, and thereby enhances the degradation rate by utilizing

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the recalcitrant compound as a secondary substrate by a cometabolic process. Hendriksen et al. (1992) have investigated the influence of a supplemental carbon source on the anaerobic dechlorination of pentachlorophenol (PCP). They observed 99% PCP (with 4.5 mg/L influent concentration) dechlorinated by the anaerobic microorganisms in an upflow anaerobic sludge blanket (UASB) reactor at a hydraulic retention time of 2–3 days. Enhanced degradation rate of atrazine was observed when citrate and sucrose were provided as supplemental carbon source (Struthers et al. 1998). Afterwards, Chung et al. (1996), used an anaerobic sediment bioreactor containing mixed culture bacteria in which mineralization of atrazine was claimed. However, information on the treatment of atrazine bearing wastewater in continuous mode using anaerobic mixed microbial consortia is scanty. Presently, the UASB reactor is one of the most widely used high rate anaerobic reactors. Although, initially it was used mainly for treating high strength easily biodegradable industrial wastes (Arceivala 1998), recently, considerable attention has been given to the assessment of its potentiality in degrading many chlorinated toxic compounds like phenol (Fang et al. 1996), tetrachloroethylene (TCE) (Prakash and Gupta 2000; Sponza 2002), pentachlorophenol, dichlorophenol, and monochlorophenol (Hendriksen et al. 1992; Wu et al. 1993; Christiansen et al. 1995). Complete dechlorination and consequent breakage of the benzene ring was observed in most of the cases. Granular sludge of an UASB reactor provides a complex microbial environment with various metabolic niches and metabolic activities having the potentiality in degrading such toxic and xenobiotic compounds. The present paper deals with a treatment system consisting of an UASB reactor followed by adsorption column for the complete management of atrazine bearing wastewater.

Materials and Methods

Chemicals

All the chemicals used in the present investigation were of analytical reagent grade. Rallis India Limited (Mumbai, India) supplied atrazine of technical grade. The synthetic waste water contained, K_2HPO_4=150; KH_2PO_4=50; $MgCl_2.6H_2O$ =300; $CaCl_2.2H_2O$=50; NH_4Cl=200; $FeCl_2.4H_2O$=5; $ZnCl_2$ =0.5; $NiCl_2.6H_2O$=0.5; $CoCl_2.6H_2O$=0.5; $MnCl_2.4H_2O$=0.5; and yeast extract=50 mg/L of distilled water. Dextrose of 150, 300, 500, and 1,000 mg/L and atrazine of 1, 5, 10, and 15 mg/L were added to water along with the above micronutrients to prepare specific characteristic synthetic wastewater according to the requirement.

Seed Sludge

Sludge collected from an anaerobic digester of activated sludge process from Bara Sewage Treatment Plant, Jamshedpur, India, was used as the seed sludge for the present investigation. This sludge was not exposed to an atrazine environment earlier. The sludge was fed with synthetic wastewater, for 1 month, to acclimate the system with the changed environment. Once the sludge stabilized, it was used for further experiments.

Adsorbent

Waste activated carbon (WAC) from a water purifier (marketed by Eureka Forbs Limited, India, with the brand name of Aqua Guard in India) was collected. About 200–300 g of activated carbon with 0.2% impregnated silver is commonly used in a small water purifier. These adsorbents need replacement after about 6 months of operation, depending on the rate of use. The activated carbon thus wasted, was used as adsorbent for the present study after giving some pretreatment. Raw waste activated carbon, which has a uniform grain size of 2 mm, was pulverized to get the grains sizes between 0.3 and 0.5 mm, washed in distilled water and being used.

Analyses

Standard methods (APHA, AWWA, WEF 1989) were used for the analyses of all the parameters unless otherwise specified. Volatile fatty acid (VFA) and alkalinity were determined as suggested by DIlallo and Albertson (1961). Activity of sludge was determined as per the procedure suggested by Valke and Vestrate (1983) and expressed as specific acetoclastic methanogenic activity (SMA). The SMA test was carried out after mixing the collected sludge from different heights of the reactor to get a better representative value.

Biogas produced in an anaerobic process was collected by the liquid displacement method and methane content was determined by passing the total gas collected through 32%(w/v) KOH solution. Volume change due to temperature variations is incorporated into the measured volumes. Periodically the biogas was analyzed in ORSAT apparatus (Borosil, India).

Atrazine was measured in both ultraviolet (UV)-visible spectrophotometer (Model: UV-160A, Shimadzu, Japan) and gas chromatograph (GC) (Model: GC 14A, Schimadzu, Japan). In both the methods, atrazine was extracted from wastewater by the liquid–liquid extraction method. Dichloromethane or ethylacetate were used as extractant in the case of UV-vis spectrophotometer or GC, respectively. In the UV-visible spectrophotometer, maximum absorbance was observed at 228.8 nm. An electron capture detector (Radioisotope Nuclide ^{63}Ni) and 1.5% OV-17 column of 3 m length and $\frac{1}{8}$ in. internal diameter using pure nitrogen as carrier gas was used for atrazine determination in GC. The operating conditions were as follows; initial and final column temperature 210°C, injector temperature 225°C, detector temperature 265°C, and carrier gas flow of 70 mL/min.

To check the buildup of atrazine in anaerobic biomass, 20–50 mL of biomass samples were centrifuged twice, resuspended in distilled water, and atrazine was extracted by using methanol by shaking in a rotary shaker (Protzman et al. 1999). Methanol was evaporated using dry nitrogen gas and residue was redissolved either in dichloromethane or in ethyl acetate for the determination of atrazine in UV-vis spectrometer or GC, respectively.

The scanning electron microscopic (SEM) picture of an averaged sized granule formed in the UASB reactor was taken after an operating period of 200 days and an attempt was made to identify the types of microorganisms grown onto the outer as well as the inner surface of the granule. For the SEM picture, sludge samples were prepared as per the procedure suggested by Glauret (1974). The samples were prepared by fixing in glutaraldehyde, washing with phosphate buffer, and dehydrating with acetone. The SEM pictures of adsorbent before and after column adsorption study were taken and (electron dispersive atomic x-ray) (EDAX) analysis was made to confirm the microbial growth on the surface of the adsorbent. In both the cases, viz. before and after adsorption column study, adsorbent samples were air dried and then kept in vacuum desiccators before analysis. The dry samples were

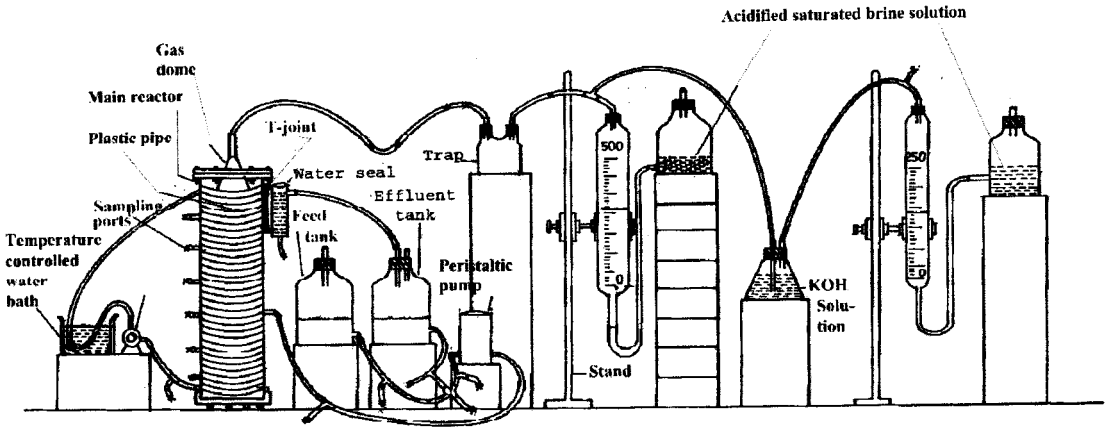

Fig. 1. Schematic diagram of laboratory scale setup of upflow anaerobic sludge blanket reactor

mounted on gold sample holder and coated with carbon in a sputter coating unit and scanned using a SEM (Model: JSM-5800, JOEL Company, Japan) at an accelerating voltage of 20 kV. The elemental composition of the adsorbent was analyzed using the Kevex apparatus attached to SEM (Model: JSM-5800, JOEL, Japan).

Reactors Used and their Operational Schedule

Two identical laboratory scale UASB reactors (UASB-1 and UASB-2) were fabricated with transparent perspex cylinders with internal cross section area of 100 cm^2 (internal diameter—11.3 cm) and a height of 78 cm. Working volume of both the reactors was 7 L. The reactors were operated simultaneously at different feeding conditions. Temperature of the reactors was maintained at $35\pm2°C$ by circulating warm water through a plastic pipe wrapped on the reactor. A schematic diagram of laboratory scale experimental setup of UASB reactor is shown in Fig. 1.

UASB-1 and UASB-2 were operated under identical operating conditions with the addition of 9 g/L of seed sludge collected from an anaerobic sludge digester as discussed earlier. In each reactor, 1 g/L of anaerobic sludge from a reactor, which was operated in semicontinuous mode for the treatment of atrazine bearing wastewater (Ghosh 2002), was added prior to startup. The reactors were operated initially with a hydraulic retention time (HRT) of 24 h and then gradually reduced to 8 h. During the startup period, the reactors were fed with synthetic wastewater containing 150 mg/L of dextrose without any atrazine. After reaching steady state condition in terms of chemical oxygen demand (COD) removal and gas production, atrazine was added in increasing concentration viz., 1, 5, 10, and 15 mg/L. Maximum solubility of atrazine in water is 33 mg/L at 20°C (Tomlin 1994). However, as the wastewater contains a large quantity of dissolved organic and inorganic material, the solubility of atrazine can be much less than the theoretical value in standard conditions. Hence, the maximum atrazine concentration used in the present study was 15 mg/L, which was the maximum soluble atrazine concentration possible in the present experimental conditions adopted.

Similar operation was done with higher strength wastewater containing dextrose of 300, 500, and 1,000 mg/L. Whenever the organic loading rate (OLR) was changed, the reactor was fed on dextrose alone (without atrazine) to acclimate the system to the changed condition. After that, raw domestic wastewater (RDW)<> spiked with 5 and 15 mg/L of atrazine in UASB-1 and UASB-2, respectively, was fed into the respective reactor and the performance was evaluated. The main characteristics of RDW used are as follows: total COD (mg/L) = 171±28, soluble COD (mg/L) = 142±12; alkalinity (mg $CaCO_3$/l) = 353±15; suspended solid (mg/L) = 20±5; volatile suspended solid (VSS) (mg/L) = 15±3, and total kjeldahl nitrogen (mg/L) = 21±4. The schedule of operation of the reactors is given in Table 1.

Fixed Bed Upflow Adsorption Column Study

Up-flow fixed bed adsorption column using WAC as adsorbent was considered as post-treatment of UASB effluent. A glass column of 50 cm length and 1.5 cm internal diameter was used as packed bed column in the present study. The bed depth was 20 cm. Wastewater was passed though the adsorption bed from the bottom to the top using a peristaltic pump (Model: pp 20, Miclins, India) with an overflow rate of 4.95 m^3/m^2 h equivalent to an up flow velocity of 8.25 cm/min. The total volume of wastewater passed (m^3/day) through the adsorption column was same as that of UASB reactor. The empty bed contact time calculated was 2.42 min. Samples were collected and analyzed at regular intervals until the column was exhausted. When effluent atrazine concentration was more than 90% to that of influent concentration, the column was regenerated.

Desorption and Regeneration Studies

Desorption study was carried out using the exhausted adsorbent after the column study. Desorption was done in two steps. In the first step, 100 mL of distilled water was passed through the exhausted column at the same flow rate as that of the influent. In the next step 300 mL of 5%(v/v) methanol in distilled water was passed through the column at the same rate as that of earlier and the effluent concentration of atrazine was measured. The adsorbent was washed with 1 N HNO_3 followed by distilled water until the pH and total dissolved solids came down to the prefixed value. After the regeneration, the column was reused for the treatment of UASB effluent containing atrazine.

Table 1. Operational Schedule and Type of Wastewater Treated in Upflow Anaerobic Sludge Blanket (UASB) Reactors

	UASB-1		UASB-2		
	Wastewater containing (mg/L)		aWastewater containing (mg/L)		
Day	Dextrose	Atrazine	Dextrose	Atrazine	Remarks
1–25	150	0.0	150	0.1	Primary startup[a]
26–55	150	1.0	150	5.0	HRT=8 h
56–80	150	10.0	150	10.0	HRT=8 h
81–90	300	0.0	300	0.0	HRT=8 h
91–105	300	1.0	300	5.0	HRT=8 h
106–120	300	10.0	300	15.0	HRT=8 h
121–130	500	0.0	500	0.0	HRT=8 h
131–155	500	1.0	500	5.0	HRT=8 h
156–160	500	10.0	500	15.0	HRT=8 h
161–170	1,000	0.0	1,000	0.0	HRT=8 h
171–185	1,000	1.0	1,000	5.0	HRT=8 h
186–200	1,000	10.0	1,000	15.0	HRT=8 h
201–214	RDW[b]	0.0	RDW[b]	0.0	HRT=8 h
215–230	RDW[b]	5.0	RDW[b]	15.0	HRT=8 h

Note: Two UASB reactors were operated in parallel to reduce the study duration.

[a]HRT=hydraulic retention time.

[b]RDW=raw domestic wastewater.

Results and Discussion

Performance of Upflow Anaerobic Sludge Blanket Reactors Treating Atrazine-Bearing Wastewater

Chemical Oxygen Demand Removal

During the startup period, the HRT was reduced from 24 to 12 h and then to 8 h.The reactors could achieve more than 85% in terms of COD_{TT} and COD_{ST} removal within 1 week time and remained steady for the next 3 days at a HRT of 8 h. Effluent COD during the startup period is shown in Fig. 2. The biogas production was on the order of 300 mL/g of COD reduction, which contain methane of about 81%. pH and VFA of the reactors remained well in the specified limit. After primary startup, both the UASB reactors were operated in the sequence given in Table 1.

The reactors were operated at least 5 more days (=15 HRT) after they reached pseudosteady state for each feeding and operating conditions. At pseudosteady state condition COD in terms of COD_{TT}, COD_{ST}, and COD_{SS} was measured regularly and the average of the measured data are reported in this paper (Table 2).

In the case of synthetic wastewater COD_{SS} is equal to COD_{ST} as suspended solid in the influent (synthetic wastewater) was nil. At an influent dextrose concentration of 150 mg/L, high COD_{ST} reduction on the order 86.3, 85.7, 84.5, and 83.2% from the reactors at an influent atrazine of 1, 5, 10, and 15 mg/L, respectively (Table 2) was observed. However, COD_{ST} reduction was reduced by 2–3% when atrazine concentration was increased to 10 and 15 mg/L. The COD_{TT} removal efficiency followed almost the same trend as that of COD_{ST} reduction. Effluent COD_{ST}/COD_{TT} was more than 0.95. An almost similar performance was observed at an influent dextrose concentration of 300, 500, and 1,000 mg/L and the results are given in the Table 2. Measurement of COD_{TT} is important in view of effluent discharge standards, whereas COD_{ST} represents the treatment potential of the reactor. In actual domestic or industrial wastewater, suspended organic material imparts a significant amount of total influent COD. The removal of the suspended organic material may be due to the entrapment in the sludge bed by physical means but not by a biological process. In that case COD_{SS} gives the reduction of organic matter by biological activity.

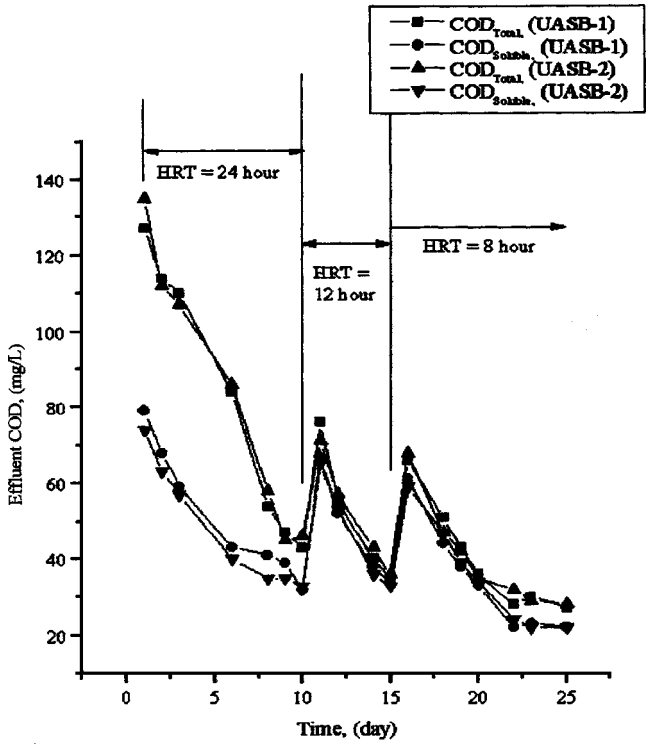

Fig. 2. Effluent chemical oxygen demand profile in upflow anaerobic sludge blanket reactors during startup period

Table 2. Performance of Upflow Anaerobic Sludge Blanket Reactors (UASB) (in Pseudosteady State Condition) Treating Various Strength Wastewaters

Dextrose	150 mg/L						300 mg/L					
Atrazine	0 mg/L[a]		1 mg/L	5 mg/L	10 mg/L	15 mg/L	0 mg/L		1 mg/L	5 mg/L	10 mg/L	15 mg/L
Reactor	UASB-1	UASB-2	UASB-1	UASB-2	UASB-1	UASB-2	UASB-1	UASB-2	UASB-1	UASB-2	UASB-1	UASB-2
COD_{TT} (%)	84.5	83.9	84.5	83.9	83.2	82	86.6	86.0	86.0	85.4	83.4	82.4
COD_{ST} (%)	86.4	86.4	86.3	85.7	84.5	83.2	88.8	88.4	88.4	87.2	85.7	85.2
Total gas[b]	304	305	302	292	284	267	348	345	348	341	317	300
Methane[b]	246	246	245	240	237	221	267	259	267	256	235	224
Methane/Total	0.811	0.812	0.810	0.821	0.834	0.830	0.768	0.752	0.761	0.753	0.743	0.745
Atrazine (%)	—	—	40.3	45.2	45.0	42.1	—	—	41.0	48.24	47.1	44.3
SMA[c]	0.3849	0.3748	0.3799	0.3621	0.3394	0.3267	0.3925	0.3824	—	—	0.3494	0.3394

Dextrose	500 mg/L						1000 mg/L					
Atrazine	0 mg/L		1 mg/L	5 mg/L	10 mg/L	15 mg/L	0 mg/L		1 mg/L	5 mg/L	10 mg/L	15 mg/L
Reactor	UASB-1	UASB-2	UASB-1	UASB-2	UASB-1	UASB-2	UASB-1	UASB-2	UASB-1	UASB-2	UASB-1	UASB-2
COD_{TT} (%)	86.1	86.2	86.2	85.1	82.7	80.5	87.8	87.3	87.8	86.1	84.6	83.8
COD_{ST} (%)	88.1	87.7	87.7	86.6	84.0	83.3	88.5	88.1	88.1	87	85.4	84.3
Total gas[b]	361	354	360	344	327	320	388	386	380	374	365	362
Methane[b]	273	265	272	258	236	228	273	276	268	269	266	255
Methane/Total	0.755	0.749	0.755	0.748	0.721	0.710	0.710	0.704	0.710	0.709	0.699	0.694
Atrazine (%)	—	—	40.8	45.1	45.3	45.4	—	—	38.2	44.8	41.2	43.7
SMA[c]	0.4001	0.3925	—	—	0.3520	0.3444	0.3976	0.3900	—	—	0.3545	0.3444

[a]Start-up period.

[b]ml/g COD_{SS} reduction at 35°C and 1 atm. pressure.

[c]Specific acetoclastic Methanogenic Activity (gCH_4–COD/g VSS day).

After evaluating the performance of the reactors in treating synthetic wastewaters, RDW without atrazine was fed to the reactor (Table 1). Once the system reached steady state in terms of COD reduction, the performance of the reactor was evaluated. In pseudosteady state condition, average COD removal expressed as COD_{TT}, COD_{ST}, and COD_{SS} were 78.5, 81, and 76.8%, respectively, in UASB-1, whereas from UASB-2 those were 77, 79.5, and 75.3%, respectively. In continuation, the reactors were fed with RDW spiked with atrazine. Under steady state conditions, COD removal in UASB-1 fed with RDW spiked with 5 mg/L of atrazine was 77.8, 79.5, and 75.4% as COD_{TT}, COD_{ST}, and COD_{SS}, whereas in UASB-2 fed with RDW spiked with 15 mg/L of atrazine, COD removal efficiency in terms of COD_{TT}, COD_{ST}, and COD_{SS} was 74.8, 76.6, and 75%, respectively. The results show that there was not much adverse effect of atrazine on the anaerobic system even at an atrazine concentration of 15 mg/L though the atrazine degradation was not very promising.

Gas Production

In pseudosteady state condition, total and methane gas production was measured and the average value of 5 days gas production equivalent at 35°C and 1 atm pressure are represented in this paper. Further, methane gas production is expressed in terms of CH_4–COD as and when required for better explanation. Total and methane gas production, thus measured in the reactors treating various strength wastewaters containing 150, 300, 500, and 1,000 mg/L of dextrose are given in Table 2. Total and methane gas production in UASB-1, while treating RDW with (5 mg/L) and without atrazine were 281, 224 and 290, 231 mL/g of COD_{SS} reduction, respectively. Although in the absence of atrazine, the performance of UASB-2 in gas production was the same as that of UASB-1, but in the presence of atrazine (15 mg/L) total and methane gas production was reduced to 264 and 221 mL/g of COD_{SS} reduction, respectively.

Total and methane gas production in the reactor treating synthetic wastewater was increased with increase in wastewater strength. Gas production/g of COD_{SS} reduction was the least when the reactor was fed with 150 mg/L of dextrose. This may be due to the solubility of carbon dioxide and methane gas in the liquid phase. As the volume of liquid remained the same all throughout, the amount of biogas being dissolved also remained the same, as the pressure inside the reactor was the same throughout the study. Reduction in the amount of gas in the gas collector was more significant in the case of low strength wastewater compared to high strength wastewaters, as the total amount of gas that could produce itself was less. The percentage of methane in the biogas was the maximum at a dextrose concentration of 150 mg/L and decreased with higher strength wastewaters. In the case of low strength wastewater, due to low OLR gas production rate was less. As CO_2 is having higher solubility (632 mL/L at 35°C and 1 atm pressure) than CH_4 (26.8 mL/L at 35°C and 1 atm pressure), more CO_2 gets dissolved in distilled water compared to CH_4. This might have increased the percentage of CH_4 content though the gas production was less. For a particular strength wastewater, average methane gas production per gram of average COD_{SS} reduction was the same up to an initial atrazine concentration of 5 mg/L, whereas slight reduction in gas production was observed at an atrazine concentration of 10 and 15 mg/L. This might be due to the inhibition effect of atrazine on anaerobic systems, which was evident in the case of COD reduction also. The COD value given in the text include both by dextrose and atrazine.

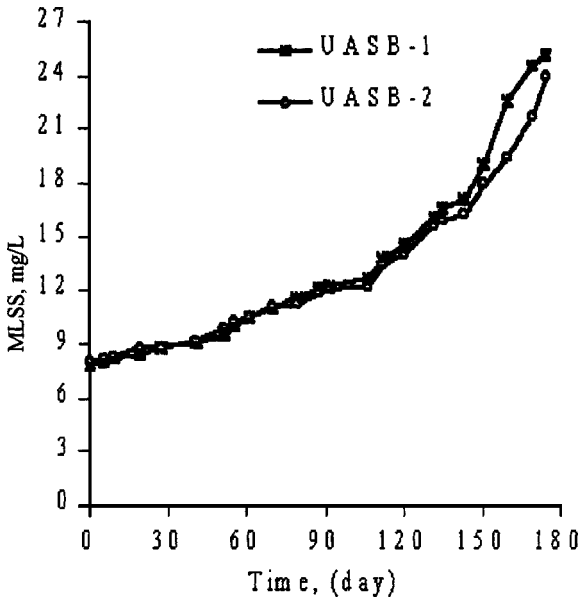

Fig. 3. Mixed liquor suspended solids profile of upflow anaerobic sludge blanket reactors treating various strength synthetic wastewaters

pH, Volatile Fatty Acid, and Alkalinity

The pH of the reactor system was monitored daily and kept within the range of 6.8–7.2 by the addition of $NaHCO_3$ or HCl. The VFA and alkalinity were measured intermittently. The VFA was quite low in all the cases and VFA/alkalinity ratio varied from 0.12 to 0.16, which was well within the specified range for a healthy reactor (Grady and Lim 1980). The low VFA value indicates the proper functioning of acetogenic and methanogenic bacterial consortia. Moreover, the domestic wastewater had a very good buffering capacity.

Sludge Production

The sludge production in both reactors was steady while treating various strength wastewaters with varying atrazine concentrations. In both the reactors, sludge profiles were similar. With the increase in wastewater strength, the slope of both the curves increased, which shows the increased rate of sludge production (Fig. 3) with due course of the reactor run.

Sludge Activity

Specific acetoclastic methanogenic activity (SMA) of the sludge at different conditions is given in Table 2. The SMA of the reactor sludge, when operated without the addition of atrazine, was varied from 0.3748 to 0.4001 g CH_4–COD/g VSS day, whereas, at an addition of 10 and 15 mg/L of atrazine SMA was varied from 0.3267 to 0.3545 g CH_4–COD/g VSS day. When the reactors were fed with 1 and 5 mg/L of atrazine, the SMA values were 0.3799 and 0.3621 g CH_4–COD/g VSS day, respectively. The SMA values show that low concentration of atrazine did not affect methanogenic activity significantly. However, at high concentrations of atrazine (10 and 15 mg/L), there was a slight decrease in the SMA value. It is evident from these results that there is some inhibition of atrazine on methanogenic bacteria. The SMA values observed were far better than that reported by Venkobachar (private communication 1985) while monitoring the performance of a full-scale UASB plant treating tannery waste mixed with domestic wastewater. The SMA was varied from 10 to 60 mL CH_4/g VSS day. Nevertheless, John (1998) while monitoring the performance of a reactor treating synthetic jaggery (a locally available form of sucrose, also known as Indian sugar) wastewater observed almost the same acetoclastic methanogenic activity (90–160 mLCH_4/g VSS day) of UASB reactor sludge. The seed used was granular sludge collected from an UASB plant treating domestic wastewater, whereas Venkobachar (private communication 1985) used a self-inoculated UASB reactor. Granular sludge is self-immobilized active biomass. The SMA values obtained in the present investigation are slightly higher than that reported by John (1998). This might be due to the use of digested sludge, which is reported to be a good alternative to granular sludge to use as seed sludge (Lettinga et al. 1980; Habets and Knelissen 1985).

Atrazine Removal

Atrazine reduction from the UASB reactors treating various strength synthetic wastewaters containing 150, 300, 500, and 1,000 mg/L of dextrose, atrazine reduction was varied from 38.2 to 48.24% depending upon the feeding conditions (Table 2). Fig. 4 shows the atrazine reduction profile from the wastewater containing 150 mg/L of dextrose. Maximum atrazine removal was from the wastewater containing 300 mg/L of dextrose and 5 mg/L of atrazine among various combinations of influent dextrose and atrazine. At an initial dextrose concentration of 150 and 300 mg/L, atrazine reduction increased with the increase of influent atrazine concentration from 1 to 5 mg/L. At elevated atrazine concentration of 10 and 15 mg/L, atrazine reduction efficiency decreased slightly. When the reactor was fed with wastewater containing dextrose of 500 mg/L, atrazine reduction was increased with the increase in influent atrazine concentration from 1 to 5 mg/L and then it remained almost constant at 10 and 15 mg/L. Nevertheless, in the case of wastewater containing 1,000 mg/L of dextrose, atrazine reduction was increased with increase in influent atrazine concentration. Maximum atrazine reduction was observed when influent dextrose concentration was 300 mg/L and of atrazine concentration of 5 mg/L.

After 15 days of operation, atrazine removal efficiency of UASB-1 and UASB-2 treating RDW spiked with atrazine of 5 and 15 mg/L, respectively, was 48.4 and 40%, respectively. Accumulation of atrazine was not observed in any cases.

Atrazine buildup in sludge was checked time to time taking sludge from different heights of the reactor. No atrazine buildup was observed in sludge samples throughout the study period. Hence, the removal of atrazine from the wastewater might be by mineralization with its probable conversion into methane and ammonia gas. However, confirmation of atrazine mineralization could be done by using the radioactive level atrazine (Chung et al. 1996).

The atrazine removal data shows that in the cometabolic process (dextrose as primary source of carbon and energy), there is a certain ratio of primary substrate and the toxic compound, at which the degradation of atrazine will be the maximum. If the concentration of primary carbon source increases drastically, due to the inhibition on the secretion of atrazine degrading inducible enzyme, its degradation rate reduces. If the concentration of the secondary component is more compared to the primary, then inhibition, lack of energy, and carbon source reduce the degradation efficiency of secondary carbon source by the microorganisms.

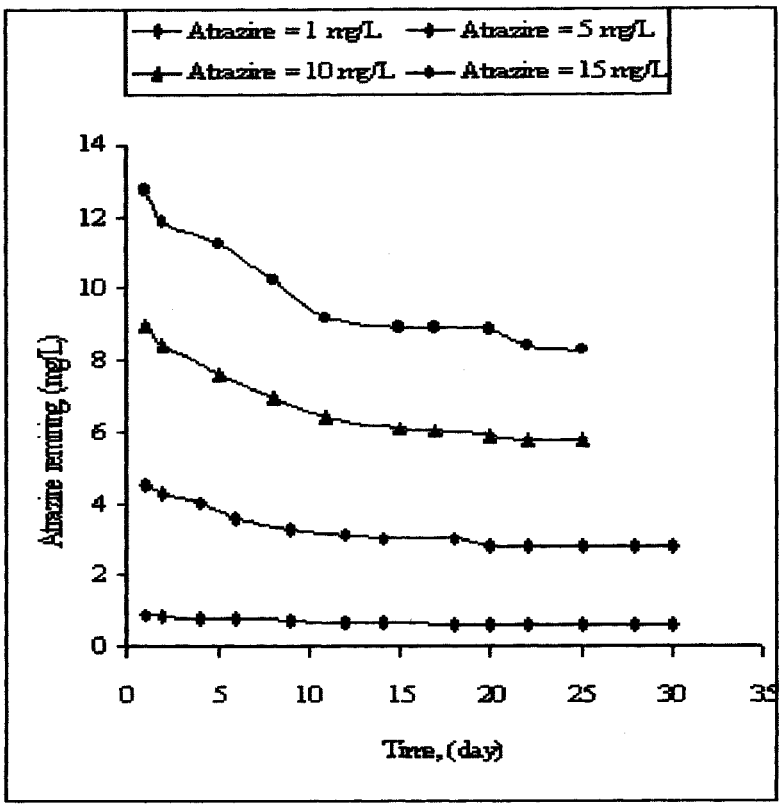

Fig. 4. Kinetics of atrazine reduction from wastewater with dextrose concentration of 150 mg/L

Granule Formation

Granule formation was noticed at the lower part of the sludge blanket in both the UASB reactors after 138 days of operation. In the present investigation, longer time taken for granulation might be due to the low OLR. The color of the granules in both the UASB reactors was black. Although very little inference can be drawn from the color of the granule, it was reported that the granules, which formed a well-defined bed with a clear supernatant and without fluffy conglomerates, were black (Dubourguier et al. 1987; Tilche and Yang 1987). The color of the granule was the same throughout the experiment. Different atrazine concentrations in the feed did not affect the appearance of the granule.

Performance of Adsorption Column

The UASB reactors could effectively remove the easily biodegradable organic matter with efficiency of more than 80%, but atrazine removal efficiency was only 40–50%, irrespective of the feeding conditions.

An up-flow adsorption column with WAC as adsorbent was used as the post-treatment unit for UASB effluent. As activated carbon is a costly adsorbent and can get exhausted soon in the presence of DOM, it was required to find a cost effective adsorbent. In India, many people use a water purifier, which consists of an adsorption column containing activated carbon and a disinfection mechanism using UV light. The adsorbents are replaced periodically. The replaced adsorbent was readily available. Waste activated carbon was pulverized to get different grain sizes and kinetic study was conducted after being pretreated by different mineral acids to choose the best possible combination. Various studies were carried out to evaluate the adsorption potential of the sorbent (results are not shown). The adsorbent having a grain size between 0.3 and 0.5 mm and pretreated with distilled water was found to be most effective for the present purpose. The WAC used in the present study had a dry density of 0.41 g/cm^3.

The breakthrough curves for both organic matter (in terms of COD) and atrazine are shown in Fig. 5. The column could effectively remove all the atrazine from UASB effluent for 26 h, which corresponds to a throughput volume of 23 L. As far as the organic matter removal is concerned, the column performance was very good. For 72 h, the effluent COD was below the detectable level. Then it gradually increased.

The COD value of the treated effluent from the adsorption column never exceeded 30 mg/L, which is the effluent discharge standard in terms of biochemical oxygen demand (BOD). Here dextrose was the primary carbon source. Hence, COD/BOD must either be close to one or even more as COD/BOD increase with increase in the extent of biological treatment. In either case, the effluent was meeting the discharge standard throughout the column run.

The breakthrough curve for organic matter (COD) was a steep curve, whereas in the case of atrazine it was relatively flat. This shows that the organic matter present in RDW is having a high affinity to WAC. As the organic matter (OM) concentration increased in the liquid phase, the percentage removal of atrazine decreased. It is reported that under the conditions prevailing in water works only 20–40% of the single solute capacity for trichloroethane has been achieved in a granular activated carbon (GAC) fixed bed absorber at a complete breakthrough of the trace organic compound (Baldauf 1986). When preloaded GAC was used for atrazine removal, the efficiency reduced to 33% compared to virgin GAC (Haist-Gulde et al. 1991). In contrast to this in some isotherm studies, the solid phase concentration of activated carbon for chlorinated hydrocarbons was not reduced in the

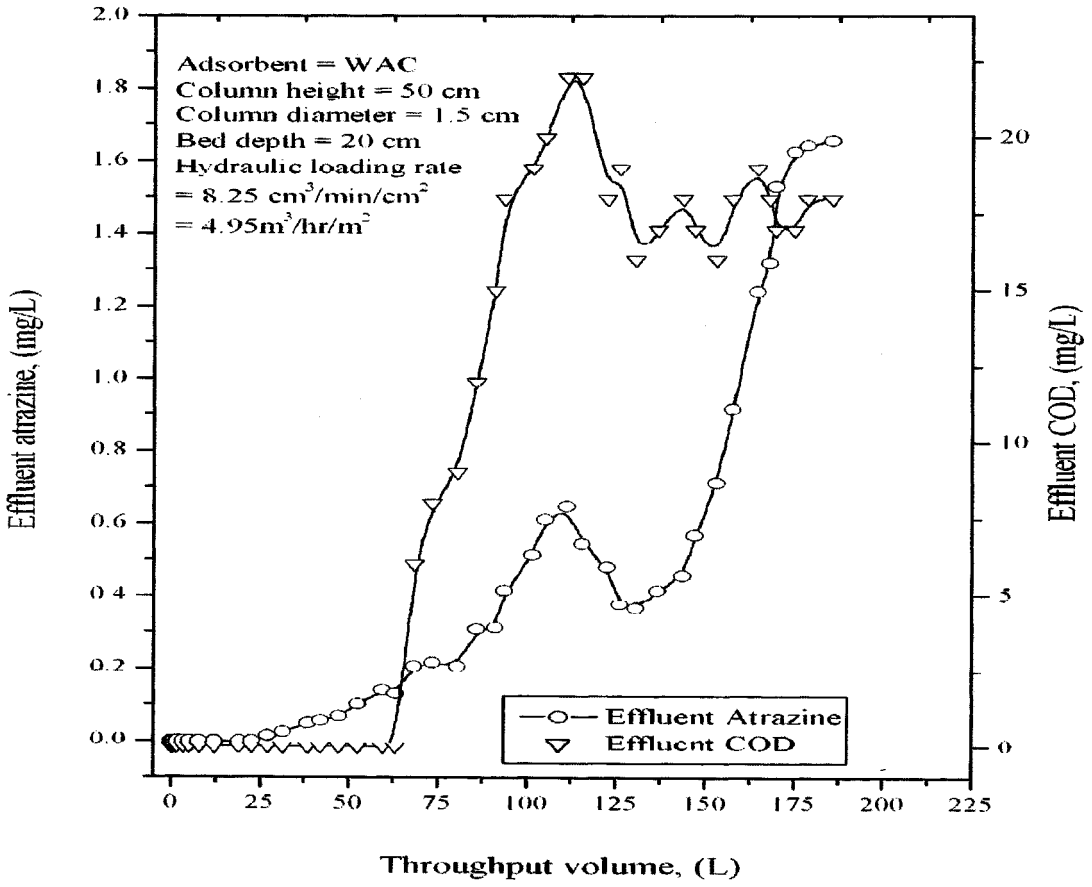

Fig. 5. Breakthrough curves for waste activated carbon removing atrazine and organic matter (chemical oxygen demand) in fixed bed adsorption column

presence of humic substances (Haist-Gulde et al. 1991). From these studies, it is evident that the adsorption capacity of GAC for a particular pollutant varies from waste to waste.

During the column run, until 100 h, the concentration of atrazine and OM was steadily increased. After this, the effluent atrazine and OM concentration started decreasing slightly though the column was operating in the same flow rate as before. This might be due to the growth of micro-organisms in the adsorbent surface. They might have degraded the adsorbed OM and atrazine partially. The OM concentration in the column effluent never increased after 100 h. In the case of atrazine, the effluent concentration remained almost constant for 50 more h, and then started increasing. As seen earlier, the atrazine degradation might have been facilitated by a cometabolic process. Initially the concentration of OM available in the adsorbent surface might not have been very high. Therefore, the micro-organisms must have degraded the atrazine. As the OM concentration increased, the atrazine degradation decreased. Moreover, WAC had a high affinity for OM compared to atrazine. Due to this, whatever traces of OM available might have been adsorbed by GAC, whereas atrazine came out along with the column effluent. Affinity of adsorbent to adsorbate is directly related to the solubility of adsorbate. Organic matter (dextrose) has more solubility than atrazine. The high concentration of OM might be responsible for its preferential sorption.

From the column results, the atrazine removal capacity of the WAC was calculated by considering the area under the breakthrough curve for the entire operational period until the column reached the exhaustion point. In the present study, the exhaustion point was considered as the time at which the effluent atrazine concentration reached was equal to about 90% of the influent concentration. Throughout the column run 223.52 mg of atrazine was removed by the column. The specific atrazine removal capacity of WAC calculated was 17.19 mg/g, whereas the Q_{max} value obtained from the batch studies using the Langmuir isotherm was 13.95 and 9.75 mg/g for treating atrazine in distilled water and wastewater with 1,000 mg/L of dextrose, respectively.

In the fixed bed adsorption column, a higher concentration gradient of adsorbate is available than in the batch reactor, which is the driving force for adsorption. This may be one reason for high atrazine adsorption capacity of WAC in the column. Another reason could be the biological degradation. Micro-organisms are expected to grow on the surface of the adsorbent during the treatment of wastewater containing biodegradable carbonaceous material. There are several reports regarding the growth of microorganism on the surface of the adsorbent during the adsorption process (Cairo et al. 1979; Schalekamp 1979; Sontheimer et al. 1988). There can be a mixed effect on the performance of the adsorption column due to the growth of micro-organisms. Adsorption of pollutants generally takes place mainly on the micropores (size 0.5 μm) of adsorbent. As the average size of microorganism is about 50–100 μm, they cannot occupy the micropores of adsorbent and thus affect the adsorption process (Committee Report 1981). Moreover, due to metabolic activity of the micro-organisms, pollutant load on the adsorbent can be reduced. On the other hand due to excessive growth of micro-

Table 3. Electron Dispersive Atomic X-Ray Analysis of Adsorbent Waste Activated Carbon

	Atomic (%)	
Element	Before adsorption	After adsorption
Na	15.01	18.55
Al	9.07	3.32
Si	17.38	9.54
S	29.15	32.15
Ca	12.37	15.28
Fe	12.80	15.45
Mg	0.084	1.43
Ag	3.11	1.55
Cl	0.06	0.31
P	1.02	2.42
Total	100	100

organisms on the surface of the adsorbent, a layer can be formed, which can reduce the pollutant transport rate from liquid phase to adsorbent through the bio-film (Committee Report 1981).

To ensure the biological growth in the adsorption column, samples of adsorbent was taken before and after the adsorption and were analyzed using SEM. The EDAX analysis of the selected spots on the WAC surface was carried out. The elemental analysis of the white spot showed that it contained high concentrations of Ca, Mg, P, S, and Fe compared to the adsorbent analyzed before the column study (Table 3). These are the inorganic components of microbial cells.

Even though there was some biomass growth in the column, there was no clogging or excessive pressure drop in the column. This may be due to a very low concentration of OM available for the micro-organism in the column. The UASB reactor itself removed almost all the OM. Hence, for excess cell growth, enough OM might not have been available. From this study it was clear that the WAC adsorption column could effectively be used as a polishing unit for the complete treatment of atrazine bearing wastewater. The atrazine concentration was below the detectable limits during the initial period of column operation. Thus by providing two or more adsorption columns in series, effluent discharge standards with respect to atrazine can be met.

Regeneration and Reuse of Waste Activated Carbon

Economic viability of an adsorption system depends upon the regeneration potential of the adsorbent. To know the regeneration potential of WAC, the desorption study of the exhausted WAC was carried out, where 5% methanol was used as the eluent. The atrazine concentration in methanol was 641 mg/L, which corresponds to 86.3% of the total atrazine adsorbed on the column. The OM concentration in the eluent was not measured as methanol, which contributed so much of the COD. Five percent methanol in water could desorb more than 86% of the total adsorbed atrazine. The remaining 14% that was not desorbed may be due to the irreversible adsorption of atrazine on some adsorption sites. The regenerated column could give 80% of the first cycle efficiency in its second cycle of operation. The concentration of atrazine in the eluent was around 50 times the influent atrazine concentration. Since the eulent has a very high atrazine concentration, it can be reused as a pesticide by properly collecting and storing it. Thus, the system described here is able to manage the atrazine bearing wastewater completely without creating many adverse environmental consequences.

Conclusion

Complete treatment of atrazine bearing wastewater is possible using a UASB reactor followed by an adsorption column. The toxicity of atrazine on the anaerobic system was negligible for a concentration range of 1–5 mg/L, whereas at high concentrations of atrazine (10–15 mg/L) the gas production and specific methanogenic activity of the sludge was reduced. The adsorption column using WAC as an adsorbent could treat the UASB effluent satisfactorily. Adsorption as well as biodegradation were responsible for atrazine removal in the column. Methanol was an effective regenerant for the system. The regenerated adsorbent and the eluent could be reused.

Appendix

The following is a list of symbols and abbreviations:

$$\mathrm{COD_{TT}}(\%) = \frac{(\text{influent } \mathrm{COD_{total}} - \text{effluent } \mathrm{COD_{unfiltered}})}{(\text{influent } \mathrm{COD_{Total}})} \times 100$$

$$\mathrm{COD_{ST}}(\%) = \frac{(\text{influent } \mathrm{COD_{Total}} - \text{effluent } \mathrm{COD_{filtered}})}{(\text{influent } \mathrm{COD_{Total}})} \times 100$$

$$\mathrm{COD_{SS}}(\%) = \frac{(\text{influent } \mathrm{COD_{Filtered}} - \text{effluent } \mathrm{COD_{Filtered}})}{(\text{influent } \mathrm{COD_{Filtered}})} \times 100$$

where MLSS=mixed liquor suspended solid; mg/L=milligram per liter; OM=organic matter; RDW=raw domestic wastewater; SMA=specific acetoclastic methanogenic activity; and WAC =waste activated carbon.

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