Combined Treatment of Domestic Wastewater using Anaerobic and Solar Photocatalytic Treatment

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The present study utilizes anaerobic and solar photocatalytic methods to treat domestic wastewater. For stage I, a granulated hybrid upflow anaerobic sludge blanket reactor (HUASB) with a working volume of 5.9 L was used. It was run in a recirculation mode for 3 days called “one cycle,” and 30 cycles were run to find out the stability of the anaerobic treatment. During stage I anaerobic treatment, 90% of the chemical oxygen demand (COD) was removed, and it increased with an increase in digestion period for each cycle. Volatile fatty acids did not cause any operational problems during the stage I anaerobic treatment, being in the range of 280 to 90 mg/L. Stage I treated wastewater was subjected to a stage II solar photocatalytic oxidation method. The optimum pH and catalyst loading for the solar photochemical oxidation were found to be 5 and 200 mg/L, respectively. Stage II, treatment at an optimized condition, removed 66% of organics from the stage I treated wastewater. The combined COD removal due to the combination of these two technologies was found to be 96%.

Key words: domestic wastewater, HUASB, biogas, solar photocatalytic treatment

Introduction

Developing and heavily populated countries in the Asian region are now facing the problem of surface water pollution by domestic wastewater (Frank 2006). According to the WHO 2003 report, about 1.2 billion people lack access to safe and affordable water for their domestic use due to water pollution caused by domestic wastewater. This scenario warrants an urgent need to develop technologies to treat huge volumes of wastewater. In the present study, an attempt has been made to treat domestic wastewater by integrating anaerobic and solar photocatalytic methods since available temperature and sunlight in these regions favour the combination of the above two technologies. The advantage of using anaerobic technology in stage I of the integrated treatment is its effectiveness with high organic concentrations (Banu and Kaliappan 2005). For stage I, a hybrid upflow anaerobic sludge blanket (HUASB) reactor was employed. It is reported that most of the negative aspects of high rate anaerobic reactors can be overcome by restricting the supported material to the top 25 to 30% of the reactor volume (Guiot and Van den Berg 1985; Banu et al. 2006a,b). This would help realize the advantages of both fixed film and upflow sludge blanket treatment. This kind of reactor is called a HUASB. The HUASB is considered to be more stable for the treatment of soluble or partially soluble wastewaters (Tilche and Vieira 1991). Over the years, HUASBs have been successfully used to treat a variety of wastewaters (Hentry et al. 1996; Shivayogimath and Ramanujam 1999; Banu and Kaliappan 2007).

The elimination of organics present in wastewater has been investigated using chemical and photochemical processes with varying success (Bhatkhande et al. 2002; Kamble et al. 2003). Photocatalysis using semiconductors is a subject of increasing interest, which has been extensively performed worldwide to find solutions for wastewater treatment since discovery of the “Honda-Fujishima effect” three decades ago (Fujishima et al. 2000). In these processes, oxidation occurs through an attack of $\text{OH}^-$, which has a rate constant billions of times higher than normal rate constants, using air as the oxidant (Neppolian et al. 2002). Among the semiconductors reported so far, outstanding stability and oxidative power makes $\text{TiO}_2$ the best semiconductor photocatalyst for environmental remediation and energy conversion processes (Hoffmann et al. 1995; Fujishima et al. 2000). Solar photocatalytic treatment has the advantage of achieving additional destruction of organics in wastewater. Ultraviolet radiation required for the photocatalytic processes can be obtained from artificial sources or the sun. There is a significant economic incentive for solar light-based photocatalytic degradations. Solar photocatalytic treatment was successfully employed for treating anaerobically treated wastewater by Banu et al. (2008) and Sigge et al. (2002). The effectiveness of a solar photocatalytic system depends on the strength of the wastewater, since high organic content wastewater is generally not suitable for solar photocatalytic treatment (Neppolian et al. 2002). Therefore, it was employed after the stage I anaerobic treatment.

Materials and Methods

The schematic diagram of integrated treatment of
domestic wastewater is illustrated in Fig. 1. In stage I, untreated domestic wastewater was treated by the HUASB reactor. The effluent from the HUASB reactor was further treated by the stage II solar photocatalytic oxidation method.

Stage I—Anaerobic Treatment HUASB

The laboratory-scale HUASB reactor was used for primary treatment of domestic wastewater. A schematic diagram of the hybrid reactor is in Fig. 1. The laboratory-scale reactor was fabricated using a polyvinylchloride (PVC) tube with an internal diameter of 11 cm and an overall height of 88 cm. The working volume of the empty reactor was 5.9 L. A screen was placed at a height of 60 cm to arrest the floating packing material, which was made with cut PVC rings. One hundred and fifty cut rings made of PVC were used as carrier material. Each PVC cut ring measured 2 cm in height and 1 cm in diameter. The effluent line was placed at a height of 72 cm. A gas headspace equivalent to 1.5 L was maintained above the effluent line. The gas outlet was connected to a wet gas meter (Ritter, Model No: TG1). A peristaltic pump (Miclins PP20) was used to feed the wastewater into the reactor. The effluent pipeline was connected to a water seal to prevent the escape of gas. The HUASB was operated in recirculation mode: 43.2 L of domestic wastewater was placed in a storage tank and it was fed to the HUASB reactor at a flow rate of 1,800 mL/h with a hydraulic retention time of 3.3 h for 3 days, called one cycle. To establish stable performance in terms of COD removal, 30 such cycles were run.

Stage II—Solar Photocatalytic Treatment

Commercially available TiO$_2$ (Degussa P-25, Anatase 70% and Rutile 30%), with a particle size of 20 nm and surface area of 50 m$^2$/g, was used as the photocatalyst. Optimization experiments were carried out in a glass tray measuring 15 by 8 cm (length by height). One litre of sample at a standing height of 5 cm was taken in the glass tray. Sunlight was used as the energy source for catalyst excitation. The tray was placed over a magnetic stirrer and exposed to direct sunlight. Samples were withdrawn at periodic intervals and analyzed for chemical parameters.

After optimization at the bench scale, the experiment was carried out in a plastic trough (20-L capacity) measuring 50 cm in diameter by 10 cm in height. The 10 L of slurry composed of stage I treated domestic wastewater (standing height of 5 cm) and catalyst were taken in the trough. A mechanical stirrer was used for maintaining TiO$_2$ in suspension at 600 rpm during the experiment. The setup was exposed to direct sunlight for a period of 5 hours. During the period of study, the daily average solar radiation and temperature were in the range of 6 kWh/m$^2$/d and 37°C, respectively. After the experiment, the setup remained undisturbed for 30 minutes to allow settling of the TiO$_2$.

Wastewater

The domestic wastewater used for the present study was collected from the Nessapakkam sewage treatment plant (STP), Chennai, India. The domestic wastewater used in the present study was analyzed for various physicochemical characteristics. These results are furnished in Table 1.

Chemical Analysis

Chemical oxygen demand (COD), volatile fatty acids (VFA), alkalinity, total suspended solids (TSS) and volatile solids of the raw and treated wastewater were analyzed following APHA et al. (1998). VFA as acetate in the treated wastewater was assessed in accordance with the procedure described in Standard Methods (APHA et al. 1998). One hundred millilitres of the centrifuged sample was taken in a 500-mL round-bottom flask. Five millilitres of 1 + 1 H$_2$SO$_4$ (50% distilled water plus 50%
H₂SO₄) and 100 mL of distilled water were added to the sample and distilled at the rate of about 5 mL/min. One hundred fifty millilitres of distillate was collected in a 250-mL conical flask and titrated against 0.1 N NaOH using phenolphthalein as the indicator. Total organic carbon (TOC) in the wastewater was analyzed using a TOC analyzer (Analytik Jena, Model: Micro C). Anions such as phosphate (PO₄³⁻), sulphate (SO₄²⁻), and chloride (Cl⁻) were analyzed employing ion exchange chromatography (Dionex, Model: DX-120) after filtering the samples through a 0.45-μm filter. The eluent was a combination of 3.5 mM bicarbonate and 1 mM carbonate; the flow rate was 1.2 ml/min with an injection volume of 25 μL. Methane content in the biogas was measured by a gas chromatograph equipped with a flame ionization detector. The column used was proapak Q.

Results and Discussion

Stage I (Anaerobic Treatment—HUASB)

Figure 2 illustrates the biogas production and pH variation during the Stage I anaerobic treatment of domestic wastewater. Gas production rates were highly variable due to fluctuations of the organic concentration in the influent (Fig. 2). The maximum cumulative gas production (3,300 mL) was recorded for cycle 2, and minimum cumulative gas production (1,550 mL day) was recorded for cycle 12. Biogas production was higher than reported by earlier workers (Kobayashi et al. 1982; Ligero and Soto 2002). This was due to the presence of high organic content in the domestic wastewater used. The COD conversion to methane ranged from 0.295 to 0.305 m³CH₄/kg COD reduced at the STP during the study period. This compares with the known equivalence of 0.350 m³ of CH₄ per kg of COD removed at the STP. The methane content in the biogas was found to be from 55 to 63%. The gas production decreased with increase in time of operation for each cycle. The daily gas production for each cycle varied from for 1,200 to 2,400 mL for day 1, 300 to 700 mL for day 2, and 200 to 50 mL for day 3, respectively. The pH of the anaerobically treated wastewater was in the range of 7.4 to 8.1, within a suitable range of 6.8 to 8.3 (Gerardi 2003). For each operational cycle, pH in the medium increased with a corresponding increase in digestion period (days). For example, in cycle 1, the pH of the medium was 7.7 on day 1, 7.9 for day 2, and 8.0 for day 3. The increase in the level of pH in each operational cycle was due to the corresponding increase in alkalinity (Banu et al. 2007).

Figure 3 illustrates the pattern of COD removal by stage I anaerobic treatment. COD removal (calculated from fig. 3) increased with an increase in time of operation for each cycle. The total COD removal was in the range of 57 to 65% for day 1, 74 to 84% for day 2, and 86 to 91% for day 3. The COD concentration in the influent domestic wastewater varied from 872 to 540 mg/L. In the treated wastewater, the COD concentration was in the range of 190 to 342 mg/L for day 1, 90 to 196 mg/L day 2, and 55 to 89 mg/L for day 3. The present study showed a decrease in the rate of COD removal with an increase in time for each cycle of operation. The COD removal efficiency was found to be 64% for day 1, 52% for day 2, and 39% for day 3. This declining COD removal efficiency from day 1 to day 3 may be due to recalcitrance of some organics in the wastewater towards COD removal and to recirculation of wastewater to the anaerobic digester causing dilution of wastewater. This decrease in the COD removal efficiency by anaerobic reactors with a decrease in feed organic concentration
has also been reported by several authors (Aiyuk et al. 2004; Chu et al. 2005).

Figure 4 depicts alkalinity and VFA concentration in the wastewater during stage I. Alkalinity of the treated wastewater varied from 626 to 690 mg/L. Alkalinity in the medium increased with an increase in treatment time for each operational cycle. An increase in alkalinity increases the pH of the medium. The VFA (as acetate) level in the medium varied from 280 to 98 mg/L. VFA concentration is the most important intermediate during anaerobic digestion (Ahring and Angelidaki 1995; Wang et al. 1999; Pind et al. 1999, 2002). Based on the VFA and alkalinity levels of this study, there was no risk of souring of the reactor by acidification. Souring of the contents of a reactor is generally not a problem in anaerobic sewage treatment and there is no need for chemical pH adjustment (Van Hanndel and Lettinga 1994).

**Stage II (Solar Photocatalytic Oxidation)**

**Optimization Studies.** Optimization of reaction variables in photocatalytic reaction is needed to get higher degradation efficiency. Hence it was planned to optimize reaction parameters such as pH and catalyst loading. The corresponding results are depicted in Fig. 5. The optimization studies for catalyst loading were done with stage I anaerobically treated wastewater at its original pH, 7.4. During optimization studies, experiments were carried out at various TiO₂ loadings to understand the influence of loading on degradation efficiency. It is evident from Fig. 5a that the rate of TOC degradation increased as the TiO₂ dose increased, and reached a maximum 0.1728 mg/L/min at a TiO₂ dose of 200 mg/L. Beyond this dose, the rate of degradation decreased with an increase in TiO₂ loading. The decrease in rate of degradation at higher catalyst loading is attributed to the deactivation of activated molecules by collision of inactivated TiO₂ molecules (Stafford et al. 1997). Solution pH is an important variable in the evaluation of aqueous-phase mediated photocatalytic reaction (Banu et al. 2008). Hence experiments were conducted to study the impact of pH on the rate of photocatalytic degradation by keeping the TiO₂ concentration constant (200 mg/L) and varying the pH of the stage I treated wastewater between 3 and 9. As can be seen from Fig. 5b, the rate of degradation increased from a pH of approximately 3.0 to a maximum of pH 5.0. The rate of TOC degradation then decreased as pH was increased to approximately 9.0.

**Treatment Studies.** After optimization, five sets of experiments were carried in a bench-scale solar photocatalytic reactor with 10 L of treated wastewater from stage I in the optimized pH of 5 and TiO₂ dose of 200 mg/L. Figure 6 shows the influence of irradiation time on the removal of organics (TOC and COD) during stage II. From the figure, it is evident that organics removal increased with an increase in irradiation time. From an initial COD concentration of 77 mg/L, COD was...
removed until it reached a minimum value of 27 mg/L at 5 h. During stage II treatment, 66% of the organics were removed from the wastewater. Similar to this finding, Bekbolet et al. (1996) obtained 70% COD removal at 5 h exposure time using solar photocatalytic treatment for biologically treated landfill leachate.

Figure 7 shows the treatment efficiency of the anaerobic and solar photocatalytic methods employed to treat domestic wastewater. The influent average COD was found to be 739 mg/L and fluctuated in the range of 520 to 980 mg/L (data not shown in the figure). This highly fluctuating COD did not have a significant effect on stage I anaerobic treatment. Stage I treatment narrowed down the fluctuation in COD significantly to result in more stable loading on stage II photocatalytic treatment. The combination of anaerobic and solar photocatalytic treatment resulted in the removal of 96 and 92% of COD and TSS, respectively, from the domestic wastewater.

To assess solids separation of suspended TiO$_2$, which is required for the process development, sedimentation experiments were carried out at pH 5 following methods detailed in Watts et al. (1995). From Fig. 8, it is clearly evident that TiO$_2$ sedimentation from its suspension was difficult and required 24 h to settle 80% (40 mg/L) of the TiO$_2$ (200 mg/L). Therefore, implementation of the suspended catalyst process requires enhanced settling, through such means as coagulation and flocculation.

**Conclusions**

HUASB treatment removed 86 to 91% of influent COD. VFA did not build up during HUASB treatment. Stage II, solar photocatalytic treatment, decreased COD from an influent concentration of 77 mg/L down to 26 mg/L, or a 66% COD removal efficiency. The overall COD removal efficiency of stage I and stage II was up to 96%.

To integrate secondary solar photocatalytic treatment using TiO$_2$, a solid/liquid separation device is required to remove the used catalyst from the liquid effluent. Further studies should focus on two aspects of this process: (1) improved filter media in the HUASB reactor to offer a better surface for biomass growth and consequent higher treatment efficiency; and (2) immobilized catalyst in the solar photocatalytic oxidation process to ensure that the use of an additional clarifier to remove the catalyst is not required.
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References


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