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ORIGINAL PAPER

An integrated approach for enhanced textile dye degradation by pre-treatment combined biodegradation

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Abstract The wastewater released by the textile industries affects aquatic, plant and human life. Though there are many conventional wastewater treatment techniques, interest on coupled treatment methods has increased in the recent times owing to their increased efficiency. In the present study, the textile wastewater was pre-treated by three different techniques, viz. sonication, photocatalysis and ozonation. Increasing the treatment time increased the biological oxygen demand to chemical oxygen demand (BOD/COD) ratio, and thus the biodegradability was about 0.6–0.73. Effluent pre-treated by photocatalysis showed relatively higher biodegradability compared to ozonation and sonication. The degradation of aromatic compounds due to pre-treatment was substantiated by Fourier transform infrared (FTIR) and proton nuclear magnetic resonance (^{1}H NMR) spectroscopy. Since pre-treatment increased the biodegradability of the effluents, further biological degradation using acclimatized sludge biomass resulted in COD removal efficiencies 94, 91 and 82 %, respectively, for photocatalysis, sonication and ozonation. The morphology of the organisms which played a major role during the degradation of pre-treated effluent was examined under scanning electron microscope (SEM).

Keywords Aerobic processes · Biodegradation · Integrated processing · Wastewater treatment · Pre-treatment

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Introduction

Textile effluent stream contains organic matters, dyes and synthetic chemicals that pollute the ground water and nearby water bodies when let out without proper treatment. As a consequence, dissolved oxygen content gets reduced and eco system in the water bodies are affected (Mandal et al. 2010). This problem may be highly important to address in future due to ever growing population and increasing number of industries. The developments in wastewater treatment systems are aimed at modifications which can enhance the contaminants removal efficiency. Many studies have reported advanced oxidation process (AOP) approach as a more viable option due to various reasons. Its applicability in the treatment of effluents containing a mixture of different dyes, efficient removal of organic matters, better reduction of odour and colour are few reasons to mention (Kuo 1992; Kang and Chang 1997; Alaton and Teksoy 2007; Srinivasan et al. 2012). The biodegradability (BOD/COD) of the dyes has been reported to improve by Fenton's and induced-Fenton's reactions (Tekin et al. 2006). Microorganisms can thereby take part in the COD level reduction of various industrial effluents. In particular, chemolithotropic bacteria have been found to play a vital role in treating the wastewater under aerobic conditions (Brock and Madigan 1998). This proves that AOP reduces the toxic level and subsequently allows bacteria to feed on the effluent, thereby improving its biodegradability. A study combining photo-Fenton and biological treatment on model and actual industrial wastewater shows different results regarding coupling strategies for different wastewaters (Malato et al. 2007; Zapata et al. 2008). Biological hybrid technologies have been reported to be the most promising techniques that can efficiently eliminate the pesticides and reduce organic content and COD in the wastewater (Oller et al. 2011). In addition, various

Table 1 Characteristics of the textile effluent

Characteristic	Value
Temperature (°C)	30–40
pH	6.5–9
Colour	Light brown–dark brown
TDS (mg/L)	800–1000
TSS (mg/L)	1000–1200
BOD (mg/L)	1800–2200
COD (mg/L)	9500–11000

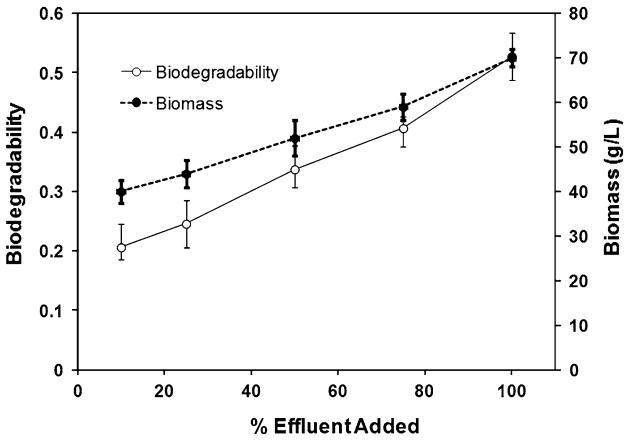

Fig. 1 Effect of effluent concentration on biodegradability and biomass growth during acclimatization

methods for large scale treatment of industrial wastewater were summarized and tabulated.

In the present study, textile effluent was pre-treated with different unit operations (viz. sonication, photo catalysis and ozonation) in order to study the treatment efficiencies to improve its biodegradability. The other objective is to provide a strategy for combining these techniques with subsequent biological treatment by aerobic processes using acclimatized sludge biomass.

Past studies on pre-treatment techniques for dye effluents

Sonication

Ultrasound was reported to generate free radicals which subsequently attack the contaminant dye molecules thereby, completely mineralizing the contaminants or converting them into less harmful or lower chain compounds (Vajnhandl and Le Marechal 2005; 2007). Researchers have been using ultrasound along with other techniques to achieve dye degradation (Vončina and Le Marechal 2003; Gogate and Pandit 2004; Sayan 2006). For example, the decolourization of six vinylsulphone reactive dyes was studied using

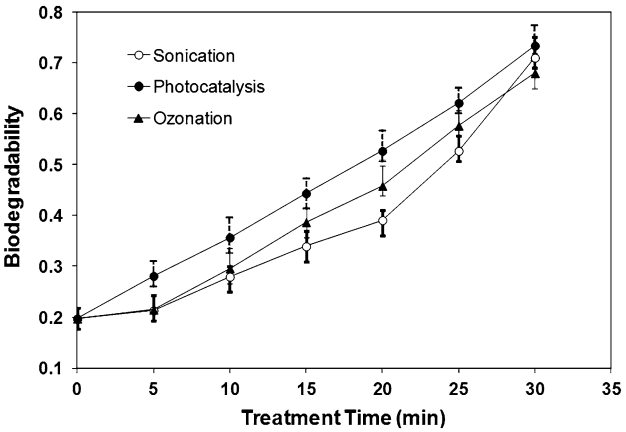

Fig. 2 Degradability studies with different pre-treatment methods

ultrasound and ultrasound/hydrogen peroxide combination (Vončina and Le Marechal 2003). The results show that ultrasound treatment was significantly enhanced in the presence of H_2O_2. Ultrasound has also been used along with H_2O_2, ozone, UV and Fenton's reagent to treat dye containing wastewater (Gogate and Pandit 2004).

Ozonation

Ozone has been used to treat textile wastewater and found to have excellent decolouring efficiency (Wang et al. 2007). Ozonation was used to effectively remove chemical oxygen demand (COD) and enhance the biodegradability of the aqueous dye solution (Wu et al. 2008; Turhan and Turgut 2009). Combination of ozone oxidation and upflow biological aerated filter has been proved as a promising technique to treat wastewater containing azo dyes (Lu et al. 2009). Ozone has also been used along with other techniques such as ultrasound, photochemical oxidation, sono-photochemical oxidation, photo-Fenton processes, catalytic advanced oxidation processes, etc. (Gogate and Pandit 2004). Ozonation has also been used in combination with other pre-treatment process, including biological aerated filter and reverse osmosis for textile wastewater treatment (Qi et al. 2011).

Photo-catalysis

Initial dye concentration, pH, flow rate and light intensity were found to affect the TiO_2 catalyzed photocatalytic dye degradation process (Liu et al. 2006). The rate of decolourization of two different dyes together in a binary dye mixture was found to be governed by the adsorptivity of the particular dye onto the surface of the TiO_2 photocatalyst (Chatterjee et al. 2008). In photocatalytic degradation of a mixture of mono and diazo dyes using TiO_2, the degradation efficiency of one azo dye was found to be improved by the presence of the other with suitable

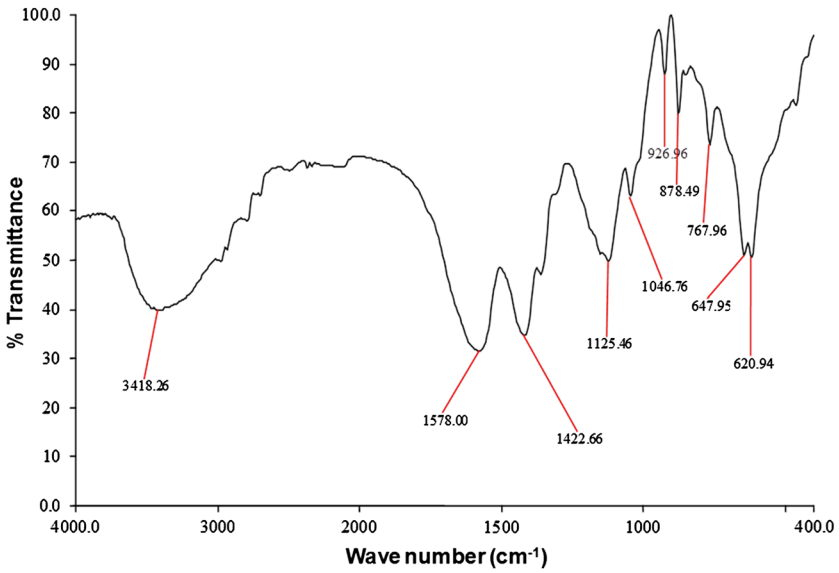

Fig. 3 FTIR spectra of untreated effluent

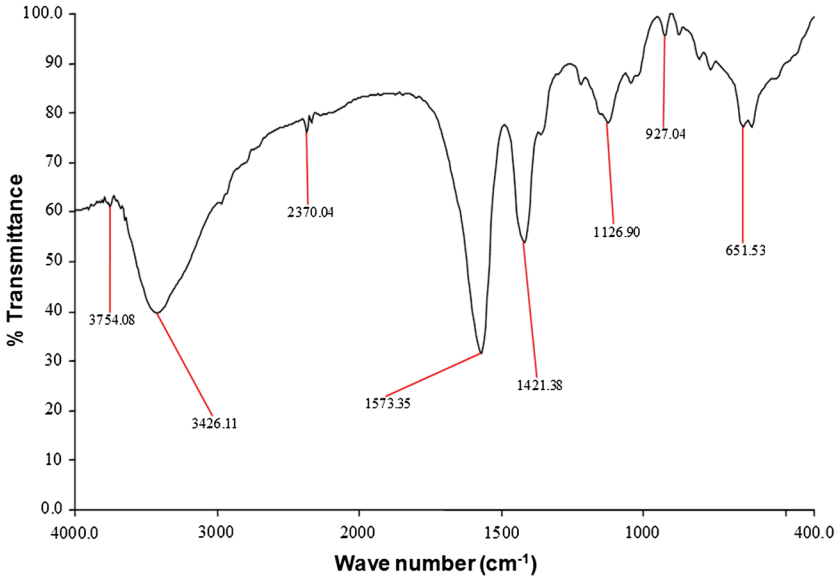

Fig. 4 FTIR spectra of ultrasound treated effluent

concentrations (Wongkalasin et al. 2011). Modified TiO_2 catalyst has been reported to perform better in dye degradation processes (Suwanchawalit et al. 2012).

Materials and methods

Textile wastewater

The characteristics of wastewater collected from the textile effluent stream are given in Table 1.

Sludge

Activated sludge with initial concentration of 37 g/L was collected from a nearby sewage treatment plant and inoculated in 100 mL of nutrient broth. Then it was incubated at 37 °C for 24 h. The resultant culture was further used for acclimatization.

Acclimatization studies

Acclimatization involves the following steps.

- The 100 mL activated sludge (culture) prepared was first inoculated in 900 mL of 10 % effluent sample (90 mL sample + 810 mL distilled water). It was subjected to aerobic process for 48 h, after which there was a considerable reduction in colour.
- In the next step, aeration was stopped and the sludge was allowed to settle. The supernatant was discarded

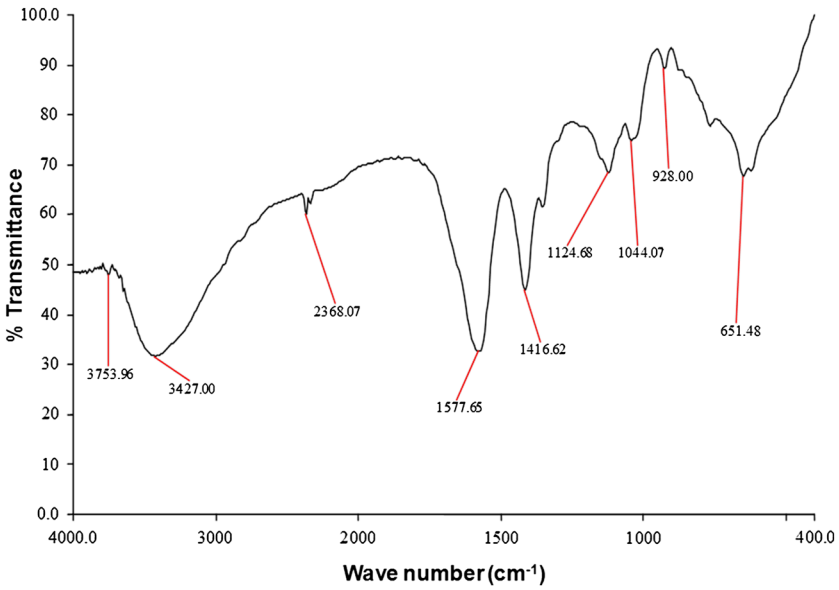

Fig. 5 FTIR spectra of ozone treated effluent

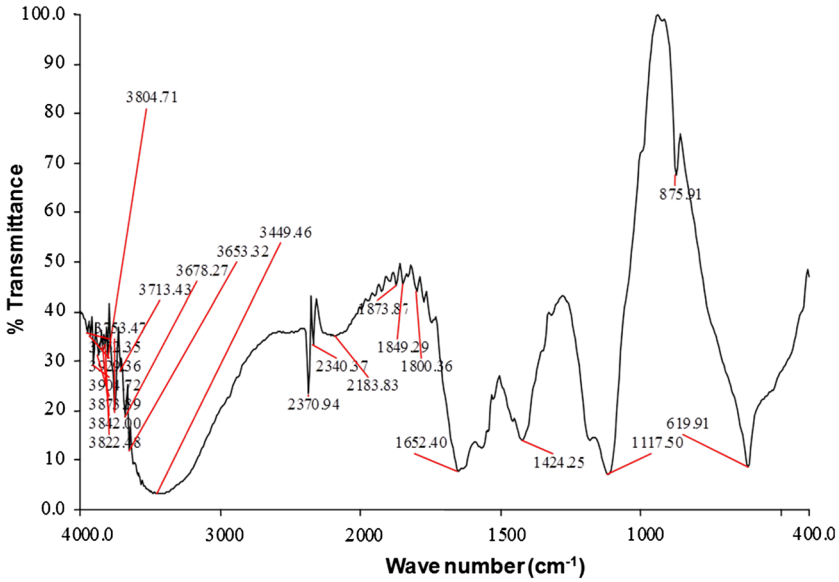

Fig. 6 FTIR spectra of photocatalytic treated effluent

leaving about 100 mL of settled sludge at the bottom. To this sludge, 900 mL of 25 % effluent sample (225 mL sample + 675 mL distilled water) was added and aerobic process was continued for 48 h. Similarly the procedure has been repeated for 50, 75 and 100 % effluent concentrations.

The biomass concentration, BOD and COD, were determined at each step, and thus the biodegradability was noted. Biomass concentrations were measured in duplicates, whereas, BOD and COD were measured in triplicates.

Pre-treatment techniques

Sonication

Sonication was conducted using a Digital Sonifier 250 model, Branson, MO, USA. Effluents with the working volume of 200 mL were treated with ultrasound at different time intervals (5, 10, 15, 20, 25 and 30 min) at 30 % amplitude (200 W) and frequency of 20 kHz. BOD and COD were determined for all the intermediate samples and biodegradability was evaluated.

Table 2 FTIR analysis of untreated and pre-treated textile effluent

Wave numbers (cm^{-1})	Groups	Remarks	Untreated	Ultra sound treated	Ozone treated	Photocatalytic treated
3520–3320	NH_2 in aromatic amines	NH stretch	–	3754, 3426	3753, 3427	3753, 3678, 3653, 3449
3420–3250	OH in alcohols and phenols	OH stretch	3418	–	–	–
2990–2850	CH_3 and CH_2 in aliphatic compound	CH antisym and asym stretch	–	–	–	–
2700–2250	Amine salts	NH_2 stretch	–	2370	2368	2370, 2181
2000–1650	Substituted benzene ring	Several bands from overtone and combination	–	–	–	1873, 1849, 1800
1680–1520	CO and NH_2 in primary amides	C O stretch	1578	1573	1577	1652
1515–1450	Benzene ring in aromatic compounds	Ring stretch	1422	–	–	1424
1400–1310	COO group in carboxylic acid	Antisym stretch	–	1421	1416	–
1285–1240	AR O in alkyl ethers	C O stretch	–	–	–	–
1250–1200	C O C in vinyl ethers	C O C stretch	1125	1126	1121	1117
1060–1025	CH_2 OH in primery alcohols	C O stretch	–	–	1044	–
950–900	CH CH_2 in vinyl compounds	CH_2	1046	927	928	–
900–750	CH CH_2 in vinyl compounds	CH_2	926, 878, 767	–	–	–
630–535	C CO C in ketones	C CO C bend	647, 620	651	651	619

Photo-catalytic reaction

Photo-catalytic experiments were conducted in a photo-reactor equipped with 125 W UV lamp as irradiation source, supplied by Heber Scientific Company, Chennai, India. Concentration of 0.5 g of TiO_2 as catalyst per litre of effluent was used. Effluents with the working volume of 200 mL were treated for different time intervals (5, 10, 15, 20, 25 and 30 min) in the reactor. Intermediate samples were analyzed for BOD and COD, and thus biodegradability was evaluated.

Ozonation

A lab-scale ozone generator (200 W, Model No. SA001, India) of 3.2 g/h capacity was used to generate ozone. Oxygen was supplied at the rate of 4 LPM to the Ozone generator. Thus, the generated ozone was used to treat 200 mL of effluent sample. Intermediate samples treated at different time intervals (5, 10, 15, 20, 25 and 30 min) were analyzed for BOD and COD and biodegradability was evaluated.

Analysis

BOD and COD values were estimated as per the standard procedures available in APHA (APHA 1998). The biodegradability was determined using the ratio BOD/COD. The effluent samples were pre-treated with different techniques, and they were subjected to biological treatment with acclimatized sludge. The inoculation was carried out with the acclimatized sludge in the ratio 1:10 and continuous aeration was given. Intermediate samples were taken for every 6 h to determine COD and biomass concentration (MLSS).

Analytical instruments

Pre-treated samples (effluent samples pre-treated with 3 different techniques, viz. photo-catalysis, ozonation and sonication for 30 min) were analyzed for FTIR (Perkin-Elmer 1000) and ^1H NMR (JEOL ECA 500 MHz high resolution liquid state NMR) spectroscopy. The acclimatized sludge was also analyzed using scanning electron microscopy (model SEM 30 ISS, UK) for supporting evidences.

Results and discussion

Acclimatization

During acclimatization, the effluent concentration was varied from 10 to 100 % and the samples were aerated for

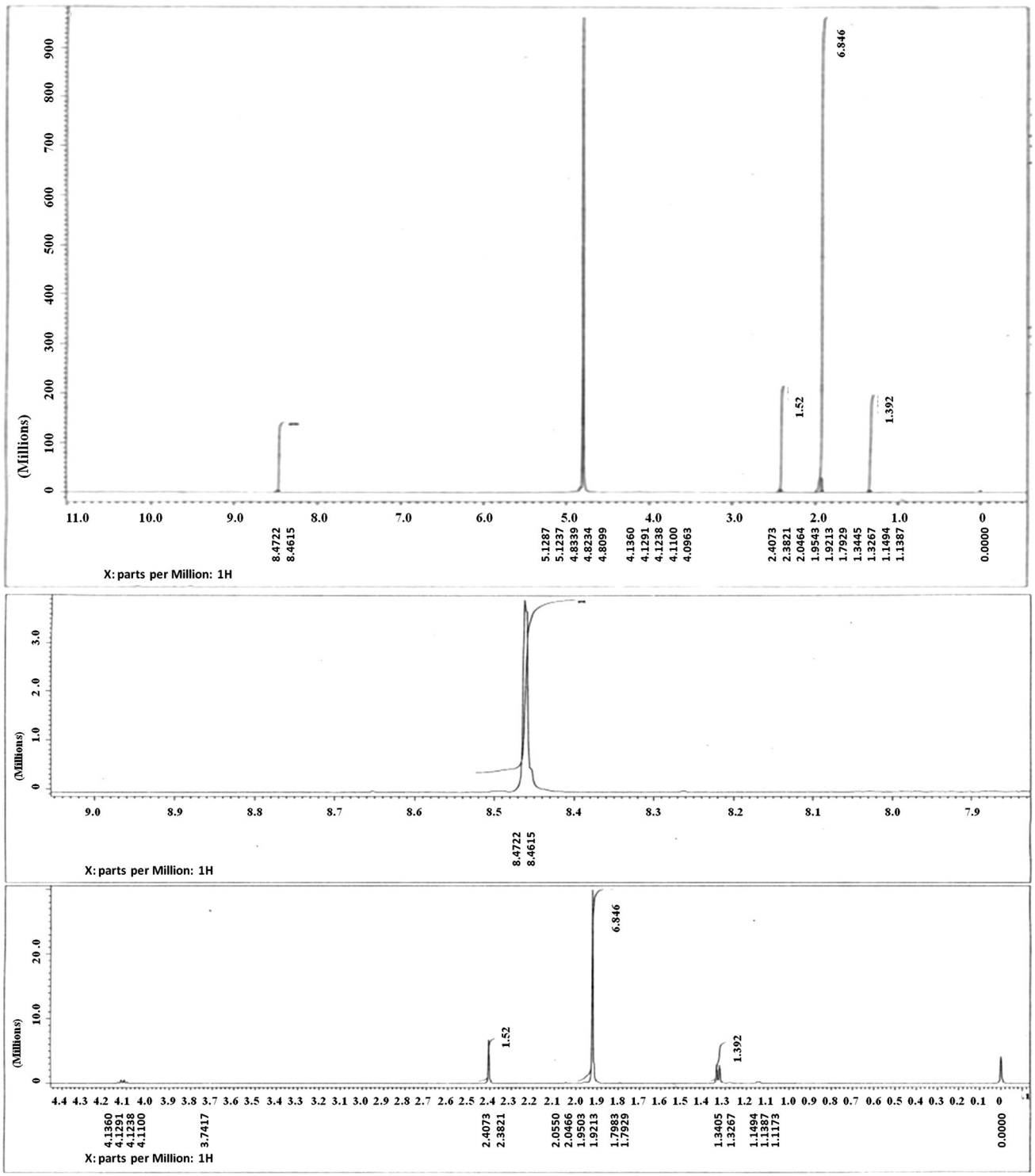

Fig. 7 ^{1}H NMR spectra of the untreated effluent

48 h. Figure 1 shows the effect of increasing effluent concentration on biodegradability and biomass concentration during the acclimatization process. The biomass concentration increased from 40 g/L (at 10 % effluent concentration) to 70 g/L (at 100 % effluent concentration) in 240 h. On the other hand, the biodegradability also increased from 0.2 (at 10 % effluent concentration) to 0.5 (at 100 % effluent concentration). Therefore, it can be concluded at this stage that the microorganisms show slow adaptation, and also good response to textile wastewater.

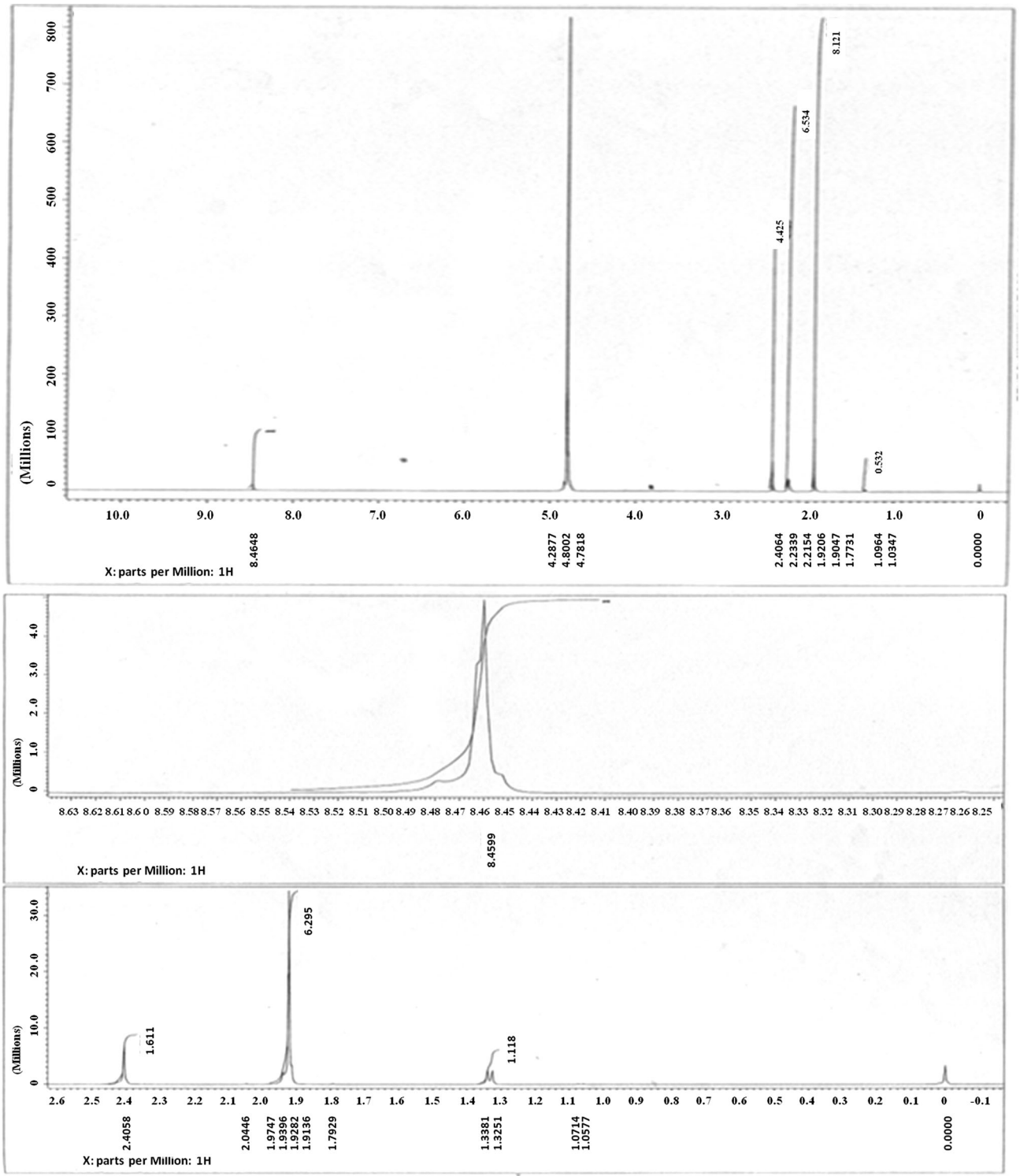

Fig. 8 ^{1}H NMR spectra of ultrasonic treated effluent

Pre-treatment degradation studies

Figure 2 shows that the biodegradability increases on increasing the treatment time for all the three techniques viz. sonication, photocatalysis and ozonation. The increase in biodegradability may be due to the conversion of refractory organics into biodegradable compounds during pre-treatment. Photo-catalysis shows relatively better

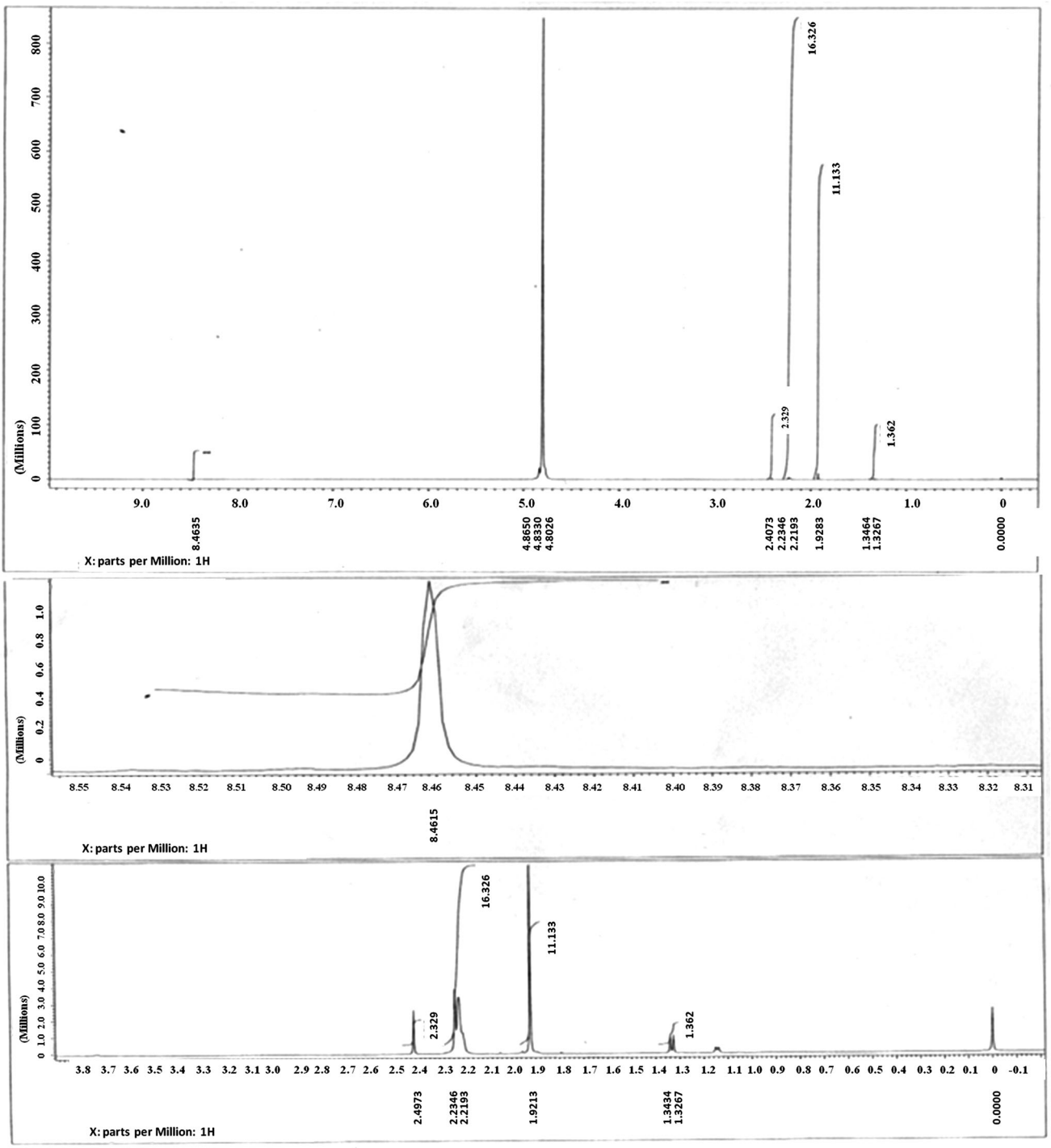

Fig. 9 ^{1}H NMR spectra of ozone treated effluent

biodegradability compared to the other two techniques. The biodegradability of the effluent by photocatalysis and ozonation was enhanced by 22.3 and 7.5 %, respectively when compared to sonication. The COD removal efficiencies using photo-catalysis, sonication and ozonation are 81, 80 and 79 %, respectively. At this point, it can be concluded that photocatalytic degradation method is a fast, effective, efficient and probably a viable method for wastewater treatment.

Functional group analysis by FTIR

The FTIR spectra of the untreated and 30-min treated effluent samples were analyzed to identify changes, if any

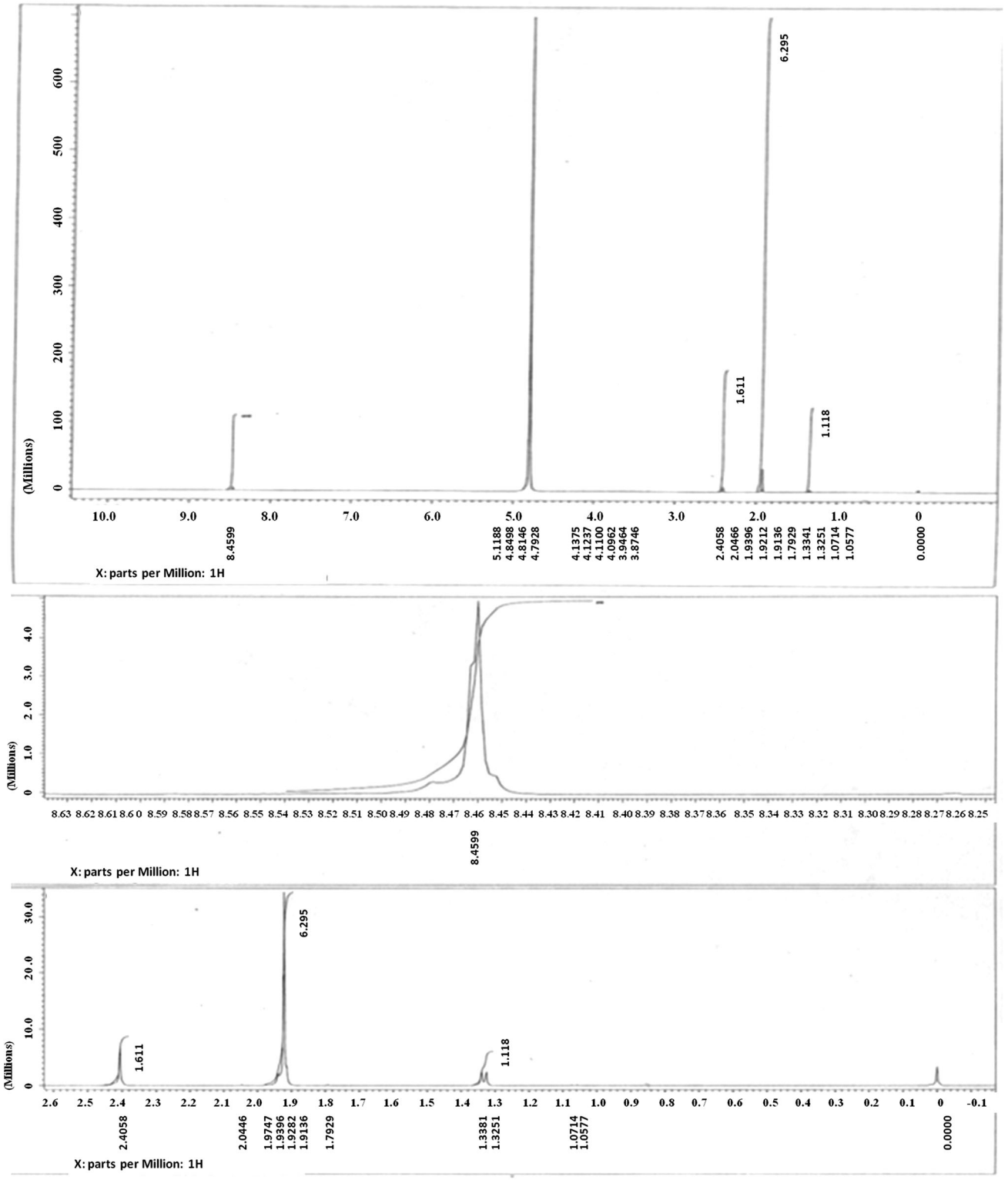

Fig. 10 ^{1}H NMR spectra of photo-catalytic treated effluent

in the functional groups. The spectra are shown in Figs. 3, 4, 5 and 6. Significant changes can be observed in the pre-treated effluent when compared to the untreated sample. The photocatalysis treated effluent shows distinct variation in the functional groups, which may be due to the ring breaking that occurs during photocatalytic process. The

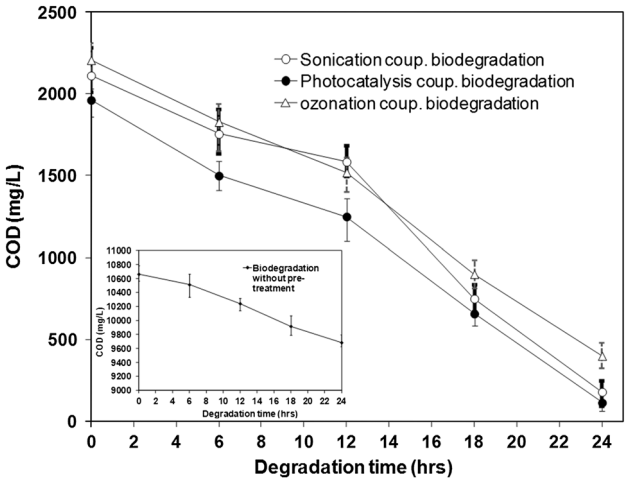

Fig. 11 Biodegradation with and without pre-treatments

absorbance bands below 900 cm^{-1} represent the aromatic ring structure which are absent in the spectra for pre-treated samples. This confirms that the aromatic structure was completely degraded during this pre-treatment. However, in the photocatalytic treated samples alone, complete functional and structural changes were observed when compared to samples treated by other two techniques. The peaks observed and the corresponding groups assigned are presented in Table 2.

Structural analysis by ^{1}H NMR

The ^{1}H NMR spectra were observed for untreated and treated effluents and are shown in Figs. 7, 8,9 and 10. The ^{1}H NMR spectrum of the untreated effluent showed 4 singlets at 1.392—$R_2C\underline{H}_2$, 1.950—$R_3C\underline{H}$, 2.40—$ArC\underline{H}_3$, 4.833—$RC{=}C\underline{H}$ and a doublet peak at 8.46—$Ar\underline{H}$. From these observations, it is evident that the untreated effluents contain aromatic ring structures with RCH and RCH_2 side chains. The photo-catalytic degraded samples show peaks at 1.325–1.338, 1.921–1.974, 2.04–2.21, 4.81 and 8.44–8.53. On the other hand 6 singlet peaks at 0.532, 1.45, 1.900–1.920, 2.215–2.233, 2.40, 4.80 and 8.46 were observed for ultrasound treated sample. Similarly, ozone degraded effluent showed doublet peaks at 1.326–1.340, 2.219–2.234 and three singlet peaks at 1.921, 2.407 and 8.461. From ^{1}H NMR results it can be concluded that breaking of aromatic ring structure has occurred during pre-treatment process.

Biodegradation studies on the pre-treated effluent

The biodegradation of untreated and pre-treated effluents was carried out using acclimatized sludge. Samples were drawn at regular time intervals (i.e.) once in 6 h for the analysis of COD. As the biodegradation time increased, the COD values were found to decrease for both untreated and pre-treated effluents, as shown in Fig. 11. The plot in the inset shows the low COD removal efficiency of 9 % for untreated effluent. Whereas, pre-treatment facilitates further biodegradation process resulting in COD removal efficiencies 94, 91 and 82 % for photo-catalyzed, sonicated and ozonated effluents, respectively. In photocatalysis coupled biodegradation, better reduction in overall COD was observed. This may be due to major COD reduction that occurred in the photocatalysis step which made the effluent more amenable for further biodegradation. Similarly, for sonication and ozonation, COD reduction was observed with marginal differences.

SEM analysis

SEM analysis of the sludge was carried out to identify the microbial species responsible for degradation of the pre-treated effluent. Figure 12 shows the presence of several morphologically distinct microorganisms, such as coccus, rod and long filamentous shaped bacteria. The cocci shaped bacteria of about 1 μm diameter were found to be of maximum population and this could have been responsible for the degradation.

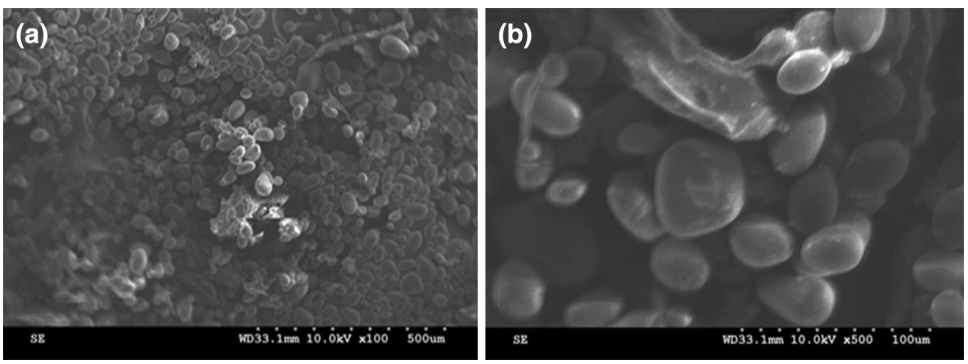

Fig. 12 SEM micrographs of different shaped bacteria at different magnification **a** 100× **b** 500×

Conclusion

This study revealed that incorporating pre-treatment unit operations prior to biological treatment enhances biodegradation. Using sonication, photocatalysis and ozonation as pre-treatment methods, it was observed that increasing the treatment time increases the biodegradability by reducing BOD and COD. Photocatalysis showed relatively higher biodegradability compared to ozonation and sonication. FTIR and ^{1}H NMR spectroscopic studies confirm that aromatics are degraded due to pre-treatment. Pre-treatment coupled with biological degradation increased the biodegradability of the effluents. Biodegradation of photo-catalyzed effluent was much effective with COD removal efficiency of 94 %. This was followed by sonicated and ozonated effluents with COD removal efficiencies 91 and 82 %, respectively. It can be concluded that pre-treatment is essential in achieving effective biodegradation. Also increasing the treatment time would improve the biodegradability process, thereby reducing the hydraulic retention time when compared to conventional treatment processes.

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