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S-rGO/ZnS nanocomposite-mediated photocatalytic pretreatment of dairy wastewater to enhance aerobic digestion

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Abstract−The treatment of real dairy wastewater by aerobic digestion is a time taking process due to the complex nature of organics present in dairy effluent. Herein, solar light-mediated photocatalytic pretreatment of the dairy wastewater was performed to decompose the complexed organic into shorter chair organics. The sulfur-doped reduced graphene oxide/zinc sulfide (S-rGO/ZnS) nanocomposite was applied as an efficient photocatalyst to solubilize and decompose the organic components in dairy wastewater under natural solar light. The results showed that the photocatalytic treatment enhanced the solubilized chemical oxygen demand (SCOD) by 113% after 6 h of sunlight exposure as compared to 28.1% of SCOD under the photolysis conditions. The aerobic digestion of the pretreated dairy wastewater showed 94% removal of total chemical oxygen demand (TCOD) after 36 days. TCOD of pretreated and untreated dairy wastewater was decreased to the level 71 mg/L and 257 mg/L after the aerobic digestion, indicating the effectiveness of the pretreatment process. A water quality analysis of photocatalysis-aerobic treatment showed that the values for various parameters such as COD, total solids, nitrogen, alkalinity, oil and grease content, electrical conductivity and pH were at acceptable limits for environmental discharge of dairy effluent. This study reveals that photocatalytic pretreatment of dairy wastewater is an effective method for solubilization of the complex organic components of dairy effluents which can be easily decomposed by the microbes during the aerobic digestion process.

Keywords: Dairy Effluent, Pretreatment, Photocatalysis, S-rGO/ZnS, Aerobic Treatment

INTRODUCTION

The processing of dairy products consumes a large amount of water, which is the leading contributor to the water footprint. Generally, 2-4 liters of pure water is required for the processing of one liter of milk [1,2]. Dairy industries release a large volume of wastewater containing a high load of the organics such as lactose, fat, protein, detergents, etc. [2]. High COD and microbial content are the major characteristics of the dairy wastewaters due to high organic load and high nutrient value [3-6]. Thus, due to its potential environmental concerns and large volumes, dairy wastewater demands serious attention for proper management and disposal [7,8].

In the last decade, several methodologies have emerged to treat the wastewater, including oxidation process, filtration, aerobic, anaerobic digestions and so forth. Biological methods are the most common for the treatment of the wastewater [6,9-11]. Aerobic digestion is the most popular method for the treatment of dairy wastewater due to low operating cost, easy handling, and applicability to large scale. The dairy effluent consists of fatty acids, lactose, and proteins [7,12] which provide a favorable environment for their growth. Although, a large volume of milk fat in the dairy wastewater provides substantial hindrance in the microbial degradation due to its water insolubility and poor biodegradability. Therefore, milk fats restrict aeration and form a continuous film over the surface of the water during the aerobic wastewater treatment. This leads to the production of high volumes of scum and foam over the surface, which hinders the penetration of air and thus reduces the microbial efficacy to degrade organic compounds. In addition, dairy wastewater also contains cleaning and hormonal chemicals [13,14], which also have an adverse effect on the microbial activity. Hence, an alternative or pretreatment method is needed to degrade these complex fatty acids to simple and soluble organics which can be easily processed by the microbes during the aerobic process.

Advanced oxidation processes (AOP's) are well known for the degradation of organic constituents by the production of active radicals. Numerous studies related to the treatment of dairy effluent have been performed with photo Fenton, Fenton, and electro Fenton-like reactions [15,16], electro flocculation and electro-coagulation [6,16] and ozonation [17,18]. However, these methods are costly in terms of energy demand and chemical uses. Among various AOPs, the application of heterogeneous photocatalysis process is an emerging technology as an alternative to treating dairy wastewater. The basic mechanism of photocatalysis involves the production $^{o}O^{2-}$, and ^{o}OH radicals under light irradiation, which is extremely

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oxidizing and reducing in nature and could decompose the complex organics [19]. These two oxidative species can degrade organic components in dairy effluent and form small chain simple intermediate byproducts which could be solubilized organic compounds.

A large number of photocatalysts have been synthesized and used for the environmental remediation application [15,20-25]. Fabrication of the visible light active catalyst is still a challenge. In recent years, semiconductor-based nanocomposites have been thoroughly investigated for photocatalytic applications. The composites based on the ZnS and graphene oxide (GO) have gained considerable attention for the degradation of organic pollutants and reduction of the toxic Cr(VI) to Cr(III) [15,26,27]. The incorporation of the GO with ZnS facilitates efficient charge separation and inhibits the recombination of the e^{-}/h^{+} pairs. Therefore, the use of the GO/ZnS based nanocomposite could be a good option to decompose the complex aromatics present in dairy wastewater into the soluble short chain compounds using the photocatalysis process. Moreover, the GO/ZnS based photocatalyst can be reclaimed and possesses a high level of reusability, as observed in the pioneer study [27], where up to 80% removal of organic pollutant was recorded with S-rGO/ZnS nanocomposite even after three times of reuse.

Herein, we investigated a novel photocatalytic pretreatment in natural solar light and aerobic digestion of the real dairy effluents. The application of the S-rGO/ZnS nanocomposite was investigated to decompose the organics in dairy effluent. Thereafter, pretreated dairy effluent was digested aerobically in a bioflow reactor. The effect of pretreatment on the aerobic digestion was investigated by comparing the results with control aerobic digestion of dairy effluents. The changes in the TCOD, COD, TS, nitrogen, pH, EC, etc. parameters were evaluated to find the effect of the applied treatment methods.

MATERIALS AND METHODS

1. Chemicals

The chemicals used, such as $Zn(CH_3CO_2)_2 \cdot 2H_2O$ and Na_2S, were purchased from Scharlau and BDH Chemicals Ltd. The graphite used for the preparation of GO was obtained from Sigma Aldrich. LCK514 and LCK 238 kits provided by HACH were used for the analysis of COD and nitrogen. Inoculum for aerobic treatment was prepared by using culture media Nutrient broth.

2. Dairy Effluent Sampling

The dairy wastewater sample was obtained from Saudi Dairy and Foodstuff Company (SADAFCO) Jeddah, Kingdom of Saudi Arabia in the month of October. The wastewater samples were collected according to the standard method no. 1060 of APHA, 1999 [28]. The fresh samples of wastewater were collected in vinyl plastic containers and stored at 5 °C in cold storage units prior for use in analysis and experiments.

3. Preparation S- rGO/ZnS Nanocomposite

S-rGO/ZnS nanocomposite was prepared according to the previously reported method using a solution of GO, $Zn(CH_3CO_2)_2$ and sodium sulfide [27]. Briefly, GO was synthesized by Hummers' method and S-rGO/ZnS nanocomposite was prepared by mixing the 50 mL of 1 M $Zn(CH_3CO_2)_2$ solution with 25 mL of 10 mg/mL GO solution under continuous stirring for 30 min. Thereafter, 30 mL of 1.3 M Na_2S solution was added dropwise and left for 3 h for stirring. This solution was transferred into the hydrothermal reactor and keep for 16 h at 140 °C. After cooling the reactor, the material was filtered and washed with de-ionized water, acetone, ethanol to remove the impurities. The obtained black S-rGO/ZnS nanocomposite was air dried at 105 °C and stored for the further applications.

4. Pretreatment of Dairy Wastewater

The dairy effluent was photocatalytically pretreated in a 4 L capacity batch reactor operated under sunlight, continuous aeration and stirring for six hours between 10:00 am to 4:00 pm. A fixed amount of 0.5 g/L of S-rGO/ZnS was added to the dairy effluent. A similar experiment was set under solar light without the addition of any photocatalyst to estimate the effect of photolysis on dairy effluent. The dairy effluent was sampled at a regular interval using an

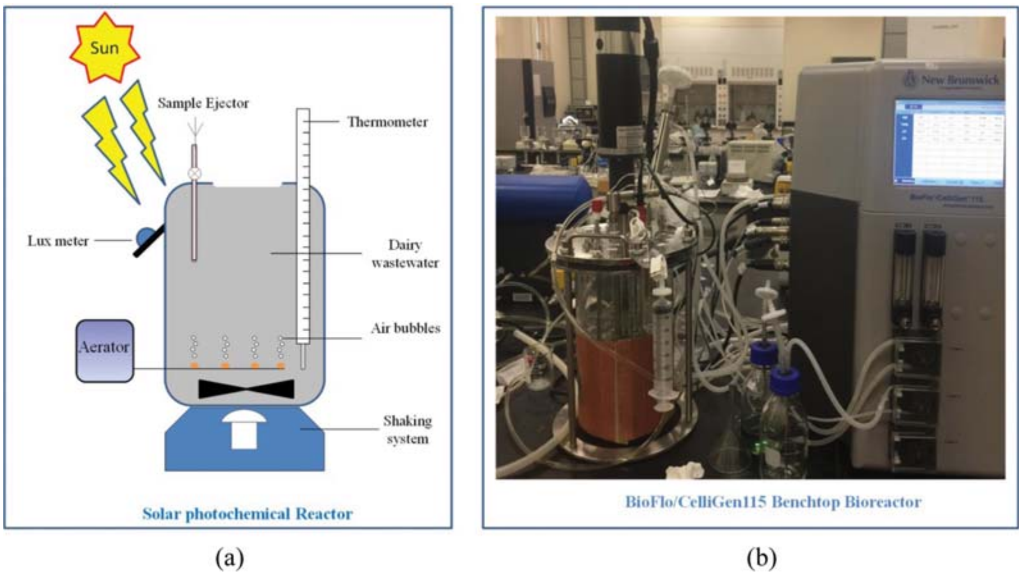

Fig. 1. Solar photochemical rector (a) and BioFlo/CelliGen115 Benchtop Bioreactor (b).

ejector, while pretreatment efficiency was measured by analyzing soluble content of COD. The temperature variations were recorded after each hour of photocatalysis for 6 h. A schematic diagram for the photocatalytic pretreatment reactor is shown in Fig. 1(a).

5. Aerobic Digestion of Dairy Wastewater

5-1. Inoculum Preparation

The aerobic bacterial inoculum was prepared from the same dairy effluent. The liquid culture medium was prepared by adding an appropriate amount (as per supplier recommendation) nutrient broth (Sigma Aldrich) in 1,000 ml of deionized water. The final composition of the nutrient broth contained D(+)-glucose (1 g/L), peptone (15 g/L), sodium chloride (6 g/L) and yeast extract (3 g/L). The culture media was initially sterilized in autoclave at 120 °C for 20 minutes. Thereafter, an appropriate amount of dairy effluent was added in the autoclaved media and incubated at 35±1 °C for 48 h. Once visible colonies could be identified in the incubated culture and optical density approached to 1, the inoculum was read to be applied for the aerobic treatment system.

5-2. Reactor Setup and Configuration

Aerobic treatment of dairy wastewater was performed in Brunswick BioFlo®/CelliGen® 115 Benchtop fermentor and bioreactor. The reactor configuration is controlled by the process control software (Table 1). The aerobic treatment was performed in two runs in which photocatalytic dairy effluent was used as a substrate in the first run, followed by untreated dairy effluent in the second run. In each run, 4 liters of the substrate was added in the main vessel and mixed with inoculum at a substrate-inoculum ratio of 9 : 1 at the start-up. An agitation motor (removable) positioned on the middle top of the head plate bearing housing was the connected shaft of agitation. The agitation speed was adjusted at 150 rpm through the system. The temperature of the bioreactor was controlled (35±1 °C) by either a heater blanket or cooling coil connected to the main vessel. For aerobic treatment oxygen was supplied through the aeration system connected with ring spurger in the vessel and the flow rate was controlled by a thermal mass flow controller. Dissolved oxygen in the substrate was controlled by the DO electrode sensor, which is linked to the changing speed of agitation and, P and I (proportional and integral) thermal mass flow controller. The pH was maintained at 6.5, which was sensed by a pH gel-filled probe. pH control was maintained by a P and I controller for the peristaltic pumps, allocated to execute addition of acid and base buffers. An image of the aerobic reactor setup is displayed in Fig. 1(b).

6. Analysis

The collected samples during photocatalytic pretreatment and aerobically treatment of dairy effluent were analyzed for different operating parameters to estimate the efficiency of the processes. The chemical oxygen demand (COD) as total and soluble fraction was measured using wastewater COD cuvette test (LCK514) through HACH LANGE DR-6000, (Germany). The total solid fractions (TS) and total suspended fraction (TSS) were analyzed using standard test methods of APHA, 1997 [29]. The volatile solids fraction (VS) was estimated by US-EPA test methods no. 1684 [30]. Total carbon content in the samples was calculated on the basis of the method reported by Brake [31]. Nitrogen content was measured by using the LCK 238 cuvette test on DR-6000 detector. Electrical conductivity (EC) of the effluent samples was recorded on JENWAY 4510 EC, while pH values were recorded on pH meter (SensIon PH3, HACH). The water quality parameters were analyzed using standard test methods of APHA [28].

RESULTS AND DISCUSSION

1. Characterization of S-rGO/ZnS Nanocomposite and Dairy Effluent

The S-rGO/ZnS nanocomposite was characterized by scanning electron microscopy (SEM), X-ray diffraction, photoluminescence analysis, UV-visible absorbance, Raman and X-ray photoelectron spectroscopy (XPS) techniques. A brief description of the physicochemical characteristics of S-rGO/ZnS nanocomposite is reported elsewhere [27]. The applied characterization tools clearly showed the successful deposition of ZnS onto S-rGO, while XPS analysis confirmed the doping of sulfur in rGO. Optical analysis techniques (photoluminescence analysis, UV-visible absorbance) confirmed the visible light absorption properties of S-rGO/ZnS nanocomposite and better electron-hole pair separation which facilitated the higher photocatalysis.

The physiocochemical characteristics of wastewater were analyzed initially for the parameters, including chemical oxygen demand (COD), total solids (TS), carbon, nitrogen, C/N ratio, alkalinity, oil and grease content, electrical conductivity (EC) and pH. The data are presented in Table 2.

Table 1. Configuration of the photochemical reactor and bioflow aerobic reactor

Solar photocatalytic reactor		Bioflo benchtop bioreactor	
Reactor type	Solar photochemical	Reactor type	BioFlo/CelliGen115 Benchtop Bioreactor
Reactor Mode	Batch	Reactor Mode	Batch
HRT	6 h	HRT	35 d
Working volume	4 L	Working volume	4 L
Light	Visible Range (Solar)	Aeration	sparger
Catalyst type	ZnS/RGO	Inoculum	100 ml/L
Catalyst dose	0.5 g/L	Substrate: Inoculum	9.1
Temperature	Ambient outdoor	Temperature	35 °C
pH	5.7	pH	6.5
Agitation	150 rpm	Agitation	150 rpm

Table 2. Physiochemical properties of dairy wastewater sample

Parameters	Units	Value	SD*
tCOD	mg/L	1212	98.1
sCOD	mg/L	267	29.3
Total solids	mg/L	1524	41.7
Carbon	g/L	9.2	1.02
Nitrogen	g/L	1.78	0.1
C:N		76.0	3.5
Oil and Grease	g/L	168	4.76
EC	µS	5.2	5.75
pH		5.75	0.7

*SD=standard deviation

2. Photocatalytic Pretreatment of Dairy Effluent

The high content of oil, grease, and fats in dairy wastewater inhibits the biological treatment process [32]. Thus, pretreatment of dairy effluent is needed prior to biological treatment. The S-rGO/ZnS composite was evaluated for its applicability as pretreatment to dairy wastewater. Fig. 2(a) shows the SCOD conversion in photocatalysis and photolysis experiment. After six hours of pretreatment, SCOD in S-rGO/ZnS nanocomposite photocatalysis experiment was increased from 267 mg/L (0 h) to 570 mg/L, which means 113% higher SCOD as compared to the initial value. In the case of the photolytic experiment (without S-rGO/ZnS), it can be seen, Fig. 2(a), that the increase in SCOD in negligible; thus photolysis has no effect on dairy wastewater as pretreatment solubili-

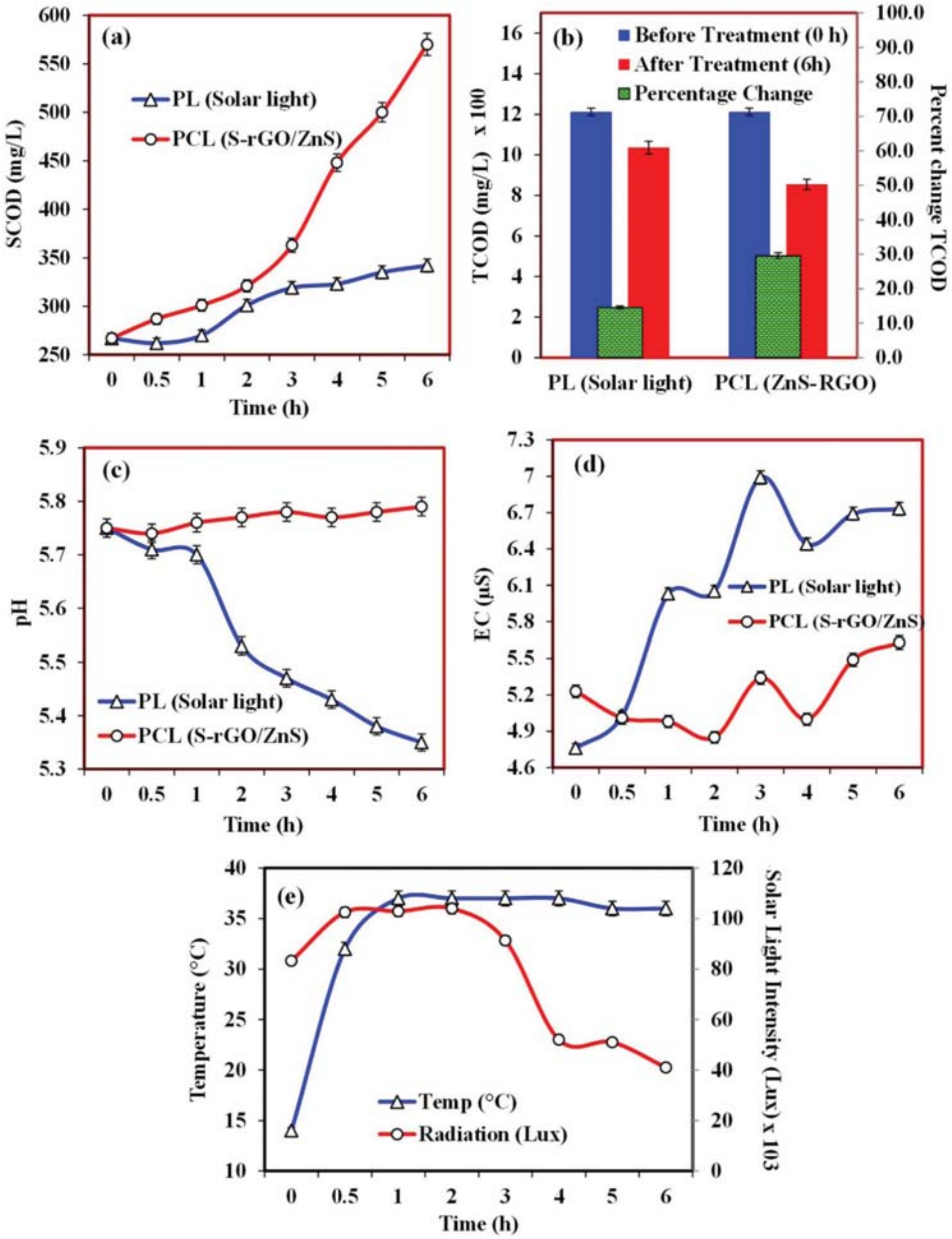

Fig. 2. Photocatalytic pretreatment of dairy wastewater (a) Effect on SCOD, (b) Effect on TCOD, (c) Variation in pH, (d) Variation in EC, (e) Temperature and solar light intensity.

Table 3. Pearson correlation (r) among various operating conditions during photolysis of dairy wastewater

	Time	Temp (°C)	Radiation (Lux)	PL-SCOD (mg/L)	pH	EC (μm)
Time	1					
Temp (°C)	0.551	1				
Radiation (Lux)	−0.849	−0.113	1			
PL-SCOD (mg/L)	0.573	0.632	−0.288	1		
pH	0.895	0.543	−0.635	0.666	1	
EC (μm)	0.667	−0.047	−0.699	0.107	0.619	1

Table 4. Pearson correlation (r) among various operating conditions during photocatalysis of dairy wastewater

	Time	Temp (°C)	Radiation (Lux)	PCL-SCOD (mg/L)	pH	EC (μm)
Time	1					
Temp (°C)	0.551	1				
Radiation (Lux)	−0.849	−0.113	1			
PCL-SCOD (mg/L)	0.945	0.326	−0.901	1		
pH	−0.971	−0.601	0.758	−0.906	1	
EC (μm)	0.828	0.767	−0.485	0.758	−0.872	1

zation. The improved SCOD in photocatalyst is linked to the photocatalytic degradation of organics present in dairy wastewater. Under the solar light irradiation, S-rGO/ZnS produce the active radical species, which attacked the triglycerides of fatty compounds present in dairy wastewater, which results in the degradation of fatty acid chains into lipid precursors fatty acids and glycerols and fatty acids. These byproducts are more soluble in water as compared to lipids, thus more easily available to microorganisms for subsequent biological treatment of dairy wastewater.

The TCOD removal was evaluated after S-rGO/ZnS photocatalysis of dairy wastewater and explicit in Fig. 2(b). The data indicated a slight lowering in TCOD in both photolysis and photocatalytic experiments. The photocatalytic process showed up to 29% removal in TCOD (1,212 mg/L to 854 mg/L), while photolytics of the dairy effluent showed only 14.5% removal in TCOD. The lower TCOD provide more favorable conditions for subsequent biological treatment as more organic matters are in the soluble form, which would be available in the system during aerobic digestion.

The pH and EC are important factors that may affect the performance of photocatalysis and biological treatment of wastewater. During the pretreatment of dairy wastewater, the variation in pH and EC values was also evaluated. The pH was maintained in the system in the range of 5.75-5.35 and no significant variation was found (Fig. 2(c)). However, in the case of EC, a slight increase in the photocatalytic reactor (from 4.76 μS to 6.73 μS) was observed after 6 hours of pretreatment experiment (Fig. 2(d)). The increase is probably linked to the formation of various salts and ions during the degradation process of dairy wastewater.

The photocatalyst efficiency highly depends on temperature and solar radiation intensity during the experiment. The temperature variation and solar intensity were measured at regular intervals during the experiment and results are presented in Fig. 2(e). To evaluate the relationship of these factors with photocatalytic efficiency, Pearson correlation analysis was performed.

The photocatalysis process is dependent on various factors, including temperature, and the intensity of light plays a crucial role. The role of temperature and solar radiation on photocatalysis was evaluated by conducting the Pearson correlation of various quantities as explicit in Table 3 and Table 4. It was observed that time had a positive correlation with SCOD in both photolysis (r=0.573) and photocatalysis (r=0.945) of dairy wastewater, which means that the increase in SCOD was 57% and 94% in relation to time. The lower correlation in photolysis revealed that there was no improvement in SCOD production even with longer exposure to light. pH showed a positive correlation (r=0.895) with time in photolysis, while in photocatalysis a negative correlation (r=–0.971) was observed. Thus, with an increase in duration of exposure to light, a positive effect on photolysis could be observed, while pH was decreased in case of photocatalysis. The change in SCOD also affected the EC of the photocatalytic system where 75% dependency (r=0.758) of EC was directly linked to the SCOD production. On the other hand, no relationship (r=0.107) between EC and SCOD was observed, while in the case of photolysis, low SCOD production was observed.

3. Aerobic Digestion of Photocatalytic Dairy Effluent

3-1. Chemical Oxygen Demand

COD, which is widely applied as an organic pollution indicator, is a parameter useful to determine the concentration of organic pollutants liable to degrade [3]. The TCOD in during both runs of aerobic treatment of photocatalytic pretreated (Run 1) and untreated (Run 2) dairy effluents were analyzed and results explained in Fig. 3. Maximum COD removal (94%) was achieved under photocatalytically pretreated dairy effluent, while 79% removal in TCOD was shown by untreated dairy effluent. During 36 days of aerobic treatment, a continuous decreasing trend was observed in both cases. However, photocatalysis of the wastewater gave a higher rate of COD removal, where after 36 days the TCOD values was lowered to 71 mg/L from initial 1,126 mg/L concentration. Tocchi et al. [33] tested the aerobic treatment of dairy wastewater where they achieved the TCOD reduction up to 160 mg/L. However, in

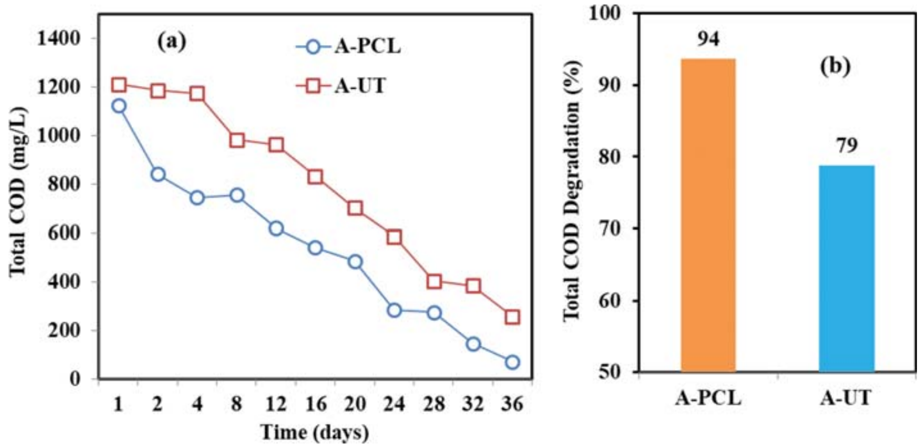

Fig. 3. Aerobic digestion of pretreated (A-PCL) and untreated dairy wastewater (A-UT) (a) effect on TCOD content, (b) percentage removal of TCOD.

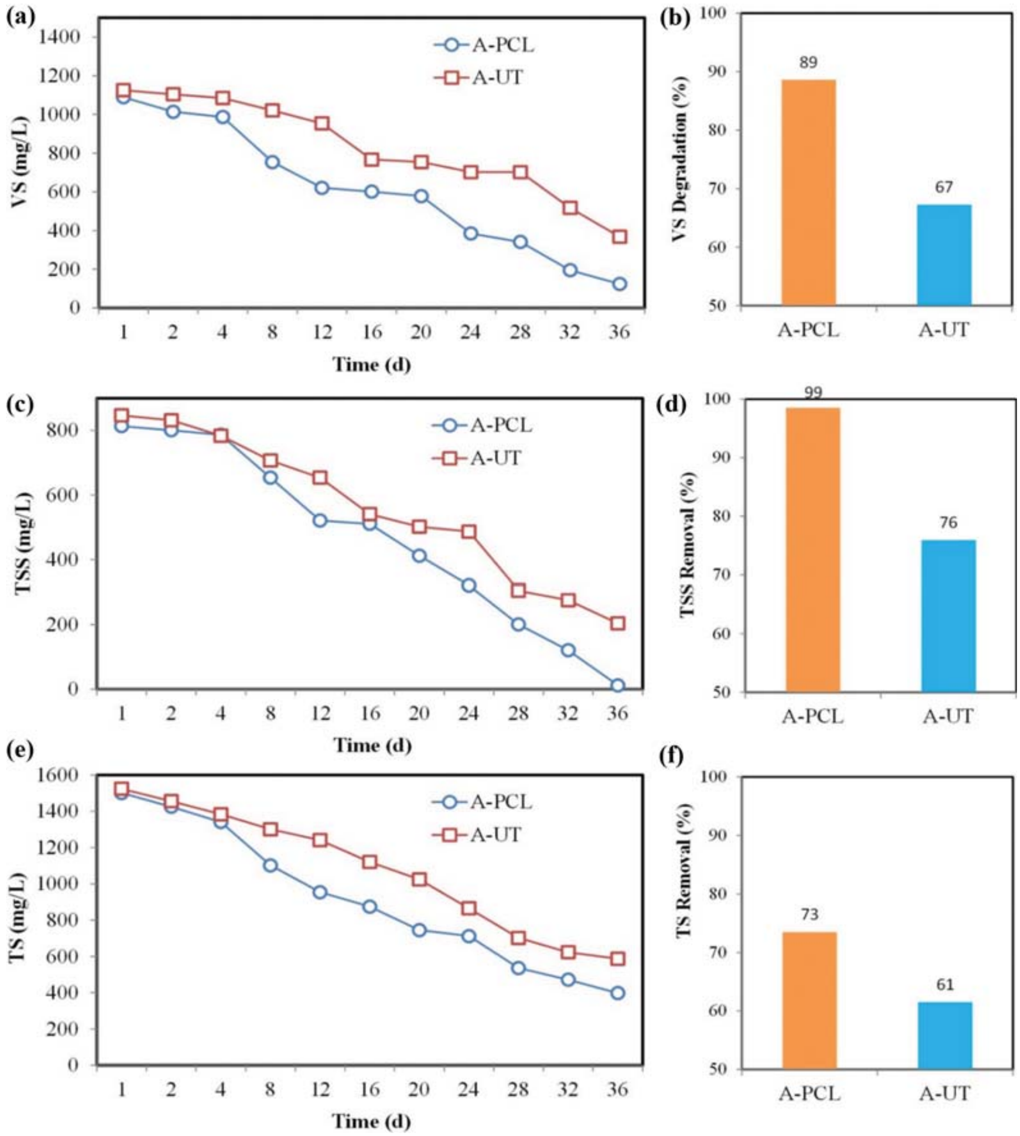

Fig. 4. Aerobic digestion of pretreated (A-PCL) and untreated (A-UT) dairy wastewater: (a), (b) effect on VS content, (c), (d) effect on TSS degradation, (e), (f) effect on total TS degradation.

the current case, the least COD up to 71 mg/L was achieved, which is possibly because of photogeneration of superoxide radicals and hydroxyl radicals during photocatalytic (S-rGO/ZnS) pretreatment, acting as oxidants to complex organics such as fatty acids [3], and converting to the soluble compounds available for aerobic microorganisms. Contrary to that, the untreated dairy effluent showed the minimum value of TCOD 257 mg/L from initial 1,212 mg/L after 36 days. Biological treatment is often hindered by various factors, which include the presence of fats and poor nutrient removal [34,35], where photocatalysis ultimately counters this inhibition and supplies soluble and balanced nutrient.

3-2. Effect on Solid Content (TS, VS, and TSS)

The effect on the removal of solid content in dairy effluent treated under aerobic conditions is explained by various factions of solids which include volatile solids, total suspended solids, and an overall total solid content and results are described in Fig. 4. The VS degradation explained the organic removal efficiency during biological treatment of wastewater. The determination of the biodegradability of organic compounds is an important parameter [36] while studying waste treatment. The VS-based organic removal efficiency during aerobic treatment of photocatalytic dairy effluent, in comparison with untreated dairy effluent, is presented in Fig. 4(a) and 4(b). It was observed that VS decreased from 1,089 mg/L (Day 1) to 124 mg/L (36^{th} day) in photocatalytically pretreated dairy effluent with a maximum organic removal efficiency up to 89%. In the second run, untreated dairy effluent showed the organic removal efficiency stopped by 67% at the 36^{th} day of aerobic treatment. The photocatalytic dairy effluent achieved about 21% increments in organic removal efficiency compared to untreated dairy effluent. This was because the photocatalytic dairy effluent possessed more soluble organic compounds as discussed in the previous section, which are available in solution for microbial degradation.

The results regarding the removal of TSS in dairy effluent are illustrated in Fig. 4(c) and 4(d). Similar to VS, the TSS was removed at a more significant rate in pretreated dairy effluent as compared to untreated effluent. The maximum TSS removal was 99% in photocatalytic dairy wastewater, which was 23% higher compared to untreated dairy effluent (76%). TSS was reduced to 12 mg/L form 814 mg/L after aerobic treatment using photocatalytic pretreated dairy effluent. Overall, up to 73% solids in dairy effluent were removed from pretreated dairy effluent compared 61% in untreated dairy effluent (Fig. 4(e) and 4(f)).

3-3. Effect on pH and EC

During biological degradation processes, pH plays a crucial role that determines the microbial activity of the process [37]. The results in Fig. 5(a) show that the pH remained in the close range of 6.5-7.56 in photocatalytic dairy effluent and 6.5-7.45 in untreated dairy effluent. Initially, pH values were slightly increased in both runs, thereafter pH values dropped to 7.12 (A-PCL) and 6.91 (A-UT) after 36 days of treatment. The optimum pH range lies between 6.8-7.2 for biological treatment process of wastewater, where in the present study, both runs showed that the pH remained under the optimum conditions after eight days of the startup process.

EC is widely applied as a parameter to determine different ion and salt concentration during the biological degradation process

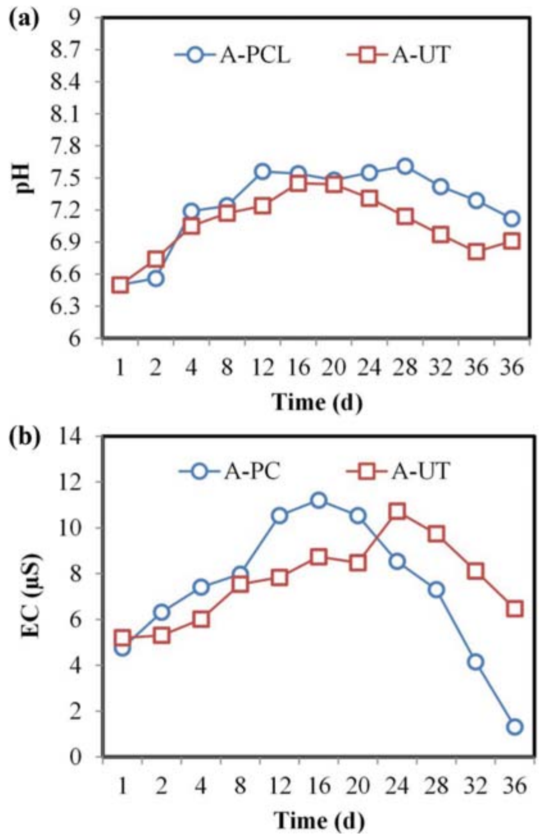

Fig. 5. Aerobic digestion of pretreated and untreated dairy wastewater (a) effect on pH, (b) effect on EC.

[38]. The results regarding the effect on EC valued during aerobic digestion of dairy effluent are presented in Fig. 5(b). There was no significant difference observed in both cases. In the first run, using photocatalytic dairy effluent EC 11.21 µS after just 16 days. This increase in EC values during aerobic digestion is attributed to the successful degradation of the content of dairy effluent and production of several ions in the solution. Thereafter, EC continuously dropped in both runs due to the microbial activity where the lowest values of 1.31 µS and 6.47 µS were observed in photocatalytic dairy effluent and untreated dairy effluent, respectively.

3-4. Dairy Effluent Quality Analysis

To identify the real success of the photocatalytic-aerobic treatment employed in the present work, a wastewater quality analysis was performed before and after treatment. The wastewater quality analysis was performed for aerobically digested photocatalytic and untreated dairy effluent and compared with the PME General Environmental Regulation, 2001 of Saudi Arabia [39] (Fig. 6 and Fig. 7). The results showed that the aerobic treatment of photocatalytic dairy effluent achieved the values for water quality parameter under permissible limits compared to the untreated effluent. The COD was reduced to 71 mg/L (94% lowering) after 36 days of aerobic treatment, while untreated dairy effluent achieved up to 257 mg/L (79% lowering) of COD, which was quite higher than permissible limits (150 mg/L). TS content was reduced by 73.5% and 61.5% in photocatalytic and untreated dairy effluent, respectively. The nitrogen content also showed lowering during aerobic

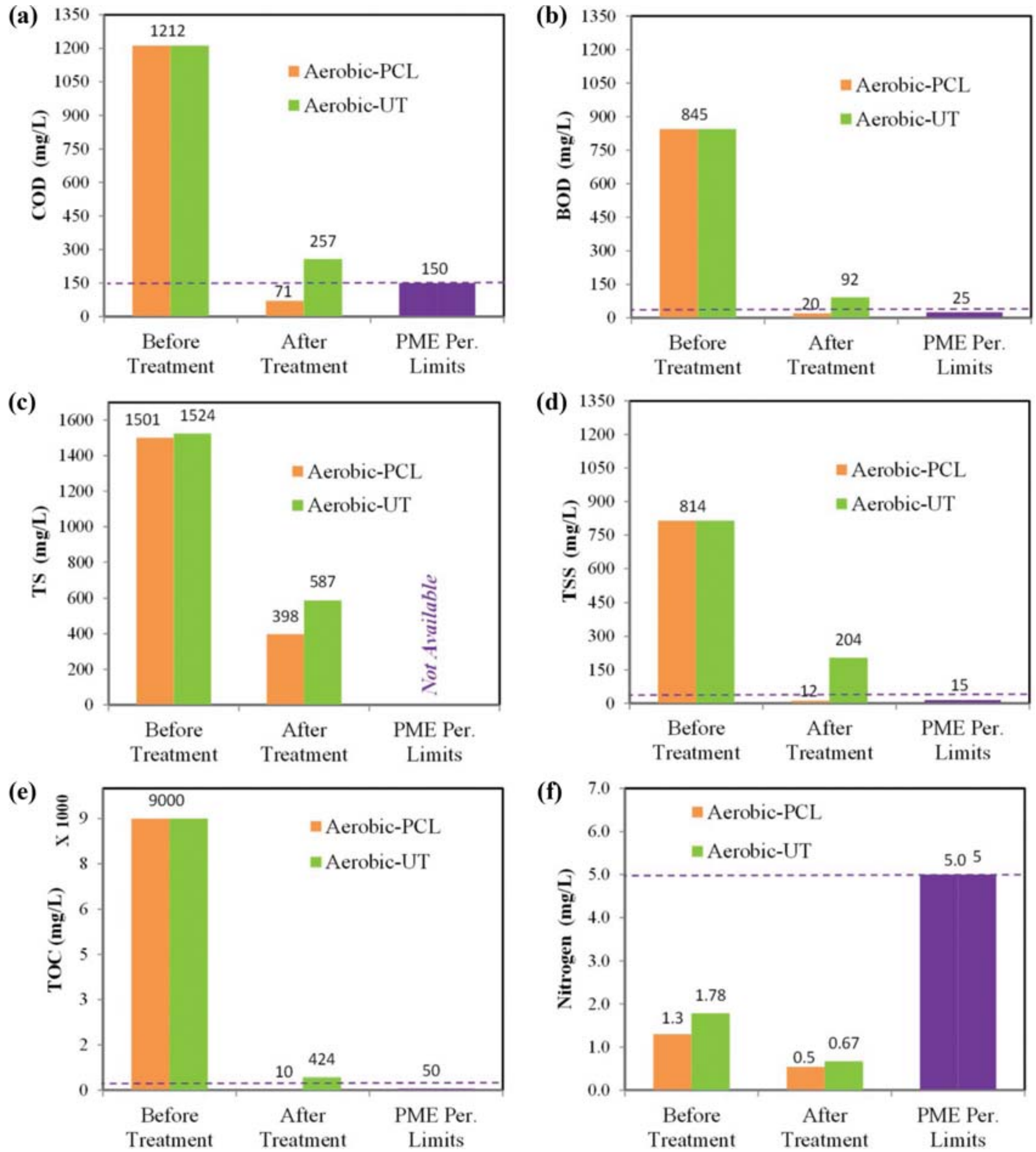

Fig. 6. Quality analysis of aerobically digested untreated and photocatalytic dairy effluent: (a) COD, (b) BOD, (c) TS, (d) TSS, (e) TOC, (f) Nitrogen (The dotted line shows the standard permissible limit, PME, 2001).

digestion of photocatalytic dairy effluent, i.e., 1.5 mg/L to 0.54 mg/L. Similarly, TOC decreased from 9,000 mg/L to 10 mg/L in photocatalytic dairy effluent ,whereas in case of untreated dairy effluent, TOC was lowered to 424 mg/L compared to 50 mg/L as a permissible limit. Similarly, the other quality parameters, alkalinity (25.8 mg/L), EC (1.31 μS) and pH (7.12), were more promising in photocatalytic dairy effluent as compared to untreated effluent. It is important for the dairy plant to discharge their effluent into the environment so as not to damage quality water bodies and confirm that Environmental Quality Standards (EQS) are met [11]. Therefore, it was found that aerobic treatment of dairy effluent using additional photocatalytic step achieved high treatment efficiency, thus achieving effluent with high water quality under acceptable standards.

CONCLUSIONS

Photocatalysis-aerobic treatment was successfully applied for dairy industrial effluent. The results indicated that the photocatalytic pretreatment using S-rGO/ZnS nanocomposite under solar light improved the solubilization of complex organic compounds, especially fats present in dairy effluent. The SCOD in dairy effluent after photocatalysis pretreatment increased from the initial 267 up to 570 mg/L, which represents an overall 113% increase. In subsequent aerobic treatment, the photocatalysis improved digestibility of dairy effluent due to improved solubilization of organic components. Maximum COD removal (94%) with the final value of 71 mg/L was achieved under photocatalytic pretreated dairy effluent, while only 79% COD removal was showed by the untreated

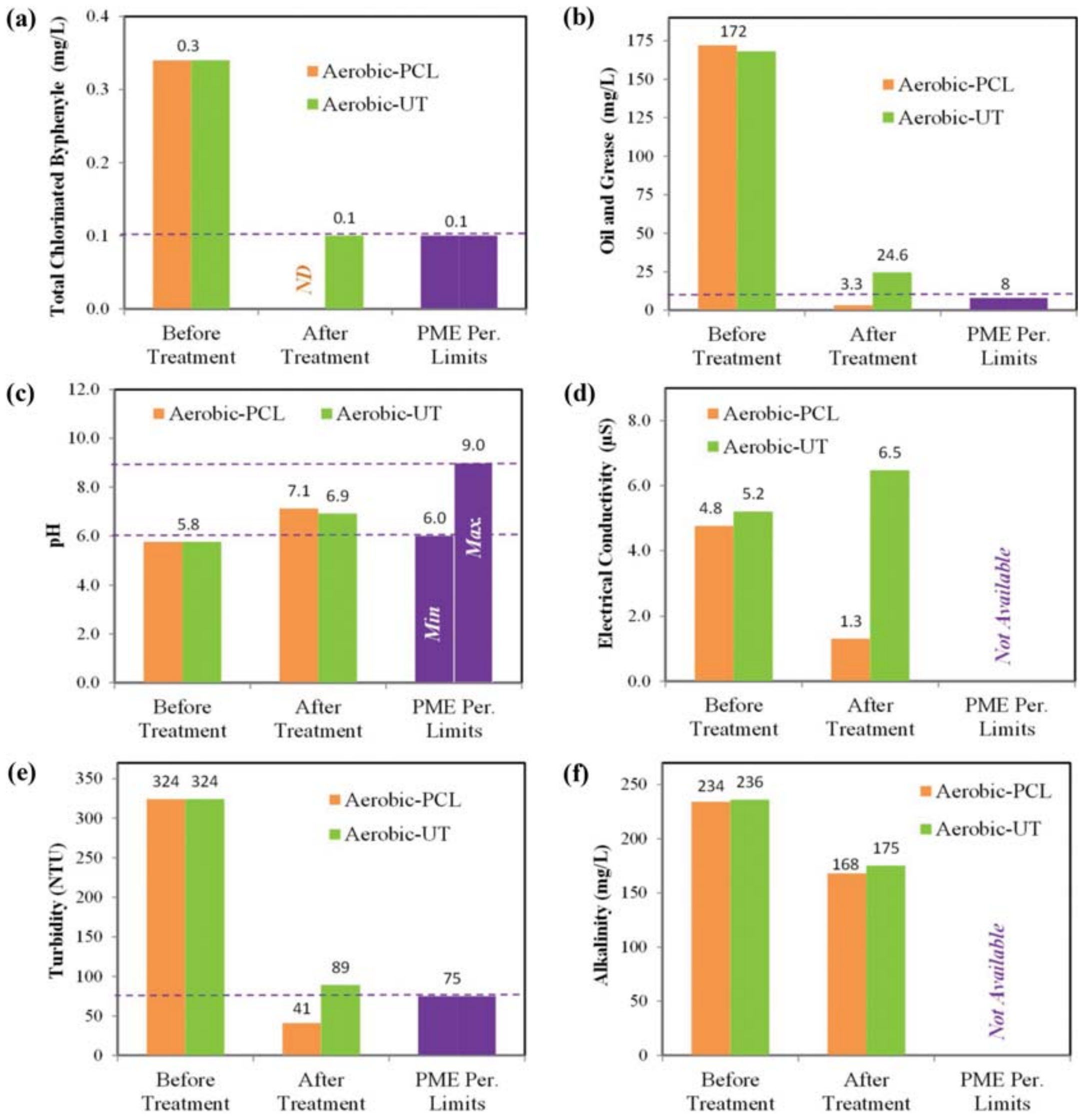

Fig. 7. Quality analysis of aerobically digested untreated and photocatalytic dairy effluent: (a) Total chlorinated biphenyl, (b) Oil and grease, (c) pH, (d) EC, (e) Turbidity, (f) Alkalinity.

substrate. Total VS decreased from 1,089 mg/L to 124 mg/L with maximum organic removal efficiency up to 89% during HRT of 36 d. Overall, this study provides a novel application of solar photocatalysis as alternative pretreatment of dairy effluent in order to establish a unified photocatalysis-aerobic treatment process.

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ACRONYMS

COD : chemical oxygen demand
SCOD : solubilized chemical oxygen demand
BOD : biological oxygen demand
EC : electrical conductivity
PL : photolysis
PCL : photocatalysis
A-UT : aerobic-untreated dairy effluent
A-PCL : aerobic-photocatalytic dairy effluent
mg/L : milligram per liter
OH : hydroxyl radical
HRT : hydraulic retention time
TS : total solids
TSS : total suspended solids
VS : volatile solids
h : hour

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