Solar Light Assisted Catalysis Process with G-C_3N_4Nanomaterialsto Improve Biological Treatment of Cheese Whey Wastewater

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ABSTRACT

In the current study, a visible light catalyst g-C_3N_4 was prepared and evaluated to be applied as a pretreatment process to enhance the biodegradability of organic pollutants in Cheese Whey wastewater. The photocatalysis pretreatment was performed using the solar photo chemical reactor for a duration of 8-9 hours, and the optimization of the process was evaluated under varying catalyst types such as traditional TiO2 and visible light g-C_3N_4, application dose of catalyst and pH of the system. The results indicated that g-C3N4 achieved the most promising results in terms of solubilization of insoluble fats and protein of cheese whey wastewater. The application dose of 0.75g/L and pH 5-6 showed the most acceptable results where soluble COD was 7876 mg/L and 7976 mg/L which were achieved from the initial values of 5765 mg/L. The follow up reaction of aerobic digestion which was performed in the continuous mixing aerobic (CMA) bioreactor for a duration of 70 day, revealed the efficient performance in terms of tCOD degradation. The lowering of tCDO from 8078 mg/L to 432 was achieved with the pretreated cheese whey wastewater in comparison with the untreated wastewater, where tCOD was lowered to 2634 mg/L. Similarly, a considerable improvement in other water quality parameters such as Nitrogen, pH, EC, sulfates, alkalinity and, oil and grease was achieved with the pretreated cheese whey wastewater. It has been concluded that, this study has a great potential to be applied at the industrial level as the pretreatment process is simple and highly economical due to its dependence on the freely available solar light

Key Words: g-C_3N_4, catalysis, cheese whey, wastewater biological degradation, solar light

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INTRODUCTION

The number of dairy industry is increasing worldwide due to the increasing demand of milk and milk products [1, 2]. One of the major effluent producing food processing industry is a dairy industry [3]. Wastewater is produced in different operations and cleaning units [4]. Dairy proceeding units involve conversion of milk to various products including yogurt, butter, cheese, ice cream, desserts and various milk based drinks. All these processes require continuous cleaning and maintenance of the equipments, therefore wastewater with mild detergents and cleaners is produced along with the processing of milk to whey, cheese and ice-cream producing large volumes of wastewater. Dairy wastewater is often characterized by high lactose, lipids, soluble proteins, minerals and low concentration of heavy metals and detergents [1, 2, 4]. Apart from these high temperatures (30-40°C), CODs [5-7] are specific characters that make dairy effluents an environmental nuisance.

Therefore, the treatment of dairy wastewater is critical to ensure the environmental security. Conventional methods usually involve aerobic processes like the activated sludge process [3]. But high organic molecules, nutrients including phosphates and minerals, fats and oils which are often hard for biological degradation affect the biological processes for wastewater treatment [8]. These sow degrading molecules are usually fats and oils that consist of straight chain fatty acids with branches of esters and glycerols. On degradation, such molecules produce long chain fatty acids that are usually toxic to the micro-organisms, hinder the overall treatment process. However, the option of pretreatment of waste could be opted to increase the efficacy of the dairy wastewater treatment. Various effective pretreatment methods are

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employed for the pretreatment of dairy wastewater, including tilted plate separators, grease-trap and dissolved air flotation. However, the pretreatment cost of these processes is usually high, and the removal efficiency of fats and oils is also low [9]. Therefore, alternate methods to reduce fats and oil contents of the dairy wastewater prior to the biological treatment are required to increase the process efficiency.

Among different alternate pretreatment options, photo catalysis using semiconductors is the most viable option due to its comparatively low cost and high efficiency [10]. The overall process involves 'Honda–Fujishima Effect' which includes the oxidation of targeted compounds by the attack of OH°, which has the strong oxidation potential where its large band gap (about 3.2 eV) and high electron-hole recombination confine its application [11]. Where, among the different semiconductors reported so far, TiO_2 is well known for its application in the environmental remediation and energy efficiency [12], however, the requirement of UV for the activation of TiO_2 increases the associated operational cost. So, alternatively the use of phototocatalyst provides significant economic incentives [13].

Different semiconductor phototocatalysts have emerged as a potential option for pretreatment and waste degradation for instance metal-free graphitic carbon nitride (g-C_3N_4) which has significant applications due to the low toixicity, high earth abundance, thermal and chemical stability [14]. Similarly, nano g-C_3N_4 structures are effective phtotocatalysts due to the high active sites [11]. It has also been reported as the most stable carbonitride [15, 16]. Therefore, it remains stable under light irradiation in water, alkalies and acids [17]. Further, its band gap energy is 2.58–2.89 eV [18]. These attributes make g-C_3N_4 a potential photocatalyst under visible light. The present study was planned to achieve the high biodegradation potential of cheese whey (CW) wastewater through photocatalytic pretreatment. The visible light active g-C_3N_4 nanomaterials photocatalysts (NPP) were synthesized using semiconductor photocatalysis in the photocatalytic pretreatment of CW wastewater. The pretreatment efficiency was also compared with the traditional TiO_2. Finally, the subsequent biological treatment was evaluated in a lab based aerobic degradation reactor using the pretreated and untreated CW wastewater.

MATERIAL AND METHODS

1. Chemicals and wastewater samples

The chemicals used for the synthesis of g-C_3N_4–NPP catalyst was melamine ($C_3H_6N_6$) (Sigma Aldrich), while the analytical grade P25 TiO_2 powder (Degussa Co.) was used as a reference catalyst. Dionized water was used for the washing and dilution purposes during chemical analysis. For adjustment of pH, 1M solutions of each NaOH and HCl were used. CW wastewater samples were obtained from a big dairy wastewater industry (name not allowed to mention), located in the industrial zone in Jeddah, Saudi Arabia. The initial physicochemical properties of CW have been summarized in Table (1).

Table 1. Physicochemical properties of cheese whey wastewater

Parameters	Units	Values
tCOD	g/L	8.287 ± 0.49
sCOD	g/L	5.765 ± 0.43
Total Solids	g/L	34.23 ± 1.9
Total Carbon	g/L	26.7 ± 1.8
Total Nitrogen	%	0.6 ± 0.01
C/N Ration	-	44.5 ± 2.3
pH	-	8.72 ± 0.12
Alkalinity	mg/L	390 ± 21.3
Sulfates	mg/L	97 ± 4.21
Oil and Grease	mg/L	174 ± 5.43

2. Catalysts preparation and characterization

For preparation of g-C_3N_4-NPP, a simple, facile thermal heating method was applied as described in the literature [11]. In a typical synthesis, about 5 g of melamine powder was measured and transfered into an alumina crucible with a cover. The crucible containing was initially heated at 250 ºC with a heating rate of 5.0 ºC/min, and thereafter, the temperature was increased up to 550 ºC at a heating rate of 10.0 ºC/min with a hold of 2 h. The yellow coloured g-C_3N_4 product was collected, and milled to a fine powder with an agate mortar for further use. The synthesized g-C_3N_4-NPPand P25 TiO_2-NPPwere characterized using X-ray diffraction (XRD), UV-visible spectroscopy and photoluminescence (PL) spectroscopy.

3. Photocatalytic pretreatment of CW wastewater

For pretreatment of CW wastewater, a solar glass reactor was used which had the ability to handle 5 litres of wastewater. The solar reactor was attached to a continuous shaking machine and air diffuser that provided oxygen from the bottom of the reactor. The catalyst was applied at a fixed dose in a reactor containing CW wastewater. The treatment was conducted for eight to nine hours under the continuous exposure of solar light. The solar illuminous was continuously monitored using a lux meter for eight hours, and found in the average range of 1908 lx. The experiments were conducted in different runs in order to optimize the effect of reaction time, type and dose of photocatalyst ,and also the effect of photocatalyst itself.

3.1. Effect of reaction time and type of photocatalyst

In the initial run, the pretreatment of wastewater was optimized for the duration of the reaction and type of the photocatalyst. Two types of catalysts were used namely, g-C_3N_4-NPPand P25 TiO_2-NPPwhich were used in separate runs at 0.25 g/L in the reactor. The photocatalyst was evaluated for the duration up to 8 hours under the continuous exposure to the sunlight. The pH of the wastewater was maintained at 6.0 throughout the reaction. The samples were taken at the regular time intervals, and were analysed for the solubilization using sCOD content. The pretreatment was also evaluated in the absence of catalyst, and only at the exposure of the sunlight as a reference test.

3.2. Effect of dosage of catalyst

After optimizing the catalyst type and duration of the pretreatment, the process was optimized for the rate of catalyst application. For this, the catalyst was applied at various doses, i.e. 0.25, 0.5 and 1.0 g/L. The pH was maintained at 6.0 , and the process was evaluated for eight hours. In a similar previous experiment, CODs were measured to evaluate the pretreatment efficiency.

3.3. Effect of pH of substrate

In this set of experiment, the pH of the pretreatment process was optimized in five runs. In each run, pH was maintained at 3.0, 5.0, 6.0, 7.0 and 9.0 ; respectively under the optimum catalyst dose and catalyst type. The pretreatment of CW wastewater showed the best results which was treated in the subsequent biological process which has been described in the later section.

4. Aerobic treatment of CW wastewater

After optimization of pretreatment process, the CW wastewater was subjected to post treatment thorugh aerobic biological process in continuous mixing aerobic (CMA) bioreactor. The reactor in the sequential of photocatalytic reactor had the same capacity of 5 liters. The aerobic bacterial inoclum having the source consortium was added after the enrichment using Lorelei broth liquid media. The inoculum was incubated for 48 hours in a shaking incubator at temperature of 35±1 ºC. Thereafter, the enriched culture was applied at a rate of 10 % in the aerobic reactor. The aerobic degradation process was operated for 70 days, and compared with the reactor containing untreated CW wastewater. The efficiency of the process was analysed by measuring COD remo val and the rate of organic matter degradation.

5. Procedures

The pretreatment efficiency was analysed by measuring variations in sCOD, whereas the efficiency of biological degradation was analysed by tCOD removal. Other water quality parameters were analysed before and after the treatment process which included VS, TS, C, C:N, pH, EC, alkalinity, sulfates, oil, and grease content. All the parameters were analysed by using APHA, 2005 [19] test methods. The significance of the data was statistically analysed by applying ANOVA using Microsoft office excel program 2013.

RESULTS AND DISCUSSIONS

1. Characteristics of Catalysts

The characterizations of the nanomaterial catalysts were conducted using various techniques including UV-visible spectroscopy, photoluminescence (PL) spectroscopy, and X-ray diffraction (XRD). The optical properties of g-C_3N_4 NPP and TiO_2 NPP were investigated with UV-visible spectroscopy, which have been shown in figure 2. TiO_2 NPP showed the absorbance of light in less than 400 nm wavelength, due to the wide band gap (3.2 eV) of TiO_2 [20]. Contrary to this, g-C_3N_4 NPPshowed more absorption of light in visible range from 400 to 480 nm, and thereafter a constant absorption was observed in a visible range.

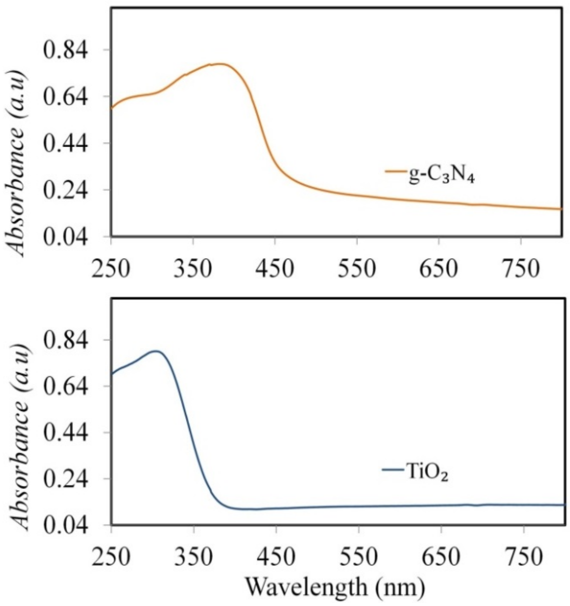


Fig. 1. UV-visible spectroscopy of g-C3N4 and TiO2 nanomaterials

To examine the charge transfer and separation properties of carriers of prepared NNP, PL spectra were tested, and the results have been described in Figure 2. The PL intentsity was higher in case of TiO_2 NPP as compared to that of g-C_3N_4 NPP. It has been known that at lower PL intensity, there will be less chance of the electron-holes recombination [21]. Thus, the recombination of charges (electrons and holes) was considerably prohibited at the surface of the surface catalyst, which resulted in the generation of more photo induced electrons-holes [17].

The phase and plane of the prepared materials were investigated by XRD spectra which have been shown in Fig. 3. The pure g-C_3N_4 NPP showed two main peaks at angle (2θ) of 13.0 ˚ and 27.4˚ which have also been reported by [22]. Another strongest peak at 2θ of 27.4˚ was recorded which was associated with 110 diffraction planes with the DB card no. 050-512. Probably, this strongest peak was linked to the stacking and conjugated aromatic rings structure in the discotic system. In case of TiO_2 NPP, the diffraction peak at 2θ of 24.2 having plane 101, settled the anatase crystal phase structure of TiO_2 NPP [11].

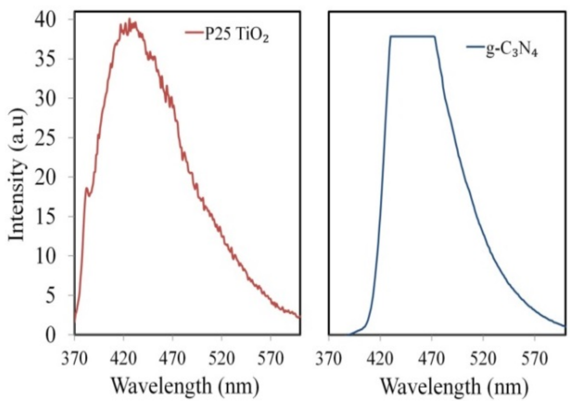


Fig. 2. PL-Spectra of g-C3N4 and TiO2 nanomaterials

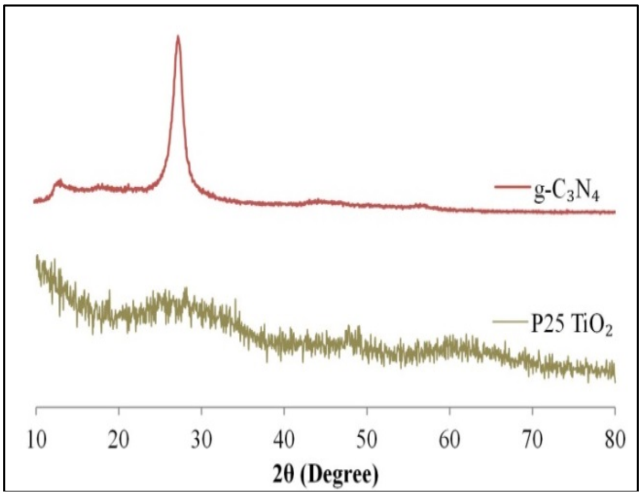


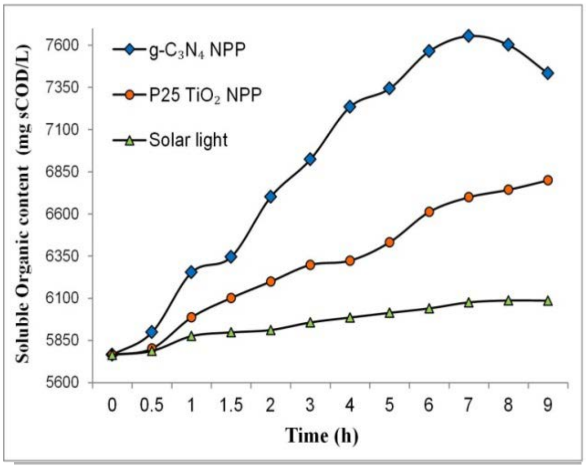
Fig. 3. X-ray diffraction of g-C_3N_4 and TiO_2 nanomaterials

2. Optimization of photocatalysis process (pretreatment of CW wastewater)

CW wastewater is rich in insoluble fats and lipids, thus it has a part of the insoluble organic content in its wastewater. To improve the degradation of complete organic matter in CW wastewater, a pretreatment was performed using photocatalysis process. The pretreatment was optimized for various factors which have been explained in the following sections.

2.1. Effect of reaction time and type of photocatalyst

The effect of reaction time and the type of photocatalyst such as g-C_3N_4-NPP, and the traditional Titania were examined using catalyst application dose of 0.25 g/L at the constant pH of 3.0. The results have been depicted in Figure 4. During the nine hours of reaction under the sunlight, it was observed that the soluble organic content increased more rapidly with g-C_3N_4 NPPas compared to that with TiO_2. After 9 hours, the highest sCOD was attained up to 7432 mg/L which was improved by 28.9 %, from its initital value with g-C_3N_4-NPP. Comparitivley, COD was improved by only 17.93% with TiO_2-NPP where the values were incremented to 6799 mg/L from 5765 mg/L in the first hour. The higher improvement in COD with g-C_3N_4 NPPwas associated with its capacity to absorb more visible part of the solar light [23] as compared to the that with TiO_2-NPP. As shown in the figure, the peak of sCOD (7654 mg/L) was obtained at 8th hour of reaction which revealed that the optimum time for solar phtocatalysis with g-C_3N_4-NPPwas seven hours. In contrast with the pretreatment of CW wastewater without catalyst i.e. only under the sunlight exposure, no significant change in sCOD (4.1 %) was observed which showed that catalyst had a higher potential of pretreatment compared to the sunlight only.



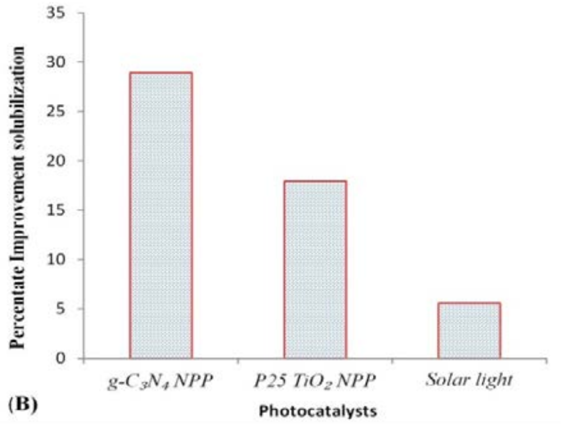


Fig. 4. Effect of light assisted preatretment using g-C3N4, TiO2 and solar light on solubilization of cheese whey wastewater (NPP = nano particles photocatalyst)

2.2. Effect of dosage of catalyst application

In this set of experiments, the raw CW wastewater was pretreated at different dose of catalyst and compared with TiO_2-NPPas a reference catalyst. The experiments were performed in separate runs at varying amounts of each catalyst that were 0.25 g/L, 0.75 g/L and 1.75 g/L, while the pH 6.0 and the duration of monitored 7 hours (optimum) were fixed throughout the reaction. A comprehensive description results have been explained in Figure 5. It can been in figure 5a that the sCOD was improved with the increase in the dosage of the catalyst where sCOD content of 8064 mg/L (g-C_3N_4 at 0.75 g/L) and 7976 mg/L (g-C_3N_4 at 1.25 g/L) were observed compared to 7601 mg/L (g-C_3N_4 at 0.25 g/L). Both of the higher doses of catalyst showed a significant higher solubiliztion efficiency compared to the lower dosages of the catalyst, however, the difference between both of the higher doses was quite low, and could be ignored. Thus, it can be said that g-C_3N_4-NPPat a dose of 0.75 could be ideal for pretreatment of CW wastewater. The effect of catalyst dosage in case of TiO_2, no promising results were observed, where even the highest rate of TiO_2 showed lower sCOD (6932 mg/L) as compared to sCOD (7601 mg/L) with the lowest rate of catalyst application.

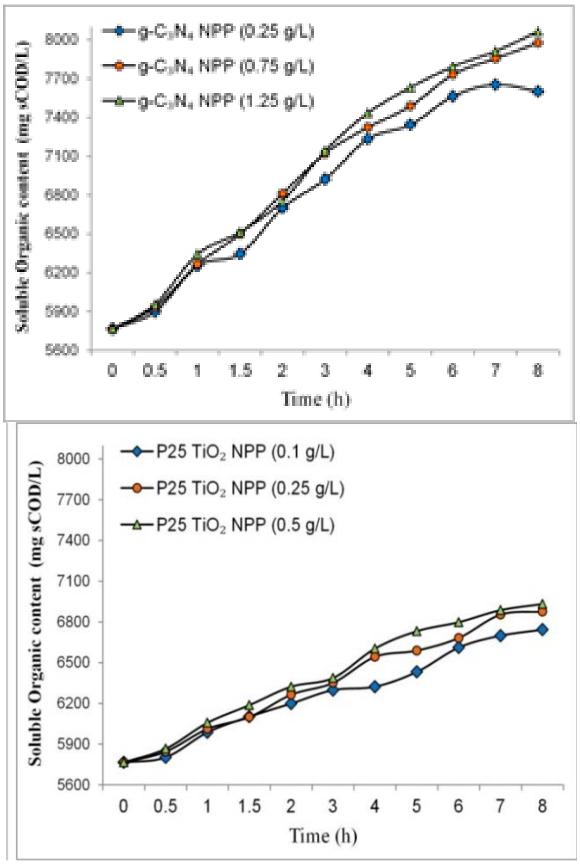


Fig. 5. Effect of various doses of g-C3N4, TiO2 and solar light on solubilization of cheese whey wastewater (NPP = nano particles photocatalyst)

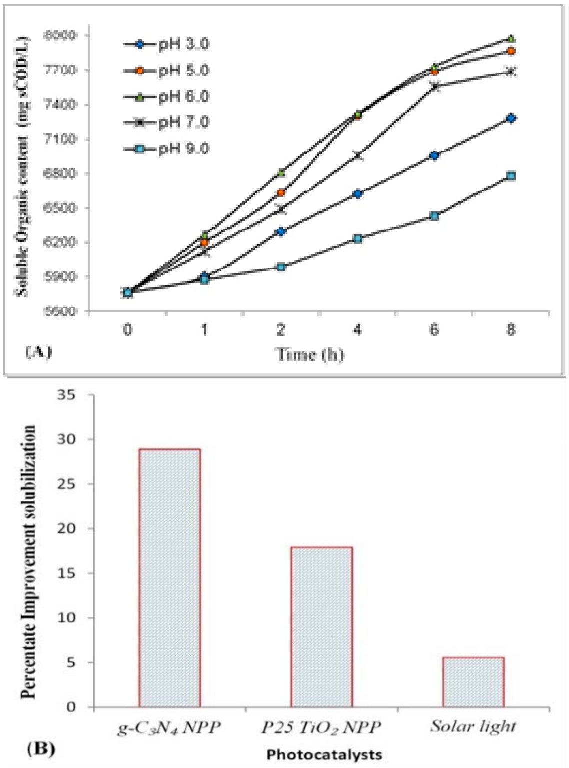


Fig. 6. Effect of pH on solubilization of cheese whey wastewater using g-C3N4 (NPP = nano particles photocatalyst)

2.3. Effect of pH of substrate

pH is one of the most important operating parameters which affects the process of photocatalysis. Various pH levels (3.0-9.0) were maintained in the CW wastewater during the pretreatment process. Other conditions such as catalyst time, type and dosage of catalyst (g-C_3N_4-NPP) were maintained at the optimum level as achieved in the previous section. The results in figure 6 explained that the change in pH significantly affected the solubilization of the organic matter in the CW wastewater. The pH range between 5-6 showed the most acceptable results where the soluble sCOD of 7876 mg/L and 7976 mg/L were achieved. On the other hand, as the pH was lower than 5 to 3, COD was lower as compared to the acidic range. Similarly, the higher pH beyond the neutral range also lowered the COD (6781 mg/L). The maximum improvement in COD formation was remained intact up to 39.3 % at pH 6.0 which revealed that the catalyst g-C_3N_4–NPP was highly active in a higher acidic range. The basic mechanism of the photocatalytic reaction was related to the production of some active species like hydroxyl radicals (OH), hydroperoxyl radical (HO), the superoxide radical (O_2), and the holes. Under visible light source, the hydroxyl radicals (OH) acted as the primary oxidants which were produced by the direct hole oxidation or might be photogenerated electron induced multistep reduction of the O_2 dissolved in the solution [24].

3. Effect of pretreatment on aerobic digestion of CW wastewater

The aerobic digestion of the pretreated CW wastewater with g-C_3N_4 –NPP at 0.75 g/L, pH 6.0, and 6 h) was performed in the CMA bioreactor for the duration of 70 days. The results regarding the degradation efficiency of tCOD have been explained in Figure 7. It can be found in Figure 7A that aerobic digestion of pretreated CW wastewater showed the considerable higher rate of degradation as compared to the untreated CW wastewater, as the wastewater from dairy industry basically was composed of carbohydrates (lactose), and large organic molecules such as fats, proteins' oil and grease. They had a high molecular weight and a low biodegradability coefficient, therefore outlined by high COD [25]. This problem could be solved by using catalysis preatreament of the wastewater. In the experimental results, both untreated and pretreated reactors initially showed sudden peaks (190 mg/L/d and 202 mg/L/d, respectively) within 2 days of digestion, which was due to the suddenly available organic matter to the microorganisms, thereafter, the degradation rate became stabilized. With the gradual increment, the highest rate of degradation (254 mg/L/d) was achieved at 60th day in the pretreated reactor. The degradation was monitored for 70 days which showed a sharp decline due to the low availability of organic matters in the system.

Figure 7B and 7C depict the overall removal of tCOD during aerobic reaction. In pretreated reactor, tCOD was lower than 432 mg/L after 70 days of the digestion process, whereas the untreated reactor with lower potential of degradation achieved 2634 mg/L of tCOD values. As a whole, tCOD removal was only 68.2 % of its initial value in untreated CW wastewater, where 94.7 of tCOD removal was achieved by photocatalytic pretreated CW wastewater. It has been reported that the cheese whey wastewater usually has increased the concentration of tCOD varying between 800–7700 mg/L [26], where the approach used in the current study showed the higher tCOD removal efficiency of the aerobic digestion which revealed that the process had a great potential to attain the clean water under the compliance of the local environmental standards.

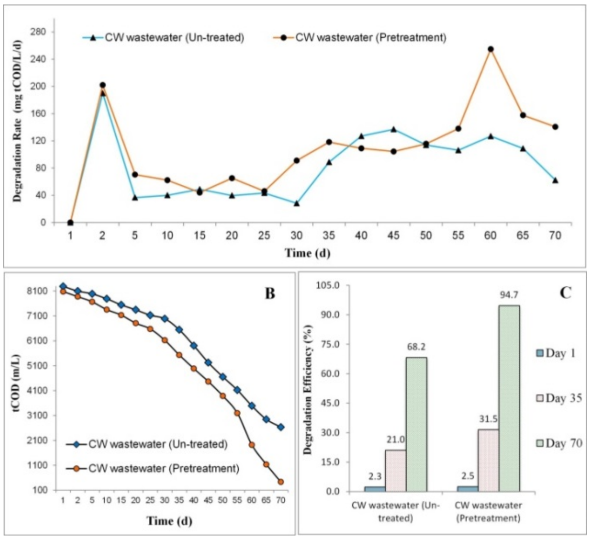


Fig. 7. Aerobic treatment of pretreated cheese whey wastewater (A) Rate of COD degradation, (B) tCOD removal, (C) Percentage of degradation of organic matter (COD based)

4. Evaluation of performance efficiency of treatment process

The performance efficient of the treatment process was evaluated by analyzing various water quality parameters such as COD, TS, N, C/N ratio, pH, alkalinity, sulfates, oil and grease content. The analytical results in the Table 2 depict the physiochemical properties of CW wastewater before and after the treatment processes. It was found that all of the water quality parameters showed more improvement under the aerobic digestion of the pretreated CW wastewater as compared to that with the untreated CW wastewater.

In dairy wastewater, such as CW processing, there were high COD values as observed 8.28 g/L. This was due to the hgih organic content mainly represented by the assimilable carbohydrates and slowly degradable lipids and proteins characterised by COD values up to 100 g/L [7, 27, 28]. In the current study, the tCOD was decreased efficiently to 0.43g/L by the pretreated CW wastewater which was 6 times lower as compared to the tCOD (2.63 g/L) by the untreated wastewater. This was due to more rapid degradation of total solids (5.43 g/L) i.e. 84 % by the pretreated wastewater from the initial TS content of 34.23 g/L.

The nitrogen and C/N was recorded as 06% and 44.5 respectively in initial samples of CW wastewater. Nitrogen exists usually as amino groups of milk proteins and nitrogenous compounds such as uric acids, urea and, NO_3^- NH_4^+ and NO_2^- ions [26, 29]. The nutrients as C/N were observed in more optimum range (16.5) required for the microorganism in pretreated wastewater. The C/N mainly linked to the amount of N presented in the system where lower N content was lower down to 0.35% and 0.2 % from 44.5% in the pretreated and untreated wastewater.

pH of the CW wastewater was recored as 8.72 which was lowerd to 6.71 and 6.81 after the aerobic digestion of the untreated and pretreated CW wastewater; respectively. Contrarily , it was previously reported that the pH in cheese manufacturing wastewater was slightly acidic in the range of 5.9–6.6 [26].

Alkalinity has been one of the crucial parameters in the wastewater treatment process which has been defined as the ability to neutralize acid and/or to absorb hydrogen ions in the wastewater. Dairy effluents have been characterised by very low alkalinity (approx. 2.5 g/L expressed as $CaCO_3$ in milk permeate), thus bringing about a potential for the rapid acidification and increased reagent costs for pH maintenance during the purification [30, 31]. Similarly, in the present study, the alkalinity was recorded as very low that is 390 mg/L in CW wastewater, which was further lowered to 276 mg/L and 124 mg/L after the aerobic degradation of the untreated and pretreated CW wastewater samples; respectively.

Similarly, the other pollutants such as sulfates (97 mg/L) and, oil and grease content (174 mg/L) also showed significantly more removal efficiency in the pretreated CW wastewater (22 mg/L and 5.0 mg/L) as compared to that by the untreated CW wastewater (32 mg/L and 45 g/L); respectively

Table 2. CW wastewater characteristics before and after the treatment process

Parameters	Initial values (Day 1)	Final values (Day 21)	
		Biological treatment of Raw CW wastewater	Biological treatment of pretreated CW wastewater
tCOD (g/L)	8.287	2.63	0.43
sCOD (g/L)	5.765	1.87	0.34
Total Solids (g/L)	34.23	9.65	5.43
Total Carbon (g/L)	26.7	7.43	3.21
Total Nitrogen (%)	0.6	0.35	0.20
C/N Ration	44.5	21.2	16.5
pH	8.72	6.71	6.85
Alkalinity (mg/L)	390	276	124
Sulfates (mg/L)	97	32	22
Oil and Grease (mg/L)	174	45	5.0

ACKNOWLEDGEMENT

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CONCLUSIONS

This work successfully demonstrated the applicability of the emerging g-C_3N_4-NPP to be used for the pretreatment of CW wastewater to supply more solubilized organic matters for biological degradation. The solar light harvesting ability of g-C_3N_4-NPP revealed the significantly improved generation of photo-excited electrons in comparision with the conventional UV light active TiO_2. Moreover, the efficient charge carrier separation restricted the recombination process thus improved the photocatalytic process. The efficient pretreatment efficiency was achieved by g-C_3N_4-NPP at the optimum dose of 0.75 g/L and pH range of 5-6. Further, the aerobic digestion that pretreated the wastewater achieved the COD degradation up to 94.7 %. In general, there has been no doubt in applicablity potential of this which has been approved in industry under the consideration of the utilization of the natural solar as the source of light for the photocatalysis process.

Highlights

- Visible light catalyst g-C3N4 was prepared.
- The pretreatment of cheese whey's wastewater was conducted using a solar light catalysis process with g-C_3N_4 .
- The highest solubilization was achieved at 0.75g/L of catalyst and pH 5-6.
- In the follow-up aerobic digestion, lowering of tCOD from 8078 mg/L to 432 was achieved.

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