

Experimental analysis on the synergistic effect of combined use of ozone and UV radiation for the treatment of dairy industry wastewater

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The present study focused on the various advanced oxidation processes; Ozone, UV radiation, O₃/H₂O₂, O₃/UV, UV/H₂O₂ and O₃/UV/H₂O₂ for treatability of dairy industry wastewater. With this aim, the trials were carried out in cylindrical reactor fortified with UV radiation and Ozone injection. Efficiency of the treatment process was evaluated considering Chemical Oxygen Demand (COD), lactose reduction and process parameters were determined to be reaction time, pH, circulation rate, and H₂O₂ dosage. 32.5%, 35.2%, 25%, 83% COD and 40.6%, 43.6%, 38.2%, 80% lactose reduction efficiency were obtained under the operating conditions for O₃/H₂O₂, O₃/UV, UV/H₂O₂ and O₃/UV/H₂O₂ processes, respectively. As per this outcome, UV/H₂O₂/O₃ process gave more than 65% of COD and 52.36% of lactose reduction efficiency than other hybrid processes. Optimum conditions for $UV/H_2O_2/O_3$ process (pH = 5, time = 180 mins, circulation rate = 50 mL/h and H_2O_2 dosage of 0.5 mL) resulted in 88% of COD and 93.4% lactose reduction.

Keywords: Advanced oxidation process, Chemical Oxygen Demand, Dairy industry, Ozone, UV radiation, Wastewater treatment

1. Introduction

Among the food industrial sectors, dairy industry consumes more amount of water. Dairy plants include milk processing, butter manufacturing, cheese/whey manufacturing, ice-cream manufacturing and milk powder productions were generating the maximum volume of effluent in a day by day activities [1]. In India, approximately one liter of milk processing produces 10 L of effluent and it may vary in different countries and dairy plants [2]. Wastewater from these dairy plants composed of carbohydrates, protein, fats, nutrients, sanitizers and detergents [1]. Among these one kg of protein produces 1.36 kg of COD, lactose produces 1.13 kg of COD, fat produces 3 kg of COD [3]. The pollution load was represented in terms of Biological Oxygen Demand (BOD) (40-48,000 mg/L), Chemical oxygen demand (COD) (80-95,000 mg/L), Total Suspended Solids (TSS) (24-88,000 mg/L) and pH (4.2-9.4) and

its values could be varying with season conditions [4, 5]. Discharging of dairy effluents to water bodies prior to treatment creates various human diseases such as yellow fever, dengue fever, chicken guniya, diahria, lunk cancer and kidney failure etc., [6]. Continuous degradation of casein, lactose and presence of microorganisms create oxygen depletion in receiving water body causes odor, turbidity and eutrophication which was hazardous to fish and algae [5, 7]. The selection and design of proper treatment methods were essential to increase the treatment efficiency of dairy effluent plants [8].

Biological processes such as aerobic and anaerobic, physicochemical processes such as electrocoagulation, membrane process and adsorption were widely used to treat the dairy effluent due to the presence of rich in organic matter [9, 10]. However, the above-mentioned treatment processes produce maximum amount of sludge, periodical maintenance, hydraulic/solid retention time, requirement of pretreatment, cost of electrodes/coagulants/adsorbents, recovery



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of coagulants/adsorbents, difficulties faced in disposal of sludge, cost of electricity and membrane, periodical replacement of electrode/membrane and toxicity of effluent leads to limitation of the process [11-14]. Although these methods produce considerable results in pollutant removal, its not give complete elimination of pollution load in dairy effluents.

In order to achieve the complete degradation of pollutants, the usage of Advanced Oxidation Methods (AOPs) in dairy wastewater was considerably increasing. In AOP, the generation of highly active chemical species as hydroxyl radicals which has a tendency to react with pollutants and converted into CO₂ and H₂O [15, 16]. Ozone was one of the AOP, which was directly or indirectly (in the form of secondary radicals) reacts with organic compounds [17]. As the ozone alone in dairy treatment process should not promote complete mineralization of organic compounds. Hence, the efficiency of ozone process was enhanced by the addition of catalytic reactants such as UV radiation, fenton and H₂O₂ [18-20]. Nowadays most of the researchers were concentrating on AOP due to the following advantages such as generation of ozone consumes less energy, no sludge production, decrease in volume of sample, less treatment time, gaseous state, easy maintenance, simple and reliable operation which considerably increased the treatment performance of dairy wastewater [18, 19, 21]. In the AOP process, compared to an individual, hybrid processes such as O₂/H₂O₂, O₃/UV and UV/H₂O₂ processes were mostly used to treat the different industrial wastewater includes hospital, pharmaceutical, winery, olive oil and textile [22]. Although AOP has notable merits, the presence of residual ozone and un-oxidized ozone from the reactor could create harmful effects on the human being. Proper installation of ozone destruction system in wastewater treatment plants considerably reduces the above-mentioned problems [23].

Efficiency of combined AOP process depends upon the buffering conditions of effluent, concentration of pollutants, temperature, Total Solids (TS), TSS, turbidity, COD and BOD load, ozone concentration, ozone diffusion rate and ozone decomposition rate [24, 25]. The combination of AOP with Biological or physicochemical methods superiorly promotes the treatment performance which creates a possible way to achieving zero pollutant discharge. László, Kertész [26], also proved that the pre ozone treatment with nanofiltration greatly increases the biodegradability of dairy wastewater to 96.4%. This was due to the application of preozonation consid-

erably reduces the membrane flux that could promote the filtrate properties of membrane [27]. In contrast, when applying a fenton as a post-treatment of membrane process, it does not give possible results in pollutant removal due to the formation of ion compounds during fenton reaction [28, 29].

This present study aims to investigate the performance of synergisation of UV radiation with ozone/ H_2O_2 system in simulated and real dairy effluent. The effect of various parameters such as circulation rate, H_2O_2 concentration and pH on pollutant removal interms of BOD, COD, turbidity and color removal were studied. The real dairy industry effluent was treated under the optimum conditions obtained in simulated dairy effluent treatment.

2. Materials and Methods

2.1. Dairy Wastewater and its Characterization

Real time dairy industrial wastewater was collected from the local industry located in Tamilnadu, India and the samples were collected in accordance with standard methods of sampling. Polyethene cans were properly washed with mild detergent and then leached with 1:1 HCl overnight. The containers were rinsed with deionized water before the sampling at the point of discharge. Two different sets of samples were taken in 1,000 mL bottles initially and then poured into other two different five liter cans for homogenization. All the samples were stored in ice box containing well frozen ice until they were taken to the laboratory.

Similarly, simulated dairy wastewater was prepared by dissolving 4 g of skimmed milk powder in one liter of distilled water [30-32]. The milk powder used were of commercial grade and used throughout the experiments without further purification in order to represent the actual conditions. Per 100 g of skimmed milk powder consists 22 g of protein, 18 g of fat and 50 g of carbohydrates. To achieve uniformity throughout the experiment, simulated dairy wastewater was newly prepared before the experimental studies. The prepared simulated dairy wastewater was considered as a representative sample equivalent to the characteristics of real time dairy effluent.

The initial characterization of real and simulated dairy wastewater was characterized as per the standard analytical techniques described by APHA [33] was presented in Table 1.

Table 1. Characterization of Dairy Wastewater

Parameters	Real effluent 1	Real effluent 2	Real effluent 3	Mean	Simulated effluent		
pН	4.58	5.25	4.44	4.76	5	7	9
COD (mg/L)	1,092	975	1,321	1,129	1,920	2,000	2,080
BOD (mg/L)	194	178	245	206	148	152	165
DO (mg/L)	7.44	6.81	9.32	7.86	7.39	7.53	7.79
TDS (mg/L)	9,500	3,500	7,320	6,773	2,310	1,296	1,733
Turbidity (NTU)	1,630	1,390	1,870	1,630	2,051	1,734	1,675
Color	White	Light white	Slightly dark white	***	White	White	White
Lactose (mg/L)	350	305	420	358	298	300	314.52
Conductivity (ms/cm)	3.78	3.24	4.05	3.69	0.5	0.26	0.3
Chloride (mg/L)	370	360	410	380	237	245	260

2.2. Experimental Setup

The experimental setup for Ozone/UV/H₂O₂ system was shown in Fig. 1. It was divided into five parts: (1) Photo reactor, (2) H₂O₂ feed tank, (3) Circulation tank, (4) Ozonator, and (5) Ozone destructor. The photoreactor was made up of glass tube with a diameter of 3 cm and a length of 20 cm. The photoreactor was equipped with the provision for the insertion of UV lamp (Philips) of 16 W power supply 254 nm wavelength at the top of the reactor and ozone gas from the ozonator (Faraday ozone FVP10-136) was introduced from bottom of the reactor through a diffuser at the rate of 800 mg/h. Ozone destructor was used to destruct the unreacted ozone coming out from the reactor. The required quantity of H₂O₂ was fed into the reaction chamber from the peroxide tank during circulation of the simulated dairy effluent. A programmable peristaltic pump was used to circulate the dairy wastewater at a different flow rate into the reactor at room temperature. A simulated dairy wastewater sample was drawn at a definite time interval from the reaction chamber to analyze the performance of the system during the course of the treatment process.

In the present study, the treatment efficiency of system was studied by varying operational parameters such as pH from 5 to 9, $\rm H_2O_2$ concentration from 0.5 to 0.15 mL/L, circulation rate from 50 to 150 mL/h at a fixed ozone dosage of 800 mg/h. pH of the simulated dairy effluent was adjusted using sodium hydroxide and hydrochloric acid. All the experimental trials were carried out in a circulation mode with a sample volume of 160 mL.

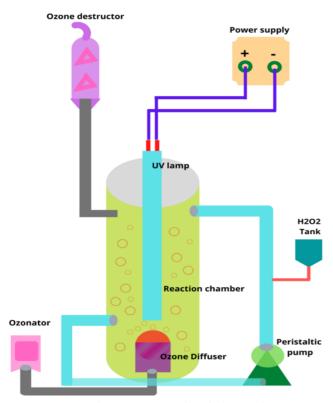


Fig. 1. Experimental setup on ozone based photocatalytic reactor.

2.3. Analytical Methods and Determination

The measurable parameters such as pH, conductivity, Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), turbidity, Total Dissolved Solids (TDS), turbidity and lactose were measured in dairy wastewater before and after the treatment to ensure removal efficiency of the system. Standard analytical methods were used as per IS 3370 and APHA standards. The pH and conductivity were measured by using digital pH meter (Elico LI 120) and conductivity meter (Elico CM 180). Potassium dichromate and sulfuric acid were used to determine the COD. TDS was determined using TDS analyzer (Elico CM 183). Lactose content present in the sample was analyzed spectrophotometrically using Elico CL 223 Colorimeter. Nephelometer (Elico CL 52D) was used to determine the turbidity of the sample. DO meter (Hach HQ430d flexi) was used to analyze BOD present in the dairy effluent.

3. Results and Discussion

3.1. O_3/H_2O_2 , O_3/UV and UV/H_2O_2 System

The preliminary experimental work was carried out by using advanced oxidation processes such as ozone, UV and $\rm H_2O_2$ either in individual or combination of these processes. From Fig. 2 (a) and (b), when adopting ozone, UV and $\rm H_2O_2$ process individually, COD and lactose reduction efficiency was less than 10% which was in agreement with the literature Slavov [34]. However, the combined hybrid process such as $\rm O_3/H_2O_2$, $\rm O_3/UV$ and $\rm UV/H_2O_2$ was carried out at a pH level of 7 and these processes gave notable COD and lactose reduction in dairy wastewater treatment was shown in Fig. 2 (a) and (b).

In O_3/H_2O_2 system, addition of H_2O_2 in wastewater considerably enhances the COD and lactose reduction of 32.5% and 40.61%, respectively. When H_2O_2 combined with ozone, the ozone was decomposed into OH^* radicals and form a peroxone process in aqueous solution. The H_2O_2 was a strong oxidizer having an oxidative potential of 1.78 eV and fastly react with HO_2^- ions rather than O_3 and generates more OH^* radicals as seen in the following reaction [22] (Eq. (1)-(3)).

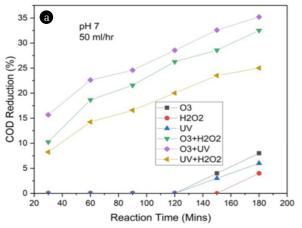
$$H_2O_2 + H_2O \to HO_2^- + H_3O^+$$
 (1)

$$O_3 + HO_2^- \to H_2 O + O_2^- + O_2$$
 (2)

$$2O_3 + H_2O_2 \rightarrow 2OH^* + 3O_2$$
 (3)

It can be seen that the O_3 disintegrates into two OH^* radicals which generate more OH^* radicals than ozone alone process with the presence of H_2O_2 oxidant. The efficiency of COD and lactose reduction was depended upon the H_2O_2 dosage.

In O₃/UV system, COD of 35.2% and lactose of 43.68% reduction was attained during the 3 h treatment process. When ozone was directly irradiated by UV, a maximum quantity of OH* radicals were produced than UV or Ozone processes in individuals. As from the following reaction, the photodegradation of O₃ molecules



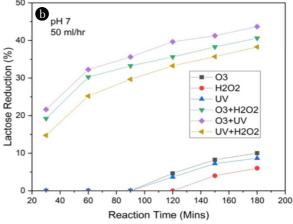


Fig. 2. Synergistic effect of hybrid AOP on COD and lactose reduction.

in water produces H_2O_2 and O_2 ions further decomposed into OH* radicals [22] (Eq. (4)-(5)).

$$O_3 + H_2O + UV \rightarrow O_2 + H_2O_2$$
 (4)

$$2O_3 + H_2O_2 \to 2OH^* + 3O_2 \tag{5}$$

 UV/H_2O_2 system also gave a considerable result in COD and lactose reduction of 25% and 38.25%, respectively (Fig. 2 (a) and (b)) which was slightly higher than the O_3/H_2O_2 and O_3/UV system. When H_2O_2 was exposed through UV radiation in solution phase, the OH* radicals were generated in accordance with the following reaction [22] Eq. (6).

$$H_2O_2 + UV \to 2OH^* \tag{6}$$

As of hybrid processes such as O_3/H_2O_2 , O_3/UV and UV/H_2O_2 , the O_3/UV process gave slightly better results in COD and lactose reduction than other two processes of O_3/H_2O_2 and UV/H_2O_2 was proved by Pourgholi, Jahandizi [35].

3.2. UV/H₂O₂/O₃ System

During the process, decomposition of H_2O_2 produces more secondary species such as exited superoxides, hydrogen peroxide and hydrogen atoms. Although this chemically formed secondary species have a tendency to react with organic matter in the dairy wastewater. The combined use of $UV/H_2O_2/O_3$ in dairy wastewater enhances the OH^* radicals formation which ultimately increases the COD and lactose reduction. In this present study, $UV/H_2O_2/O_3$ system was further analyzed at the different operational parameters (circulation rate, reaction time, initial pH and H_2O_2 dosage) and verified with COD and lactose reduction.

It can be explained by the fact that addition of UV and H_2O_2 into O_3 system greatly enhances degradation efficiency. UV irradiation accelerates the decomposition rate of O_3 and H_2O_2 into hydroxyl radicals formation by the following chain reaction Eq. (1)-(5).

$$O_3 + H_2 O_2 + UV \rightarrow OH^* + O_2 + HO_2$$
 (7)

$$O_3 + OH^* \to HO_2^* + O_2$$
 (8)

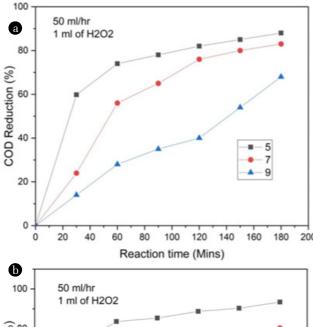
$$O_3 + HO_2^- \to H_2 O + O_2^- + O_2$$
 (9)

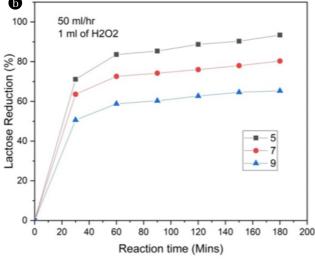
3.2.1. Effect of pH

To study effect of solution pH on the treatment efficiency of the dairy simulated wastewater, the experiments was carried out by adjusting the initial pH of solution from 5 to 9.

Effect of pH on the COD and lactose reduction of the dairy wastewater by O₃/UV/H2O2 process was studied at various pH ranges of 5, 7 and 9 as illustrated in Fig. 3 (a) and (b). This result shows that the COD and lactose reduction was low in neutral (pH 7) and alkaline medium (pH 9), and it was protuberant in acidic medium (pH 5). During the treatment process, in higher pH ranges, ozone was continuously oxidized the suspended molecules into dissolved molecules and consequently, ozone demolishes those suspended molecules into small molecules though enhances the COD level in solution [36]. Moreover, decomposition of ozone was quite high at higher pH ranges (7 to 9) subsequently causes a scavenging effect on the solution than pH 5 [37]. In contrast, in acidic medium (pH 5), ozone was directly influenced by the UV radiation and Hydrogen peroxide which was decomposed into OH radicals enhances the COD and lactose reduction. The maximum COD and lactose reduction were attained at a pH value of 5 as 88% and 93.4%, respectively. On comparing the treatment efficiency of the system on dairy wastewater, lactose reduction was very fast than the COD reduction. About 50.0% of lactose reduction and 40.0% of COD reduction was achieved within 30 minutes. Faster and higher lactose removal efficiency and lower and slower COD removal efficiency ensures that fragmentation of lactose takes place initially. But further increase of the COD removal efficiency with time proves the degradation of the fragmentation of bulkier molecules during the reaction.

At different initial pH values, variation in the pH value of dairy wastewater during the treatment with respect to the reaction time were shown in Fig. 3 (c). As we clearly have seen in Fig. 3 (c), although we maintain the initial pH value of wastewater at 5, 7 and 9, within 30 mins of an interval, solution initial pH value





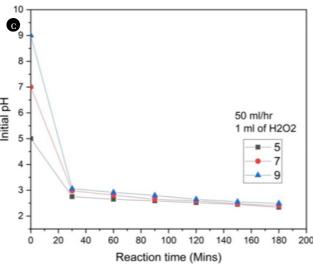


Fig. 3. (a) Effect of pH on COD reduction (b) effect of pH on lactose reduction and (c) Variation of initial pH levels with respect to reaction time.

was dropped between 3.2 to 2.5. This was due to the formation of organic and inorganic acids during the ozone-based photocatalytic process. In dairy wastewater, lactose was one of the major components which undergoes either degradation or fragmentation during the treatment process. Due to this continuous fragmentation of lactose, it was converted into 4-O- β -galactopyranosyl-D-gluconic acid as shown in Fig. 6 [38]. Although an increase of circulation rate and H_2O_2 concentration could not much influence in the variation of pH ranges. At the end of the treatment process (180 mins), almost 80% of the lactose was degraded into lactobionic acid. Besides, the increase of treatment time beyond the 3 h not much influence in the variation of pH ranges.

Increasing the circulation rate (50 to 150 mL/h) of the wastewater, solution pH of the wastewater rapidly falls to 2.2 during the treatment process. The same result was observed by maintaining an initial pH of the solution 7 and 9. But increasing the circulation rate of simulated dairy wastewater, the increased time required to fall of solution pH during the course of the reaction.

3.2.2. Effect of circulation rate

The experimental trials were carried out for the simulated dairy wastewater with the circulation rate of 50-150 mL/h at a constant H_2O_2 of 1mL with different pH levels were shown in Fig. 4 ((a)-(f)).

As can be seen from the Fig. 4 (a) and (b), at pH 5, maximum COD and lactose reduction were attained at a minimum circulation rate of 50 mL/h. Increase of circulation rate from 50 to 150 mL/h clearly showed that the decrease of COD and lactose removal efficiency. Similar results were attained at a pH of 7 and 9 as shown in Fig. 4 ((c), (d), (e) and (f)). On all the pH cases, more than 60% of COD and 70% of lactose reduction was attained at a circulation rate of 50 mL/h and reaction time of 180 mins. From Fig. 4 (a) and (b), At low circulation rate (50 mL/h), the acidic condition (pH 5) improves more than 80% COD and lactose reduction than basic and alkaline conditions of solution within 180 mins. Nevertheless, Fig. 4 ((c), (d), (e) and (f)) reveals that the increase of pH to basic (pH 7) and alkaline (pH 9) condition considerably reduces the COD and lactose reduction about 10 to 15% compared to acidic condition with the same time and circulation rate. The maximum reduction of COD and lactose reduction was may be achieved at the higher circulation rate even at higher pH of 7 and 9 by increasing the reaction time beyond

It could be clearly explained by the fact that the effluent detention time in the photocatalytic reactor of the dairy wastewater was considerably reduced on increasing the circulation rate from 50 to 150 mL/h. At higher circulation rate, detention time between target molecules and generated oxidative species in the reactor during the treatment process was considerably low which subsequently affects the reduction efficiency of COD and lactose removal. Since the hydroxyl radicals and superoxides were short in life which could not be effectively utilized in the treatment process at the higher circulation rate which could be maximum destruction of oxidative species. Contrariwise, an acquaintance of chemically oxidative species (OH radicals, O_3 and HO_2) with target molecules of dairy wastewater was maximum at a low circulation rate of 50 mL/h which considerably enhances the COD and lactose reduction efficiency.

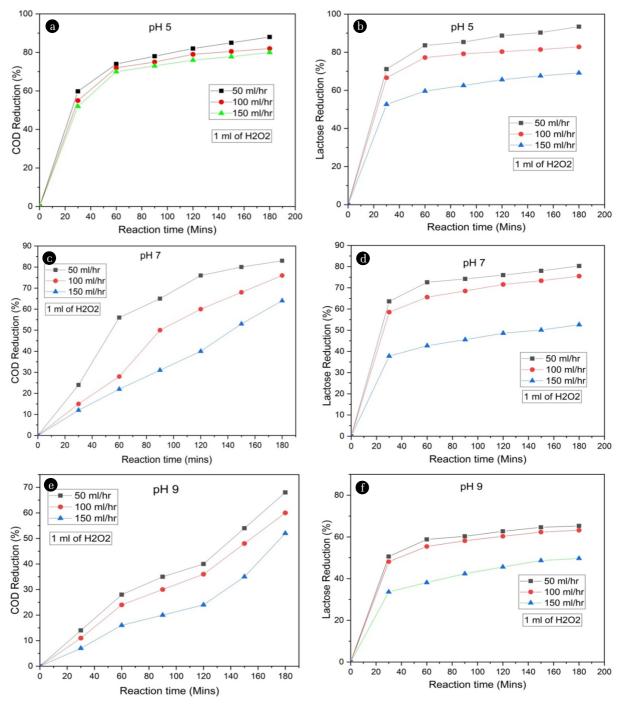


Fig. 4. Effect of circulation rate on the reduction of COD and lactose content.

3.2.3. Effect of H_2O_2 dosage

During the treatment, the $\rm H_2O_2$ dosage was varied from 0.5 to 1.5 mL per 100 mL of dairy wastewater with a constant circulation rate of 100 mL/h throughout the process.

Effect of H_2O_2 dosage on COD and lactose reduction with respect to time was illustrated on the Fig. 5. As from Fig. 5 (a) and (b), the result reveals that the increase of H_2O_2 dosage from 0.5 to

1.0 mL/h consequently enhances the COD and lactose reduction of 82% and 77% respectively at the pH of 5. Further increase of H_2O_2 dosage to 1.5 mL decreases the COD and lactose reduction efficiency of 10% and 11% from the H_2O_2 dosage of 1.0 mL.

Similarly from Fig. 5 ((c), (d), (e) and (f)), the experimental trials were repeated for the dairy effluent with the pH value of 7 and 9 and the result reveals that the decrease of COD (< 88%)

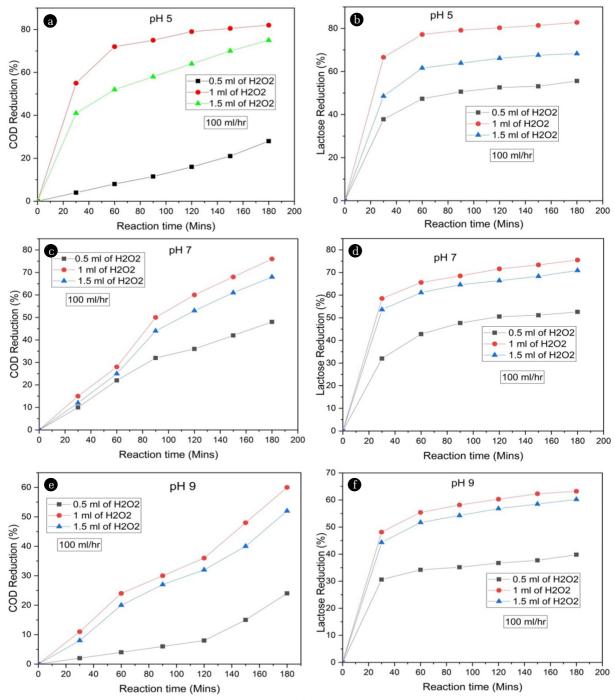


Fig. 5. Effect of H₂O₂ concentration on the reduction of COD and lactose content.

and lactose content (< 75%) by way of increasing H_2O_2 dosage from 1.0 to 1.5 mL/h. From these results, the performance of oxidation process greatly depends upon the formation of the hydroxyl radicals [39].

The supplementary addition of H_2O_2 into photocatalytic oxidation also enhances the production of more number of hydroxyl radicals. The lowest COD and lactose reduction efficiency at 0.5

mL of H_2O_2 dosage causes insufficient radical formation during the photocatalytic reaction. Upon increasing the H_2O_2 dosage from 1.0 mL/h increases the number of reactive radical formation by photochemical synergistic $O_3/UV/H_2O_2$. Maximum COD and lactose reduction efficiency of 82% and 82.8% at the 1.0 mL/h of H_2O_2 dosage and pH of 5, confirms the formation of more number of highly reactive radical formation during the course of the reaction.

In contrast, a decrease of COD and lactose reduction of 28% and 55.6% at the H_2O_2 dosage of 1.5 mL and pH of 5. Ineffective utilization of reactive radicals due to the scavenging of hydroxyl radicals during the oxidation process continuously decreases the degradation efficiency of organic matter [40].

This result shows that the lactose and COD reduction ensures that the fragmentation followed by degradation of the organic molecules may take place during the treatment process. Excess amount of H_2O_2 in wastewater generates a maximum number of hydroxyl radicals which promotes secondary reactants like hydroperoxide instead of increasing the degradation efficiency of the pollutants. This hydroperoxide was less reactive than hydroxyl radicals was unfavor of organic and inorganic removal. It was concluded that the rate of generation of hydroxyl radicals should be controlled by the dosage of H_2O_2 .

Based on the H_2O_2 dosage on the dairy wastewater, the hydroxyl radicals were formed. At alkaline pH of 9 the ozone was quickly decomposed and rapidly formed more number of hydroxyl radicals than at pH 5 and 7 [39]. Nevertheless, at a higher dosage of H_2O_2 , there was a high risk for H_2O_2 acted as a radical scavenger which possibly decreases the OH* radicals concentration in the solution as per the following reaction [22] (Eq. (10)-(11))

$$OH^* + H_2O_2 \rightarrow OOH^* + H_2O$$
 (10)

$$20H^* \rightarrow H_2 0 \tag{11}$$

Lactose was directly related to the COD reduction. During the treatment process, the lactose reacts with hydroxyl radicals and it was partially oxidized into lactobionic acid as a byproduct in COD reduction. The presence of H_2O_2 , OH° , HO_2° radicals in dairy effluent during the photocatalytic process, continuously reacts with the carbonyl group of lactose and subsequently degraded into 4-O β -galactopyranosyl-D-gluconic acid due to the free radical mechanism as shown in Fig. 6 [38]. During this mechanism, presence of secondary oxygen shown in (Eq-5) could be possible to react with lactobionic acid and finally converted into H_2O .

This could be further supported by Fig. 7 describes that the electrical conductivity and total dissolved solids (TDS) of the wastewater samples were continuously increased during the treatment process. At the initial stage, the conductivity and TDS of wastewater were measured as 0.5 ms/cm and 230 ppm respectively and it was continuously increased to 2.9 ms/cm and 1,247 ppm respectively. The changes in EC and TDS were explained by the fact that fragmentation of bulkier molecules in the dairy wastewater

Fig. 6. Schematic representation of lactose to lactobionic acid conversion.

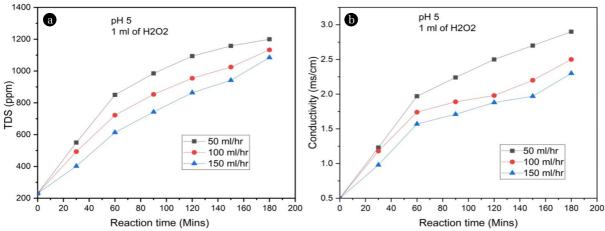


Fig. 7. Variation of TDS and conductivity with respect to circulation rate.

into smaller ionic species, which may correspondingly, increases the conductivity as well as the TDS.

3.2.4. Optimum conditions

From the above sections, the result concluded that the efficiency of COD and lactose reduction was greatly influenced by the initial pH (5 to 9), circulation rate (50-150 mL/h), H_2O_2 dosage (0.5 to 1.5 mL) and reaction time (30 to 180 mins).

Table S1 presents the comparison results of COD reduction on ozone-based photocatalytic process to other treatment processes. Generally, dairy industry wastewater contains organic mater in which most of the researchers were carried out the biological and physicochemical processes. From Table S1, the hybrid AOP process gives more COD reduction in dairy wastewater than other methods. Torres-Sánchez, López-Cervera [41], reveals that the maximum COD reduction of 95% was achieved when combining the AOP process of ozone and fenton into the electrocoagulation process. The present work exposes that the $\rm O_3/UV/H_2O_2$ system gave better results in a COD reduction of 88% compared to other biological and physicochemical processes. In the future, more than 90% of COD reduction was may be achieved by a combination of the hybrid process of $\rm O_3/UV/H_2O_2$ and membrane technology.

The synergistic effect of a hybrid process such as $O_3+H_2O_2$, O_3+UV , $UV+H_2O_2$ and $O_3+UV+H_2O_2$ were carried out and its corresponding results were illustrated in Fig. S1 (a) and (b). The hybrid $O_3+UV+H_2O_2$ process gives the yield of 65% of COD and 52.36% of lactose reduction than other hybrid processes such as $O_3+H_2O_2$, O_3+UV and $UV+H_2O_2$ at the pH of 7.

From Fig. S1 (c) and (d), when the treatment time of effluent was increased from 60 to 180 mins, the removal efficiency of COD was increased from 74 to 88% and lactose conversion was raised from 83.6 to 93.4% in the $\rm O_3+UV+H_2O_2$ process. In all the buffering conditions, the acidic medium (pH 5) was found to be more significant on the COD (88%) and lactose (93.4%) reduction efficiency. Also, the result reveals that the optimum condition for maximum COD and lactose conversion was taking place at an initial pH of 5, circulation rate of 50 mL/h, reaction time of 180 mins and $\rm H_2O_2$ dosage of 1 mL.

Based on this optimum condition, the performance of $O_3/UV/H_2O_2$ process was carried out in simulated and real dairy industrial effluent by measuring the parameters such as COD, BOD, lactose, turbidity and color were presented in Table S2.

The maximum removal efficiency of COD, lactose, turbidity and color were attained by 88-92, 97-98, 97-99% and colorless respectively. During the treatment process, more than 92% of the biological oxygen demand (BOD) was removed in both simulated and real wastewater which represents the elimination of the maximum amount of microorganisms present in dairy effluent.

4. Conclusion

In this research, the synergistic effect of advanced oxidation processes such as ozone, UV radiation; O_3/H_2O_2 , O_3/UV , UV/H_2O_2 and $O_3/UV/H_2O_2$ for treatability of dairy industry wastewater were studied. Effect of different process variables such as initial pH, reaction time, circulation rate and H_2O_2 dosage was observed. This

study exposed that $O_3/UV/H_2O_2$ system can be a better marginal to other hybrid AOP processes and conventional methods when worked under ideal circumstances.

When conducting experiments with individual processes such as ozone, UV radiation and H2O2, there were no noticeable results (< 10%) that were found in COD and lactose reduction. COD of 32.5%, 35.2%, 25%, 83% and lactose of 43.6%, 38.2%, 80% reduction efficiency were attained during the hybrid AOP process of O₃/H₂O₂, O₃/UV, UV/H₂O₂ and O₃/UV/H₂O₂ processes at a pH of 7 and circulation rate of 50 mL/h, respectively. From these results, the hybrid O₃/UV/H₂O₂ process was attained maximum COD, lactose reduction of 88% and 93.4% respectively under the optimum conditions of pH of 5, reaction time of 180 mins, circulation rate of 50 mL/h and H₂O₂ dosage of 1.5 mL. Reduction efficiency of COD and lactose decreased by an increase in H2O2 dosage of 1.5 mL, initial pH of 9 and circulation rate of 150 mL/h. This is due to at an alkaline pH and higher dosage of H2O2, the ozone decomposition rate was higher eventually causes a scavenging effect while at maximum circulation rate lack of retention time between radicals and pollutants eventually decreases the COD and lactose reduction efficiency.

However, after the $\rm O_3/UV/H_2O_2$ treatment process, TDS and EC of treated wastewater were increased to 1,043 ppm and 2.5 ms from its initial level ensures the incomplete/ partial degradation of organic pollutants present in the dairy effluent. As of this optimum process/conditions, the real dairy effluent was treated while the final concentrations of COD of 105 mg/lit, BOD of 18 mg/lit, lactose of 13 mg/L were achieved.

Removal efficiency of BOD in real-time dairy effluent satisfies the effluent standards recommended by the Central Pollution Control Board (CPCB) of India. However, TDS and pH of treated effluent did not meet the permissible limits of standards, which need further treatment process before the effluent was to be discharged into receiving bodies.

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Authors Contribution

S.R. (Ph.D student) perceived the research data and wrote the manuscript. R.B. (Professor) administered the project. C.M. (Associate Professor) wrote and look over the manuscript. P.M. (Assistant Professor) assisted in wrote and manage the work.

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