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Original Research

Effects of Different Parameters on Photocatalytic Oxidation of Slaughterhouse Wastewater Using TiO_2 and Silver-Doped TiO_2 Nanoparticles

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Abstract

Our study used a photocatalytic oxidation process for degrading slaughterhouse wastewater (SHWW). Characterization of the wastewater before and after treatment with TiO_2 and Ag-TiO_2 in terms of BOD, COD, and nitrogen was done. The effect of hydrogen peroxide, ozone, and various operating parameters such as catalyst dose, pH, and reaction time on the degradation efficiency of the process were also investigated. An increase in catalyst dose and reaction time increased process efficiency. However, process efficiency was decreased with elevating pH. The results also revealed that the type of catalyst and their operating parameters have significant influence on the oxidation of SHWW. Ag-TiO_2-H_2O_2 catalyst under UV (400watt) irradiation was found to be best for the degradation of SHWW and resulted in 95% BOD, 87% COD, and 74% nitrogen removal.

Keywords: photocatalysis, slaughterhouse wastewater, catalyst, BOD, TiO_2

Introduction

The slaughterhouse industry generates massive amounts of highly polluted wastewater of environmental concern. The discharge of untreated slaughterhouse wastewater (SHWW) into water bodies may cause eutrophication, dissolved oxygen depletion, and change in water temperature, which may pose a threat to aquatic life [1-3]. The leaching/ percolation of SHWW may also lead to the contamination of groundwater resources [4]. Resultantly, people may suffer from diarrhea, typhoid fever, wool sorter diseases, pneumonia, asthma, and chest and respiratory diseases [5]. Therefore, it is highly desirable to treat SHWW before its discharge into water bodies in order to save the environment and human health [6]. The treatment of SHWW with physio-chemical (filtration, coagulation, chlorination, adsorption, sedimentation) and biological (up-flow anaerobic sludge blanket reactors, waste stabilization pond system, and sequencing batch reactors) processes, though, significantly removes its pollution load but cannot remove the recalcitrant contaminants [7]. Another disadvantage associated with physio-chemical

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techniques is that the coagulants generate a huge amount of sludge [8]. On the other hand, the efficiency of traditional biological processes is highly dependent on external factors such as temperature and climate of the region [9, 10].

Advanced oxidation processes (AOPs), however, have proven to be very promising for the treatment of wastewater [11, 12] because they generate highly reactive hydroxyl radicals (OH) that quickly react with recalcitrant organic compounds in the wastewater and tend to completely degrade them [13, 14]. Among AOPs, the photocatalysis process has gained attention because it is effective and even more environment friendly as it does not transform the pollutants into secondary byproducts but rather completely oxidizes the organic compounds into water and carbon dioxide. No chemicals are required and the catalyst used in the process remains unchanged [15, 16]. In comparison to different semiconductor catalysts (TiO_2, ZnO, Fe_2O_3, CdS, Gap, and ZnS,), titanium dioxide (TiO_2) is gaining importance as a photocatalyst because of its thermal stability, various crystalline forms, inertness to the chemical and physical environment, and high UV absorption [17]. The synthesis of TiO_2 nanoparticles can be carried out using various methods such as thermal decomposition, alkali precipitation method, sol-gel technology, hydrothermal synthesis, ion-beam methods, chemical vapor deposition, and the sputtering method [18-21]. However, sol-gel technology has been widely used for the synthesis of TiO_2 nano-particles because it gives relatively better control over the surface chemistry, crystallinity, and morphology of TiO_2 and provides high porosity [22-24].

AOPs can either be applied individually, in combination, or even sequentially [25-27]. Therefore, the degradation rate of the photocatalysis process can be significantly increased by combining it with either ozone (O_3) or hydrogen peroxide (H_2O_2). Several researchers have attempted these combinations, for example Luiz et al. [28] used photocatalysis along with H_2O_2 in the presence of oxygen for the removal of residual organic matter from wastewater. Rivas et al. [29] also investigated the effect of O_3 on the performance of photocatalytic oxidation and reported the increase in process efficiency. The photocatalytic reactions can be carried out either in slurry-type reactors wherein the catalyst lies mobilized in suspended form [30] or by immobilizing the catalyst on various inert substances [31, 32].

The aim of this study was to synthesize immobilized TiO_2 and Ag-TiO_2 catalyst, and to determine the effects of process conditions such as pH, catalyst dose, and reaction time on the treatment efficiency of photocatalytic oxidation process for SHWW. The effects of ozone and hydrogen peroxide on the process were also investigated.

Table. 1. Characterization of slaughterhouse wastewater used in this study.

Parameter	Unit	Wastewater
pH	-	6.687^a (0.2887)
BOD	mg/l	1078.45^a (137.26)
COD	mg/l	2024.5^a (679.669)
Nitrogen	mg/l	74.8^a (3.4083)

Values in parenthesis represent standard deviation and ^{a} is mean of 20 values

Experimental Procedure

Wastewater Caracteristics

Wastewater used in this study was sampled from a local slaughterhouse located at Shahpur Kaanjra, Multan Road, Lahore, Pakistan from its discharge unit. Wastewater was then characterized in terms of pH, BOD, COD, and Nitrogen in accordance with Standard Methods for the Examination of Water and Wastewater [33]. The wastewater characteristics are given in Table 1.

Photocatalytic Oxidation Reactor

A horizontal double-walled glass photocatalytic oxidation reactor (Fig. 1) with a capacity of 1-6 liters was used in this study. The reactor was composed of three parts made of transparent glass. Part one was the outer compartment (18 x 12 inches and 6.3 inches high) with circulating fresh tap water. The purpose of the water was to maintain overall temperature of the reactor at 29-32ºC.

The second part was the inner compartment (9 x 12 inches and 6.3 inches high) in which photocatalytic oxidation reactions were carried out. It was placed in the center of the outer compartment,

Fig. 1. Photocatalytic oxidation reactor.

thus making it a double-walled reactor. A 400W UV lamp (Shanghai JWFU Industry Co., Ltd. China) was placed on top of this compartment.

The third part was the lower compartment in which a magnetic stirrer (78-1 Megnetic stirrerhotplate, 0-1400 rpm) was placed for continues circulation of wastewater.

Application of Ozone

Ozonation was carried out along with photocatalysis to examine its effect on the degradation of SHWW. Ozone gas was generated through an ozone generator (L10G of Faraday, USA) providing oxygen by an oxygen concentrator (Mark 5 of Pureozone, USA) at a flow rate of 2 l/min. A continuous supply of ozone was fed to the photocatalytic reactor through a diffuser. Ozone doses varied from 2g/h to 8g/h. All the experiments were carried out on a sample volume of 1000 ml.

Applying Hydrogen Peroxide (H_2O_2)

The experimental procedure for H_2O_2-assisted photocatalysis consisted of a photocatalytic reactor. Analytical grade hydrogen peroxide (35% w/w) from Merck was used. H_2O_2 dose varied between 0.1-1.5ml/l. All the experiments were carried out on a sample volume of 1000 ml.

Synthesis of the Photocatalyst

The synthesis of the catalyst and doping process was achieved by following the standard sol gel method.

Materials and chemicals:

- Titanium tetraisopropaoxide (97%)
- Acetic acid (99.7%)
- Silver nitrate (99%)
- Nitric acid
- Ethanol
- Deionized water

Equipment and Instrumentation:

- Magnetic stirrer (0-1,400 rpm) for continuous mixing of the wastewater
- Analytical balance (Sartorius, BL 210S)
- Oven (maximum rang 250ºC)
- Furnace

Catalysts were synthesized using the modified standard sol-gel method [34, 35]. TiO_2 photocatalyst was synthesized by following the modified standard sol-gel method. A specific amount of titanium tetra butaoxide Ti $(OBU)_4$ was dissolved in ethanol with stirring. The pH of the solution was adjusted to 2 by adding nitric acid. Deionized water was then added to the solution. Ethanol, titanium butaoxide, and water were in a 20:1:2.5 molar ratio. The solution was stirred continuously for 8 hrs and then kept for several days at 30ºC to get a clear gel. The obtained gel was then dried in an oven at vacuum at 60-70ºC for two hours and milled to powder (Fig. 2). This powdered form of TiO_2 was then calcinated at 550ºC in the furnace for half an hour and then further used in experiments.

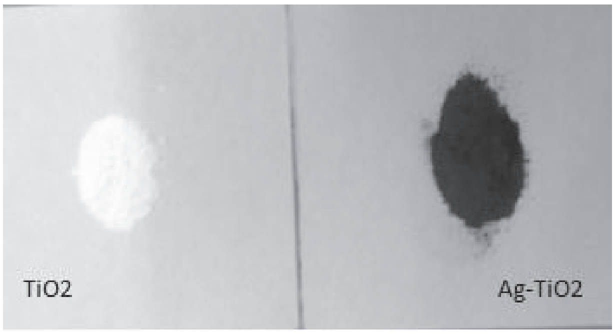

Fig. 2. Synthesized TiO_2 and Ag-Tio_2 catalysts.

Doping

For silver-doped TiO_2 nano particles, the above-mentioned procedure was repeated with the addition of silver nitrate with water (Fig. 2). The obtained powdered form of Ag-TiO_2 catalyst was then further used in experiments.

Photocatalytic Oxidation of Slaughterhouse Wastewater

Photocatalytic oxidation of SHWW using immobilized TiO_2 and Ag-TiO_2 catalysts was employed. The effect of H_2O_2, O_3, and various process parameters such as catalyst dose, pH, and exposure time under UV (400 watt) has been investigated.

Results and Discussion

Effect of Initial Catalyst Concentration

The dose of the photocatalyst is one of the most important parameters for determining process efficiency and has been widely investigated [36-39]. Catalyst concentration not only influences the efficiency of the process but also the rate of pollution degradation

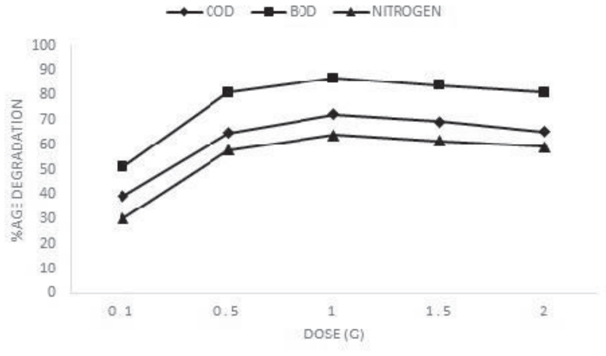

Fig. 3. Effect of catalyst concentration on degradation of SHWW.

[40]. Therefore, in order to determine the optimal dose, a catalyst amount was varied between 0.1-2 g (Fig. 3). The pH (3) and exposure time (40 min) remained constant under UV (400 watt). Initially the degradation of pollutant increases with an increase in catalyst concentration and decomposition found to be directly proportional to catalyst dose. This enhanced efficiency of the process may be due to the fact that increases in catalyst dose resultantly increase in catalyst surface area for the adsorption of pollutants [41, 42]. The effect of catalyst dose on BOD, COD, and nitrogen of SHWW shown in Fig. 3 indicates that degradation efficiency gradually increased with the increase of catalyst dose. The catalyst dose of 1g/l appeared to be optimal, which yielded 87%, 72%, and 64% degradation of SHWW in terms of BOD, COD, and nitrogen, respectively. However, further increases in catalyst dose decrease the overall efficiency of the photocatalytic oxidation process [39]. A decline in process efficiency can best be explained by two factors: 1) Increase in turbidity of the solution due to an increase in catalyst amount, which blocks or scatters the UV light and thus results in decreased light penetration and a resultant drop in the degradation rate of pollutant; and 2) Mass clumping or aggregation of the catalyst occurs, which results in less availability of catalyst active sites [43].

Effect of pH

The efficiency of the photocatalytic oxidation process is highly dependent upon the pH of the solution and is considered one of the critical parameters of process because it determines the degree of ionization and sturdily affects the photocatalyst surface charge [44-46]. Various researchers have studied the effects of different pH on the efficiency of the photocatalysis oxidation process and reported that maximum degradation by titanium dioxide occurs at low pH because in acidic medium the TiO_2 surface becomes positive and adsorbs the pollutant very easily [41, 47, 48]. Therefore, to see the effect of pH on BOD, COD, and nitrogen removal efficiency of the photocatalytic oxidation process it was varied between 1-11 (Fig. 4). The catalyst dose and reaction time remained constant at 1 g/l and 40 min. The results revealed that the process was optimized in the acidic environment and maximum removal was obtained at pH 3 because positive titanium surface efficiently adsorbs the organic matter present in wastewater on its surface. In addition, with the increases in production of hydroxyl radicals which takes part in reaction [49, 50]. The same result was reported by Prema and Kandasamy [45], who applied photocatalytic oxidation for the degradation of organic pollutants present in the seafood industry and stated that more hydroxide ions and hydroxyl radicals are formed in acidic medium, which enhances the process efficiency and found optimal pH between 2-4. Beyond pH 3 there was a gradual decrease in the degradation efficiency of the process because of the fast decomposition of hydroxyl radicals occurring at elevated pH. At alkaline conditions the TiO_2 surface is negatively charged, which also causes the repulsion of pollutants and delays the adsorption of pollutants on its surface, thus decreasing the overall efficiency of the process. Therefore, the efficiency of the process decreases with the increase in pH. The results were in agreement with the findings reported in literature [44, 45, 51].

Effect of Reaction Time

Another key parameter for the better performance of the photocatalytic oxidation process is the optimal exposure time between pollutants and photocatalyst [45]. The results of BOD, COD, and nitrogen removal of SHWW with respect to UV (400 watt) exposure time are shown in Fig. 5. The exposure time was varied in the range of 10-60 min. The reaction environment (pH) and catalyst dose remained constant at 3 and 1 g/l, respectively. The gradual increase in degradation efficiency of the photocatalytic process with the increase in exposure time has been reported. However, after optimal reaction time the degradation efficiency starts decreasing due to the fact that radicals produced at longer treatment time were unstable in nature and decompose immediately after their production [52, 53]. A gradual increase in degradation of BOD, COD, and nitrogen of SHWW with an increase in treatment time was apparent from the results

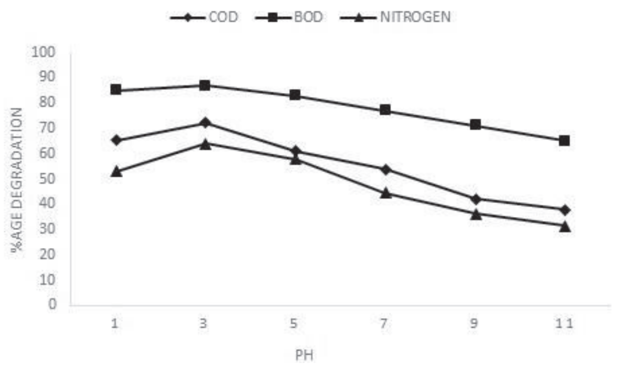

Fig. 4. Effect of pH on degradation of SHWW.

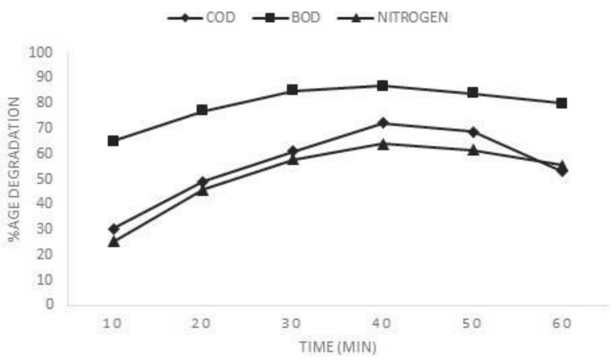

Fig. 5. Effect of reaction time on degradation of SHWW.

(Fig. 5). However, after optimal treatment time of 40 min the degradation rate significantly declined. This may be due to the fact that more radicals were produced during the longer treatment time and which were unstable in nature and decreased the degradation efficiency of the process [45].

Silver-Doped TiO_2 (Ag-TiO_2)

The process of introducing foreign elements into the catalyst to modulate its electrical properties without changing its crystalline form is referred to as doping [54]. The photo-response of TiO_2 can be increased by doping it with various metals and non-metals because doping prevents the recombination of the electron-hole by capturing the excited electron and shifts the absorption band of TiO_2 from UV to visible region to obtain the desired results [55]. For doping, various metals and non-metals have been used as dopants. However, silver-doped titanium dioxide has been extensively reported in the literature because of its broader applications in the field of the environment. Homogeneously dispersed silver nanoparticles can be synthesized through a modified sol-gel method in the presence of acetic acid [34]. The working mechanism of silver as dopant is illustrated in equations (1-4) [56].

$$e^- + Ag \rightarrow Ag^- \tag{1}$$

$$Ag^- + O_2 \rightarrow Ag + {}^{\cdot}O_2^- \tag{2}$$

$$Ag^- + Ti^{4+} \rightarrow Ag + Ti^{3+} \tag{3}$$

$$Ag^- + h^+ \rightarrow Ag \tag{4}$$

The electric potential of silver is lower than that of TiO_2, so silver deposits act as accumulation sites for photo-generated electrons from TiO_2 (Eq. 1). These electrons can react with absorbed molecular oxygen and also with the Ti^{4+} particulars (Eq. 2, 3). Silver loading results in enlarged energetic properties and silver clusters become recombination centers for photo-generated electrons and holes (Eq. 4). The influence of Ag-TiO_2 dose under UV (400) on degradation of SHWW is shown in Fig. 6a). Results revealed that when Ag-TiO_2 dose increases it results in an increase in the degradation efficiency of the process and yielded 90% BOD, 75% COD, and 65% nitrogen removal because excited electron was captured by doped silver particles, which prevents the recombination of electron-hole and thus results in better removal efficiency. The generated data also revealed that when SHWW was treated alone with TiO_2 at pH 3 it shows 87% BOD, 72% COD, and 64% nitrogen degradation. However, with Ag-TiO_2 the efficiency of the photocatalytic oxidation process was slightly enhanced, resulting in 90% BOD, 75% COD, and 65% nitrogen removal (Fig. 6b) as silver metal was always found to be favorable for the degradation of organic pollutants by different researchers [57]. Similarly, at 40 min of reaction time (Fig. 6c) Ag-TiO_2 shows slightly better degradation as compared to TiO_2 alone.

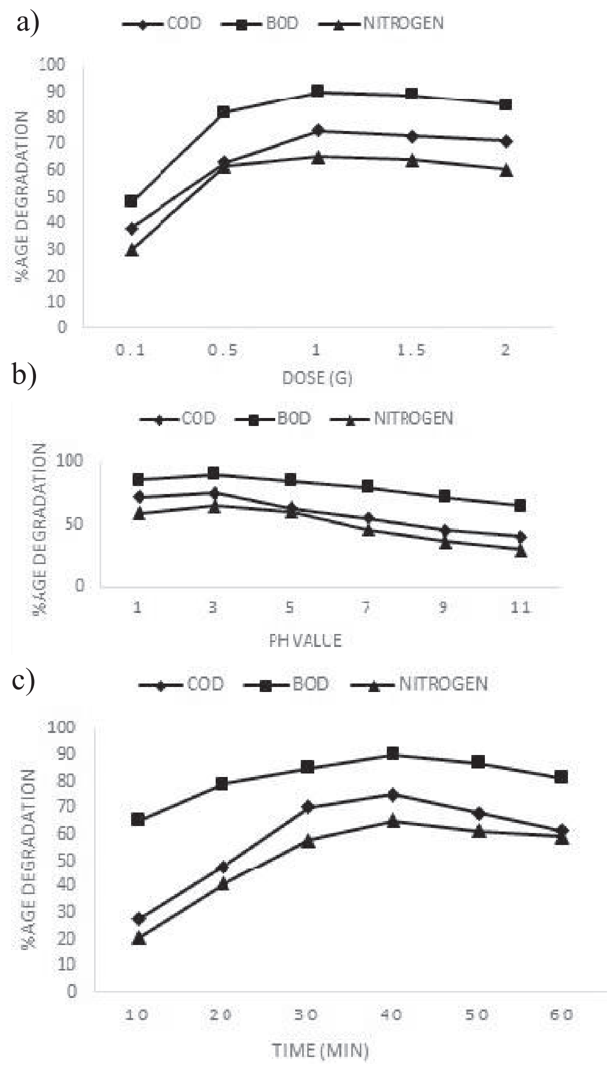

Fig. 6. Effect of dose a), pH b), and treatment time c) of Ag-TiO_2 catalyst on SHWW degradation.

Effect of Hydrogen Peroxide (H_2O_2) and Ozone (O_3)

H_2O_2 is considered a powerful oxidizing agent and produces hydroxyl radicals in water or wastewater. However, alone its degradation rate is very low but synergistic effects can be achieved by combing it with other AOPs. The addition of H_2O_2 in the photocatalysis process increases the yield of hydroxyl radicals and prevents the recombination of electrons and holes [14, 58]. This combination has been used by many researchers for complete mineralization of organic matter from wastewater. For example, Panday et al. [59] used TiO_2 photocatalysis in combination with H_2O_2 for the degradation of organic matter present in wastewater. Samsudin et al. [60] in their research have reported that TiO_2 alone was unable to completely degrade the organic matter from wastewater, but the addition of hydrogen peroxide enhanced the degradation efficiency and completely mineralized it. The effect of H_2O_2 on the degradation of SHWW in terms of BOD, COD, and nitrogen is shown in Fig 7. The concentration of H_2O_2 varied from 0.1-1.5 ml/l. It is evident from the results that degradation of the wastewater increases with the addition of H_2O_2 in both alone TiO_2 and doped TiO_2 because of the increase in OH radicals production [61]. The efficiency of the photocatalytic oxidation process increases with increasing the H_2O_2 dose up to 0.5 ml/l (Fig. 7). Beyond the optimal dose of 0.5 ml/l process efficiency starts decreasing because at higher H_2O_2 dose fewer OH radicals are produced due to the formation of oxygen and O_2H radicals [62]. Maximum degradation of SHWW was achieved by using Ag-TiO_2-H_2O_2 under (UV 400 watt) (95% BOD, 87% COD, and 74% nitrogen), which may be due to the harmony between silver and hydrogen peroxide as Ag nano particles avoid the charge recombination by trapping the photogenerated electrons, and H_2O_2 increases the production of OH radicals [63] (Fig. 9).

On the other hand, synergistic effects can also be achieved by combing the O_3 with TiO_2 photocatalysis because an addition of O_3 increases the concentration

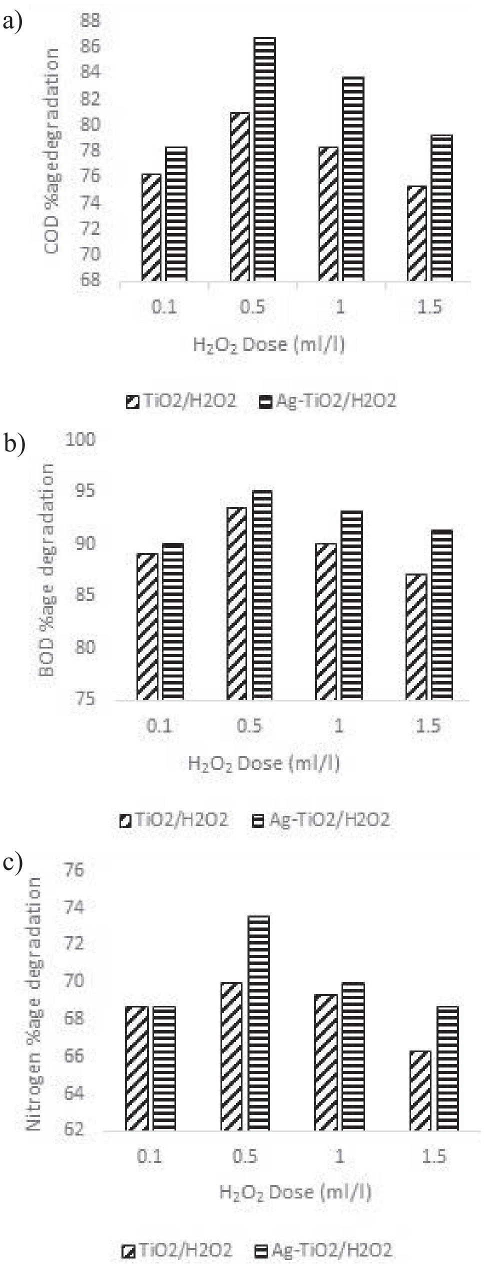

Fig. 7. Effect of hydrogen peroxide (H_2O_2) dose on TiO_2 and Ag-TiO_2 efficiencies in terms of a) COD, b) BOD, and c) nitrogen degradation.

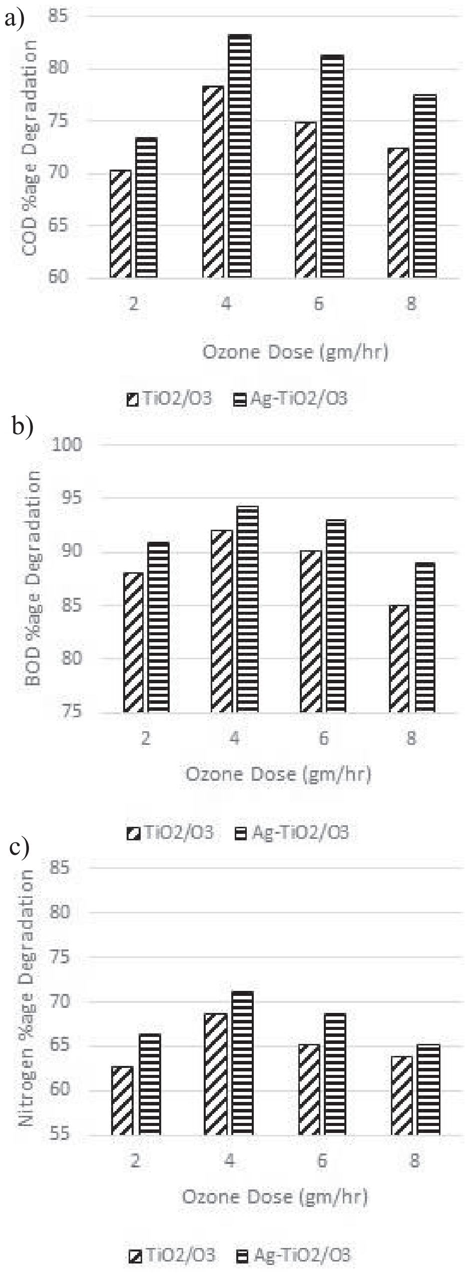

Fig. 8. Effect of ozone dose (O_3) dose on TiO_2 and Ag-TiO_2 efficiency in terms of a) COD, b) BOD, and c) nitrogen degradation.

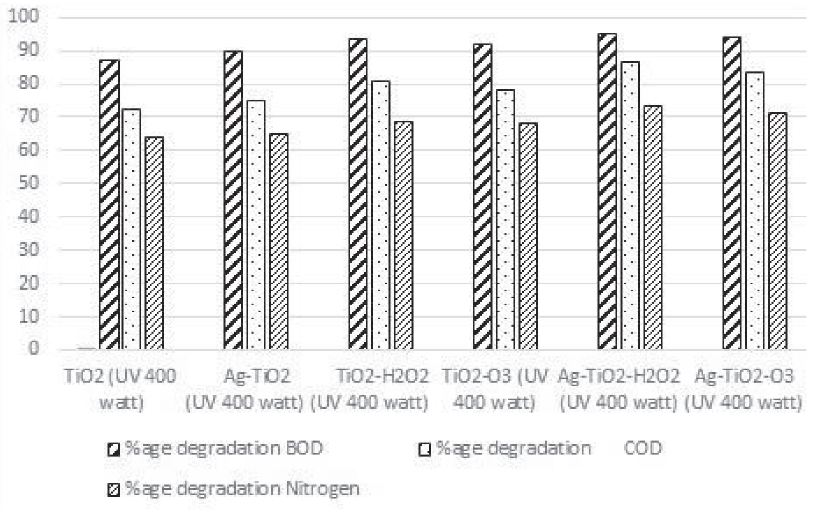

Fig. 9. Effects of different catalysts on degradation of slaughterhouse wastewater.

of highly reactive species (OH•) hydroxyl radicals in the medium, which further accelerates the process of organic matter degradation [14, 64, 65]. It is clearly evident from the results (Fig. 8) that the addition of O_3 with both TiO_2 and Ag-TiO_2 facilitates the photocatalytic degradation process by increasing hydroxyl radical production, hence speeding up the overall photocatalytic process. Horakova et al. [66] have reported the synergistic effects of photocatalytic ozonation and proven the effectiveness of using ozone with other AOPs rather than using it alone. An optimized ozone concentration is an important factor to be consider for obtaining better synergy between ozone and the photocatalytic process [67, 68]. Because at low ozone doses only hydroxyl radicals participate in reactions and complete decomposition cannot be accomplished [69]. However, at optimal dose, direct ozonation also occurs because ozone molecules are directly adsorbed on the photocatalyst surface (positive holes) and target the pollutants [70]. Hence, synergistic effects between ozone and photocatalysis can be achieved by using an optimal ozone concentration. An increase in ozone dose increased the decomposition of pollutants, but beyond optimal concentration, ozone starts to decrease the degradation process rather than increase it [71]. Therefore, in order to find out the optimal ozone dose for maximum SHWW degradation, ozone dose was varied between 2g/h-8g/h at pH 3 and reaction time of 40 min. The results indicated that degradation gradually increased with an increase of ozone dose. An ozone dose of 4 g/h was found to be optimal. Beyond the optimal dose, there was a gradual decrease in degradation of SHWW. The results were in agreement with findings reported in the literature [67]. A significant increase in degradation of SHWW in terms of BOD, COD, and nitrogen was observed by Ag-TiO_2-O_3 and resulted in 94%, 83%, and 71% removal, respectively, because doping of silver and the addition of ozone expedited the overall reaction rate due to the fact that silver enhances the electron-hole separation and act as electron reservoirs on TiO_2 surface and ozone initiates the radical chain reactions by producing the OH radicals in the presence of UV light, hence accelerating organic matter degradation [71, 72].

Table 2. One-way ANOVA results of H_2O_2 with Ag-TiO_2 effect on the percentage removal of COD, BOD, and nitrogen.

Variable	Initial dose of H_2O_2						
		Sum of Squares	Df	Mean Square	F	Sig ($p<0.05$)	Decision
Mean COD percentage Removal	Between Groups	43.1441	3	14.38135	14.38135	0.00138	Significant Mean Difference
	Within Groups	8.0000	8	1			
	Total	51.1441	11				
Mean BOD percentage Removal	Between Groups	126.6202	2	63.3101	28.1378	0.0009	Significant Mean Difference
	Within Groups	13.5	6	2.25			
	Total	140.1202	8				
Mean Nitrogen percentage Removal	Between Groups	37.2383	2	18.6192	18.6192	0.0027	Significant Mean Difference
	Within Groups	6	6	1			
	Total	43.2383	8				

Statistical Analysis

One-Way ANOVA

Statistical analysis of the data was performed by using analysis of variance (ANOVA).

Values of chemical oxygen demand (COD), biological oxygen demand (BOD), and nitrogen obtained at various H_2O_2 doses (0.1, 0.5, 1, 1.5) ml/l with Ag-TiO_2 for the treatment of slaughterhouse wastewater (SHWW) were compared through one-way ANOVA tests (Table 2). According to the results, there was a significant effect of H_2O_2 dose ($p<0.05$) as P values are 0.00138, 0.009, and 0.0027, while F values are 14.38135, 28.1378, and 18.6192 for COD, BOD, and nitrogen percentage removals, respectively. These values clearly show that there is a significant mean difference of various H_2O_2 doses with Ag-TiO_2 on the percentage removal of COD, BOD, and nitrogen, and thus this practice can be effectively used to explain the effect of H_2O_2 doses on photocatalytic oxidation process efficiency.

Conclusion

Photocatalytic oxidation was proved to be a highly feasible and promising technique for the degradation of SHWW in terms of BOD, COD, and nitrogen removal. Therefore, this process can be used to provide an effective solution to environmental issues related to this industry. It can also limit the contamination of groundwater reservoirs that occurs due to seepage of untreated or poorly treated SHWW. Results show that operating parameters influence the overall performance of the photocatalytic oxidation process such as catalyst dose, pH, and reaction time. An addition of ozone and hydrogen peroxide significantly improves the degradation efficiency of the process, and maximum degradation of SHWW was achieved with Ag-TiO_2-H_2O_2 catalyst.

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Conflict of Interest

The authors declare no conflict of interest.

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