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Removal of colour and COD from paper and pulp industry wastewater by ozone and combined ozone/UV process

Hafiz Muhammad Shahzad Munir[a,*], Nadeem Feroze[a], Amir Ikhlaq[b], Mohsin Kazmi[c], Farhan Javed[d], Hina Mukhtar[e]

[a]*Department of Chemical Engineering, University of Engineering and Technology, Lahore 54890, Pakistan, Tel. +923047223293; emails: engrsm124@gmail.com (H.M.S. Munir), drnchohan@gmail.com (N. Feroze)*
[b]*Institute of Environmental Engineering and Research, University of Engineering and Technology, Lahore 54890, Pakistan, email: aamirikhlaq@hotmail.com*
[c]*Department of Chemical Engineering, University of Engineering and Technology, Kala Shah Kaku (KSK), Pakistan, email: engr.smalikazmi@gmail.com)*
[d]*Department of Chemical and polymer Engineering, University of Engineering and Technology, Faisalabad, Pakistan, email: farhan.javed@uet.edu.pk*
[e]*Department of Chemical Engineering, NFC Institute of Engineering and Fertilizer Research, Faisalabad, Pakistan, email: hinamukhtar786@gmail.com*

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ABSTRACT

This study aims to investigate the effectiveness of ozonation alone and combined ozone/UV process for the removal of colour and chemical oxygen demand (COD) of black liquor discharged from paper and pulp industry. Moreover, the effect of several reaction parameters such as initial pH, ozone dose and reaction time were studied. Finally, pseudo-first-order considerations were applied to determine the rate of reactions in both ozonation alone and ozonation combined with UV process. The results indicate that COD and colour removal were enhanced by increasing the solution pH. The highest COD reduction and decolourization efficiencies were 56% and 71% at pH 9.8 with the O_3/UV process with ozone dose of 0.2 mg/mL. The comparative study of both ozonation and UV-Ozone processes indicate that UV-ozone process was found to be more effective as compared with ozonation alone. COD and colour removal of pulp and paper wastewater organic load follows the pseudo-first-order apparent reaction kinetics. The fastest rate constant (4.40×10^{-3}/min) at alkaline pH of wastewater was observed with O_3/UV processes. Therefore, it was concluded that O_3/UV process showed better performance than O_3 alone for the removal of colour and COD in paper and pulp wastewater near wastewater pH.

Keywords: Ozonation; Chemical oxygen demand; Black liquor; Decolorization; Paper and pulp industry

1. Introduction

The rapid increase in population and industrialization from the recent years resulted environmental problems. The wastewater generated as a result of industrial operations has a significant impact on the environment. The paper and pulp industry is one of the most important and the oldest industry in the world. This industry is considered water intensive and ranks third in the world after the metals and chemical industries [1–4]. In Pakistan, this is the second largest industry after the textile industry with more than 100 units. The capacity of all these units is about 650 thousand tons per annum [5]. Wastewater from this industry contains a variety of organic matter which is generally associated in terms of lignin, chlorinated organic compounds, cyanide, polyphenols and other aromatic compounds [6]. There are three types of organic

* Corresponding author.

compounds present in wastewater from paper industry (1) phenolic compounds due to lignin, (2) starch degradation (carboxylic acid or saccharides) products and (3) surfactants which may also present in freshwater [7,8]. Presence of dissolved inorganics and organic chemicals such as dyes, detergents and starch, etc. in wastewater may result in high chemical oxygen demand (COD), colour, turbidity, toxic compounds and inconsistent pH [9,10]. The characteristics of wastewater produced from paper and pulp industry depend on types of raw material and the type of technology and treatment methods used by the management [11].

Paper and pulp industry wastewater is highly coloured (dark brown) due to the presence of high molecular weight chlorinated lignin derivates. Lignin is a complex organic polymer with carbon–carbon and aryl/alkyl ethers linkages. Wastewater from the paper industry has dark brown colour. It is due to the degradation of lignocellulose during different processes in the paper industry. Lignocellulose indicates the amount of lignin in wastewater. Greater the amount of lignin in wastewater more will be the darkness of wastewater and there is a tendency to produce foam in wastewater [12]. Lignin and its derivates are difficult to degrade due to strong linkages within their molecular structure especially biphenyl type carbon to carbon linkages. Most of the industries use biological processes (aerated logons and activated sludge) to treat their effluents but due to this fact (presence of lignin and derivates) conventional treatment processes are less effective to degrade the pollution and decolourization of wastewater from the paper industry. Considering these limitations it is necessary to develop innovative, efficient and cost-effective technology for pulp and paper wastewater treatment [13].

Literature reveals that advanced oxidation processes (AOPs) are effective techniques to degrade the organic contaminants. These are based to produce hydroxyl radicals as oxidizing agents which are used to mineralize complex chemicals (compounds) in the effluents. The oxidation potential of hydroxyl radicals ($^\bullet$OH) is 2.8 V, so they are the strong oxidizing agents and exhibits faster oxidation reactions as compared with conventional oxidants (hydrogen peroxide and potassium permanganate) [14]. The main attributes of hydroxyl radicals ($^\bullet$OH) are that they are powerful oxidants, highly reactive, short-lived, simply produced and nonselective. The $^\bullet$OH has higher oxidation potential than chlorine, hydrogen peroxide and ozone. They react with a wide variety of compounds resulting in simple organic compounds or full mineralization described by the following reaction [15]:

$$\text{Organic species} + {}^\bullet OH \rightarrow CO_2 + H_2O + \text{inorganic ions} \quad (1)$$

Ozone and UV have long been used to stop the growth of pathogenic organisms in wastewater or water systems [16]. Similarly, ozone is a powerful oxidizing molecule that can react selectively with aromatic and unsaturated moieties for fast decolourization [17]. The combined ozone/UV process can effectively degrade the organic pollutants because the hydroxyl radicals have strong oxidation potential as compared with ozone (O_3) alone. In combined ozone/UV reactions in aqueous solution, the ozone energizes and combines with water to form hydroxyl radicals ($^\bullet$OH radicals) which are stronger and less selective than any other type of oxidants as per the following reactions:

$$O_3 + H_2O + h\nu \rightarrow H_2O_2 + O_2 \quad (2)$$

$$H_2O_2 + h\nu \rightarrow 2{}^\bullet OH \quad (3)$$

$$2O_3 + H_2O_2 \rightarrow 2{}^\bullet OH + 3O_2 \quad (4)$$

The main parameters which are responsible for the success of ozone/UV systems are pH, irradiation level and ozone dose [18,19]. Ozonation in combination with UV is widely used for the degradation and oxidation of refractory and toxic compounds present in wastewaters. In O_3/UV combined process, the oxidation power of O_3 is enhanced due to the formation of $^\bullet$OH radicals. A combination of AOPs for the degradation of sulphamethoxazole revealed a high mineralization during the O_3/UV process [20].

Hence, this work deals with ozonation and ozone/UV irradiation of black liquor from the pulp and paper industry. To the author's knowledge, the combined UV/O_3 effect have not previously been studied for COD and colour removal of real effluent (black liquor) in paper and pulp industry. The effect of ozone dose, pH and irradiation for colour and COD removal from wastewater (black liquor) was investigated. In addition, a kinetic study was performed to determine the COD removal rates for the ozone-based processes (O_3 and O_3/UV).

2. Materials and methods

2.1. Materials

A sample of wastewater (black liquor) was collected from Century Paper & Board Mills Limited, Pakistan. After collection, the effluent sample was immediately stored at 4°C until use. The initial characteristics of the black liquor were pH 6.8, COD 16,150 mg/L and the colour was dark brown. To investigate the degradation efficiency of ozonation on lignin fragments of pulping effluents, pulping effluent with COD values 400 mg/L were prepared by diluting the black liquor [21].

Major chemicals and reagents that were used for the determination of COD are potassium iodide, sodium thiosulphate, sulphuric acid, silver sulphate, mercury sulphate, potassium dichromate, ferrous ammonium sulphate and starch solution [22]. Analytical grade reagents and chemicals were used for determination of COD.

2.2. Experimental procedures

The experimental setup of the ozone/UV system used in this study is shown in Fig. 1. The ozonation and O_3/UV experiments were performed in glass reactor (bubble column with specifications: inner diameter 63.5 mm and height 914.4 mm) made of borosilicate glass equipped UV quartz tube (external diameter 22 mm and length 508 mm) which house the UV-C lamp (Fig. 1). The UV-C lamp (Atlantic 36 watt, bulb dimensions 508 mm long) used in this work emits radiations (monochromatic) at 253.7 nm. The UV intensity was 1.2 mW/cm^2.

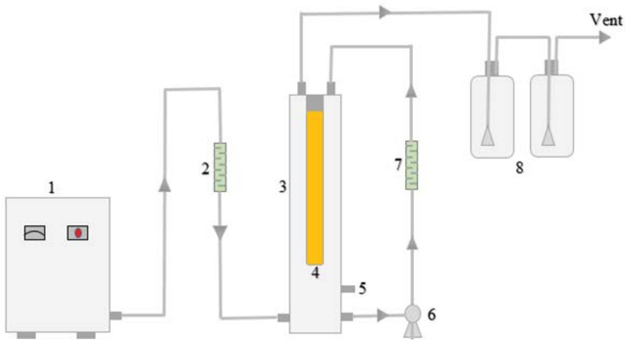

Fig. 1. Schematic representation of ozone/UV treatment system used in this study. The system consists of: (1) ozone generator; (2, 7) flowmeter; (3) ozonation reactor; (4) UV-C lamp; (5) sample port; (6) recirculation pump; (8) KI traps.

The glass reactor (bubble column) has an outlet of the sample at the bottom. A recirculation pump is also connected to the bottom of the reactor to assist recirculation of wastewater (black liquor) within the reactor. Ozone (O_3) gas was supplied to the bottom of the reactor (through a porous gas diffuser situated at its bottom) with the help of ozone generator. The gas (O_3) was regulated by a rotameter. Ozone (O_3) in the gas phase was measured by absorption method (Standard KI absorption method). The unreacted ozone from the top (leaving the reactor) was scrubbed with 2% KI solution in gas wash bottles where KI (potassium iodide) solution reacted with excess ozone (O_3) [23]. Each run (experiment) was performed three times by taking the mean value to ensure accuracy. In addition, before each run, wastewater (black liquor) was filtered to remove small particles in the effluent. pH of the wastewater (black liquor) was adjusted by 0.1 M NaOH and HCl.

2 L of wastewater (diluted black liquor) was charged into the reactor and experiments were performed by supplying ozone and ozone/UV continuously for 3 h. The wastewater was recirculated at the rate of 1 L/min to increase mixing between liquid and gas in addition to the mixing provided by the gas bubbles. Finally, the samples were collected from the bottom of the reactor at regular time intervals and analyzed for colour and COD removals by standard methods [22].

2.3. Analytical methods

Before analysis, samples were first filtered using filter paper. The organic matter in the sample was characterized in terms of COD by using standard methods. The COD removal efficiency was calculated by using the following formula [24]:

$$\text{COD removal efficiency}\left(\%\right)=\left(\frac{\text{COD}_o-\text{COD}_t}{\text{COD}_o}\right)\times 100 \quad (5)$$

where COD_o = chemical oxygen demand at time 0 and COD_t = chemical oxygen demand at time t.

The absorbance of a sample was measured by the spectrophotometer (UV-2700, PerkinEmler Lambda 35). The colour removal efficiency was quantified by using the following relation [22]:

$$\text{Colour removal efficiency}\left(\%\right)=\left(\frac{A_o-A_t}{A_o}\right)\times 100 \quad (6)$$

where A_o = absorbance at time 0 and A_t = absorbance at time t.

3. Results and discussion

The pH of a solution, ozone dose and the reaction time play a vital role in O_3 and O_3/UV processes. The effect of pH was studied in both O_3 alone and O_3/UV process for the treatment of paper and pulp industry wastewater. Then the effect of ozone dose was studied and a comparison was made between O_3 and O_3/UV processes in terms of COD and colour removal efficiencies.

3.1. COD and colour removal by ozone

3.1.1. Effect of initial pH

Initial pH of effluent plays a vital role in the ozonation mechanism since it affects ozone decomposition. Literature review reveals that the presence of OH in water or wastewater leads to the generation of hydroxyl radicals (during interaction with aqueous ozone) which react with organics [24,25]. In order to investigate the initial pH effect of wastewater on colour and COD removal, the experiments were conducted at pH 3.8, 6.8 and 9.8 with ozone capacity of 2.3 mg/min or 0.2 mg O_3/mL wastewater. COD removal efficiency and colour removal efficiency at different initial pH is shown in Fig. 2.

Fig. 2(a) shows that COD removal efficiency was increased by increasing the pH of wastewater and it varied from 41% to 52% during ozonation. Maximum COD removal efficiency was observed at pH 9.8. Thus, under alkaline conditions ozonation is favourable for COD removal of the black liquor (wastewater). This may be due to the reason that at alkaline conditions ozone decomposes to •OH radicals and then reacted with organic contaminants while at acidic conditions molecular ozone (O_3) directly reacted with organic pollutants. Since at basic conditions hydroxyl radicals (•OH) have strong oxidizing potential and less selective than O_3 (molecular ozone) which causes mineralization of organic contaminants [26].

Fig. 2(b) shows the colour removal efficiency of ozonation processes as a function of time. Colour removal efficiency was increased by increasing the initial pH of wastewater. It varied from 64% to 70% from acidic to basic conditions. This may be due to the cleavage of bonds in the colour causing lignin or polymerized tannin that are nontoxic but poorly biodegradable at basic conditions [27].

3.2. COD and colour removal by ozone/UV

3.2.1. Effect of initial pH

Previous findings show that combined O_3/UV process is more effective than ozonation (O_3) alone [28]. Therefore, experiments were conducted at different pH with the O_3/UV process. Fig. 3(a) shows that the COD removal efficiency of AOP (O_3/UV) varied from 42% to 55%. Maximum COD removal efficiency was observed at pH 9.8. The colour

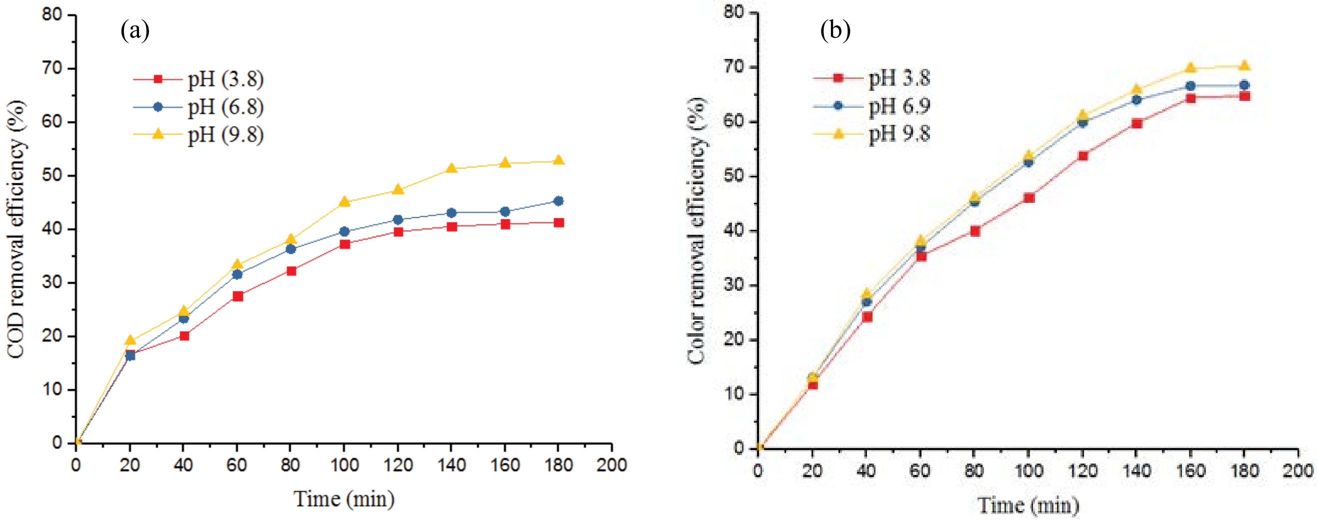

Fig. 2. Effect of initial pH on: (a) COD removal by O_3 process and (b) colour removal by O_3 process (COD_o = 400 mg/L; reaction time = 180 min; ozone dose = 0.2 mg/mL; temperature = 25°C).

removal studies presented in Fig. 3(b) indicate that the colour removal efficiency varied from 65% to 71% in acid to basic conditions, respectively. The O_3/UV process showed better performance at alkaline conditions for COD and colour removal. This may be due to the result of fast reactions of organic matter with hydroxyl radicals. At alkaline pH, ozone self-decomposition to radicals occurs as a result of initiation reaction [29,30]. Furthermore, in case of ozone/UV process, hydroxyl radicals which are surrounded by water cluster approach each other by cage effect and H_2O_2 is produced which reacts with O_3 generating more $^{\bullet}OH$ radicals [31].

$$2^{\bullet}OH \rightarrow H_2O_2 \quad (7)$$

$$H_2O_2 + O_3 \rightarrow {}^{\bullet}OH \quad (8)$$

3.2.2. Effect of ozone dose

Fig. 4(a) shows the COD variation against the ozone dosage with time. The different dosage of ozone (0.1, 0.2 and 0.3 mg of O_3/mL of wastewater) was applied for 180 min to investigate the effect of ozone dose for COD removal. The COD removal varied from 52% to 58%. By increasing the ozone dose, the oxidation process increases which results in decomposition of organic contaminants by breaking their chemical structures. Thus, at higher ozone dose there will be more radical formation, resulting in higher COD removal [32,33].

Ozone dose played a vital role during the O_3/UV process for the decolourization of paper and pulp wastewater. Different ozone doses (0.1, 0.2 and 0.3 mg of O_3/mL of wastewater) were used to investigate the effect

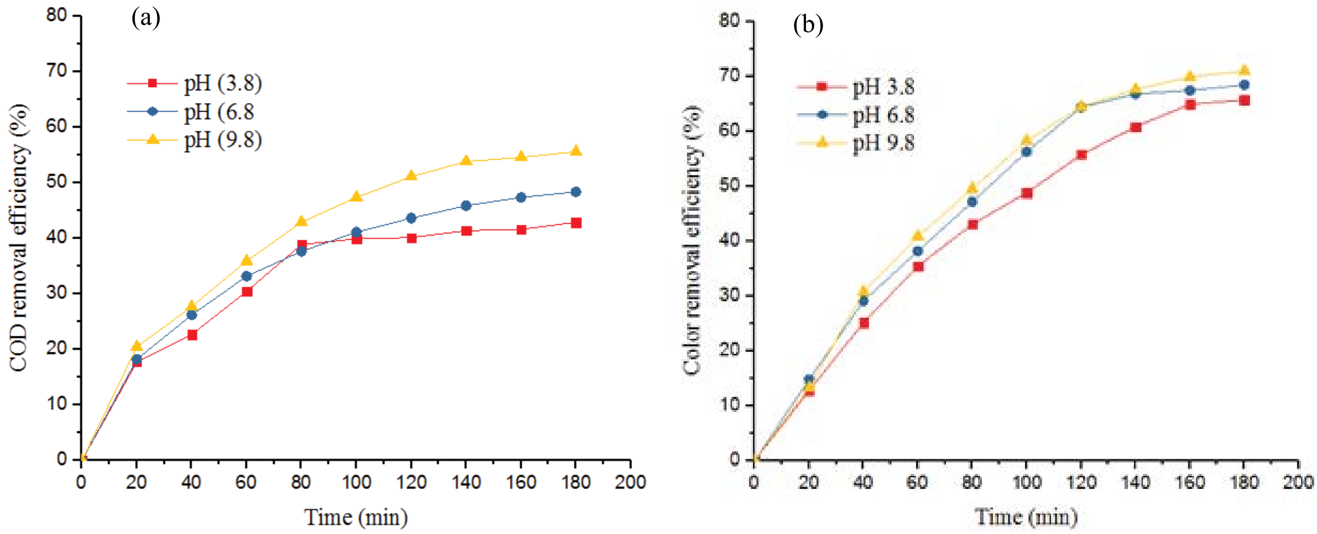

Fig. 3. Effect of initial pH on: (a) COD removal by O_3/UV process and (b) colour removal by O_3/UV process (COD_o = 400 mg/L; reaction time = 180 min; ozone dose = 0.2 mg/mL; temperature = 25°C).

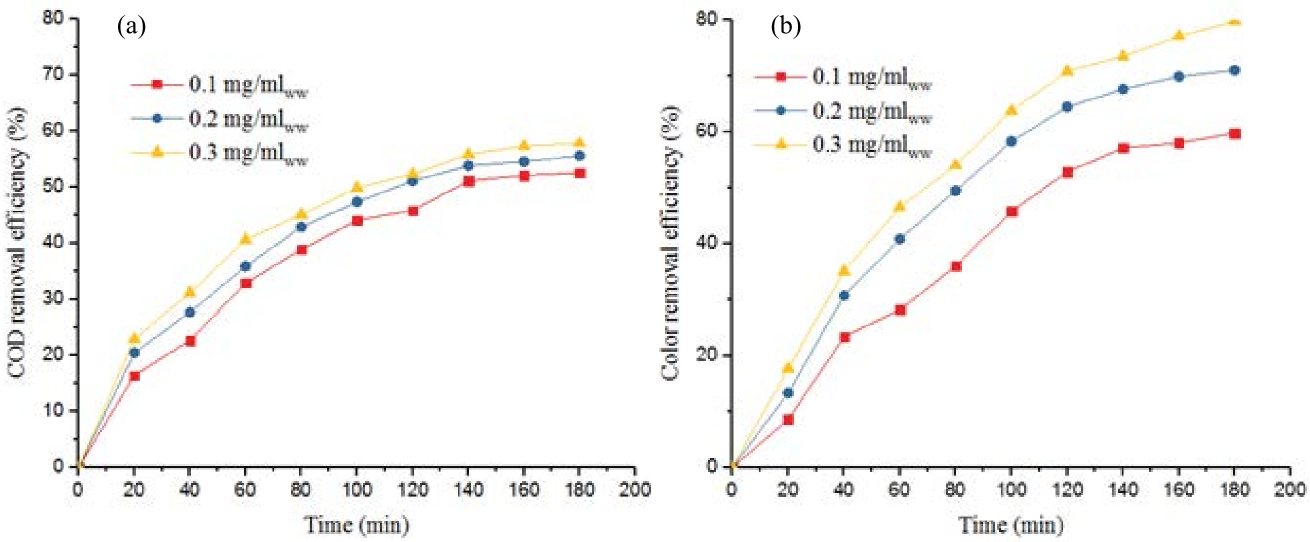

Fig. 4. Effect of ozone dose on (a) COD removal by O_3/UV process and (b) colour removal by O_3/UV process (COD_o = 400 mg/L; reaction time = 180 min; ozone dose = 0.1, 0.2, 0.3 mg/mL; temperature = 25°C).

on decolourization. Fig. 4(b) presents the colour removal efficiency at different ozone dose. By increasing the ozone dose, the colour removal efficiency was increased from 59% to 79%. This may be due to the ozone transfer from gas to liquid phase generating more hydroxyl radicals which result in more decolourization of wastewater [30]. Table 1 depicts the wastewater characteristics before and after treatment with the O_3/UV process.

3.3. Comparison of ozonation alone and O_3/UV process

Figs. 5(a) and (b) shows a comparison of ozone, UV and combined ozone/UV processes for COD and colour removal efficiencies. In O_3 alone process 52% COD removal efficiency was observed at pH 9.8, while in the case of O_3/UV, COD removal efficiency was enhanced from 52% to 55%. In O_3 alone process colour removal efficiency was observed 70% at 9.8, while O_3/UV process enhanced colour removal from 70% to 72% at pH 9.8. The higher removal efficiency obtained in the O_3/UV process may be due to the reason that UV light generates hydroxyl radicals (•OH) during interaction with ozone, while ozone (O_3) also produces radicals at alkaline conditions which results in a faster reaction between organic matter and radical species [31,32].

Fig. 6 shows the variation of pH in the effluent during the ozonation process. The pH values are slightly different when ozonation is performed at pH 3.8. However, at pH 6.8 and 9.8 the variation of the pH values can be divided into regions during ozonation: (1) continuous increase during a subsequent stage of ozonation and (2) gradual decrease during the initial stage of ozonation. A rapid reduction occurred during the initial stage of ozonation at pH 9.8. This behaviour can be explained by the dissolution of carbon dioxide in the effluent. Oxidation of organic compounds in ozonation process results in the CO_2 formation and a part of CO_2 dissolve in wastewater during this process. Due to the dissolution of CO_2, the H_2CO_3, HCO_3, H^+ and CO_3 are produced which leads to pH reduction as per following reactions [30]:

$$CO_2 + H_2O \rightarrow H_2CO_3 \quad (9)$$

$$H_2CO_3 \rightarrow HCO_3 + H^+ \quad (10)$$

$$HCO_3 \rightarrow CO_3 + H^+ \quad (11)$$

Moreover, the amount of molecular ozone decreases when it reacts with organic compounds. As a result, carboxylic acids are formed which further react with ozone (O_3) which causes pH reduction during the initial stage of the ozonation process [33]. In addition, carboxylic acid generation and solubility of CO_2 are inhibited when ozonation is carried out in acidic conditions. It is due to the presence of H^+, thus pH variation in the effluent is depressed. Similarly in case of basic conditions carboxylic acid generation and solubility of CO_2 are promoted. It may be due to the hydroxyl ions (OH) presence in the effluent which decreases the pH of effluent [26].

Table 1
Characteristics of wastewater received from the paper and pulp industry

Sr. #	Parameters	Results
1	pH	6.8
2	Chemical oxygen demand (COD)	16,150 mg/L
3	Total suspended solids (TDS)	10,632 mg/L
4	Colour	Dark brown
5	Odour	Burnt sugar

3.4. Reaction kinetics

The COD removal from pulp and paper wastewater (black liquor) by different AOPs (O_3, O_3/UV) followed

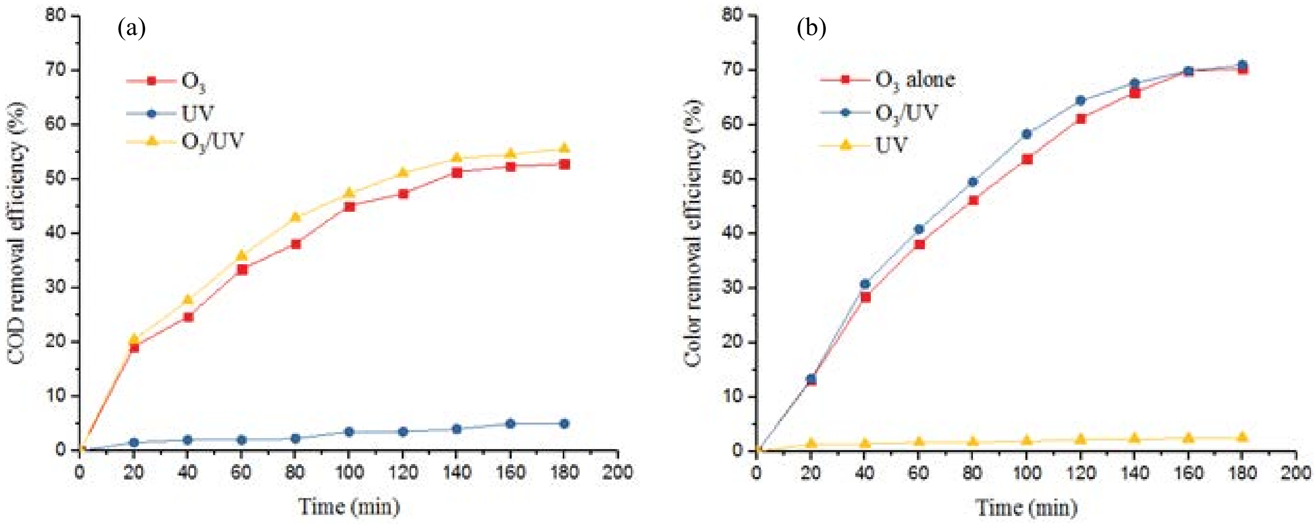

Fig. 5. Comparison of O_3, UV and O_3/UV processes for (a) COD removal and (b) colour removal (COD_0 = 400 mg/L; reaction time = 180 min; ozone dose = 0.2 mg/mL; temperature = 25°C).

first-order kinetics. The COD removal by ozone and ozone/UV process can be described by the following equation [26]:

$$-\left(\frac{dC}{C}\right) = k \times dt \tag{12}$$

Integrating the above equation gives the following relation:

$$-\ln\left(\frac{COD_t}{COD_o}\right) = k \times t \tag{13}$$

where COD_t = COD concentration in wastewater at time t; COD_o = initial COD concentration and k = pseudo-first-order rate constant for COD reduction.

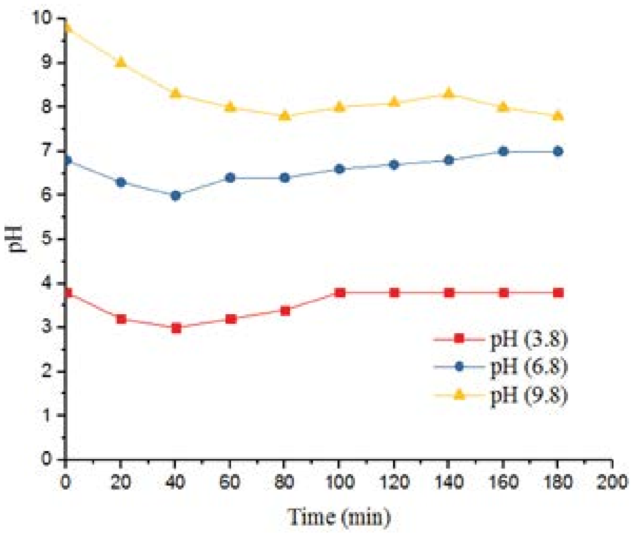

Fig. 6. pH variations during O_3/UV process (COD_o = 400 mg/L; reaction time = 180 min; ozone dose = 0.2 mg/mL; temperature = 25°C).

Table 2 depicts the model parameters for removal of COD at pH 3.8, 6.8 and 9.8. The COD rate constant with O_3/UV was higher than O_3 alone. The rate constant increases by increasing the initial pH of wastewater. This behaviour

Table 2
Model parameters for COD removal kinetics

Process	k′	R^2
O_3 (pH 3.8)	2.80×10^{-3}	0.883
O_3 (pH 6.8)	3.10×10^{-3}	0.874
O_3 (pH 9.8)	4.10×10^{-3}	0.937
O_3/UV (pH 3.8)	2.81×10^{-3}	0.807
O_3/UV (pH 6.8)	3.40×10^{-3}	0.902
O_3/UV (pH 9.8)	4.40×10^{-3}	0.927

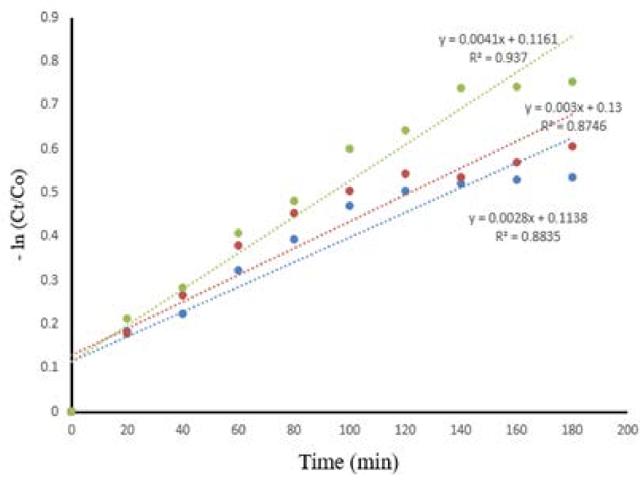

Fig. 7. Effect of pH on pseudo-first-order reaction kinetics during ozonation (COD_o = 400 mg/L; reaction time = 180 min; ozone dose = 0.2 mg/mL; temperature = 25°C).

Table 3
Wastewater characteristics before and after experiments

Sr. #	Parameters	Before experiment	After experiment
1	pH	6.8	7.5
2	Chemical oxygen demand (COD)	400 mg/L	178 mg/L
3	Colour	Dark brown	Colourless
4	Odour	Burnt sugar	Odourless

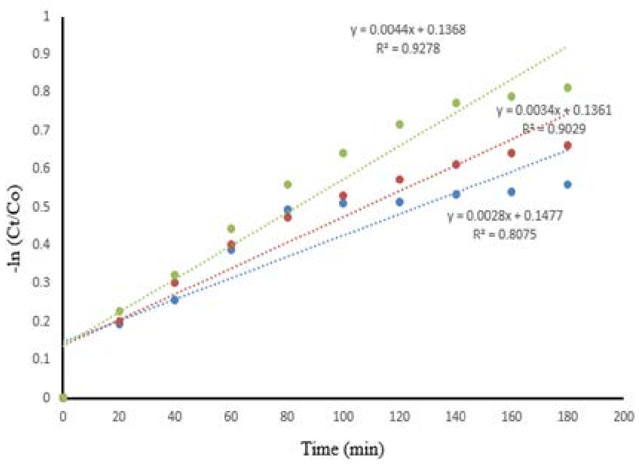

Fig. 8. Effect of pH on pseudo-first-order reaction kinetics during ozone/UV (COD_o = 400 mg/L; reaction time = 180 min; ozone dose = 0.2 mg/mL; temperature = 25°C).

is due to the oxidation of organic compounds by hydroxyl radicals (•OH) which predominates at basic conditions for COD reduction [34]. Figs. 7 and 8 presents this behaviour for ozonation and ozonation combined with UV for the treatment of paper and pulp industry wastewater. In addition Table 3 present wastewater characteristics before and after experimentation.

4. Conclusion

The results of this study indicate that O_3 and O_3/UV processes are feasible methods for the treatment of black liquor under alkaline conditions. O_3/UV process comparative to O_3 alone at basic pH (pH = 9.8) was found to be slightly better, resulting in faster degradation rates. The results further indicate that COD and colour removal are highly dependent on initial pH of the wastewater. The disappearance of pulp and paper black liquor and organic matter described by pseudo-first-order kinetics and the fastest rate constant (4.40×10^{-3}/min) was observed with the O_3/UV process at pH 9.8.

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