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The ozonation of extremely polluted petrochemical wastewater: Effect of catalysts, initial pH, volumetric flow rate and concentration of ozone on oxidation rate

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Abstract

Ozonation of an extremely polluted petrochemical wastewater from styrene and propylene oxide production and the influence of different factors on the treatment efficiency were investigated. The treatment efficiency was the highest under alkaline conditions and with the use of catalysts. Optimal values of ozone concentration and volumetric flow rate of the ozone-oxygen mixture were 20 mg L^{-1} and 400 L $(L \times h)^{-1}$, respectively. The use of H_2O_2 (0.075 wt%) as a catalyst allowed the maximum COD conversion (93%) and acetophenone removal (98%) to be achieved after 60 min. In the meantime, at an optimal concentration of $MnSO_4.5H_2O$ (0.1 wt%), the treatment efficiency in terms of COD and acetophenone removal increased up to 85% and 84%, respectively. Acetophenone was completely removed from the wastewater when the ozonation time was increased to 90 min, using H_2O_2 or $MnSO_4.5H_2O$ as a catalyst, while phenol, styrene, and ethylbenzene were entirely removed after 60 min. During the ozonation process an abnormal increase in pH appeared due to $^{\bullet}OH$-radical formation. This interesting phenomenon resulted in the possibility of increasing the treatment efficiency by lengthening the time during which the maximum pH as well as the maximum quantity of $^{\bullet}OH$-radicals were observed.

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Introduction

Currently, the chemical and petrochemical industry plays a leading role in the economy of most countries. On the other hand, it is one of the main sources of water and air pollution. If this problem cannot be solved, the ecological balance may be destroyed and humanity will lose the conditions, such as pure air and clean water, essential for its existence. Among the most common pollutants, petroleum products and by-products, and industrial chemicals exist in large amounts, which are discharged into aquatic systems mainly through industrial emissions (Petty *et al.*, 2004; Bedient *et al.*, 1999). The removal of the above substances from petrochemical wastewaters has become an important problem because different experiments have shown that these compounds cannot be removed by conventional wastewater treatment methods (3 Gallego *et al.*, 2002). In addition, existing wastewater treatment technologies require high energy consumption and are not environmentally friendly due to the production of by-products that need further treatment (Battaglin *et al.*, 2001; Hellström, 2000). Consequently, selecting the most appropriate treatment method has become an urgent task in the field of environmental protection.

It is widely known that ozone is one of the most effective reagents for removing organic substances from wastes in general and petrochemical wastewater in particular (Swietlik *et al.*, 2004). Catalytic ozonation is an effective method for removing poorly degradable organic substances from wastewater (Peixoto *et al.*, 2009). For example, the use of manganese compounds, such as manganese oxides, in the catalytic ozonation allows for the complete oxidation of aromatic compounds (Naydenov and Mehandjiev, 1993; Einaga and Futamura, 2004) due to the high level of ozone decomposition (Einaga *et al.*, 2009; Einaga *et al.*, 2011; Zhao *et al.*, 2012; Dhandapani and Oyama, 1997; Oyama, 2000). Thus, manganese compounds are good catalysts for the ozone oxidation process (Einaga and Ogata, 2009).

Apart from manganese compounds, hydrogen peroxide is also an effective catalyst for wastewater ozonation to remove aromatic pollutants and other toxic substances as well as control their color and odor. Various studies in the literature have reported that the use of ozonation together with H_2O_2 to treat wastewater from pulp and paper mills allows for a decoloration efficiency of up to 90% (Catalkaya and Kargi, 2007).

In addition, different experiments have shown that the initial pH influences the efficiency and mechanism of oxidation by ozone as well (Sumegová *et al.*, 2013). For example, the degradation efficiency of perfluorooctanoic acid and perfluorooctane sulfonate by ozonation increased by up to 85–100% at pollutant concentrations of 0.05 mg L^{-1} – 5 mg L^{-1} under alkaline condition (Lin *et al.*, 2012). For more specifically, under alkaline conditions the radical reaction mechanism predominates (Sumegová *et al.*, 2013).

Ozonation is used to treat a variety of wastewaters as has been reported in numerous studies (Parsons and Williams, 2004; Gogate and Pandit, 2004). In our work we studied the ozonation of petrochemical wastewater from the production of styrene and propylene oxide (SPO). The SPO wastewater contains a great deal of organic pollutants, including acetophenone, which is considered to be hazardous to human health and may cause many acute effects such as skin irritation and transient corneal injury (Sittig, 1985). Moreover, phenol is also observed in the SPO wastewater in large amounts. It is widely known that phenol may cause kidney damage, gastrointestinal discomfort, and headaches, pose a nuisance with detectable taste, and odors in water even at low concentrations of 1–8 ppm. There was not sufficient data on the treatment of SPO wastewater with such a high COD. Today there are effective methods of SPO wastewater treatment, using wet oxidation, a wet air regeneration system and powdered activated carbon treatment. However, these methods consume much energy and require high operating costs (Gallego *et al.*, 2002). Ozonation has been known to be an effective method for wastewater treatment in general. However, the use of ozonation on wastewater with such a high COD level has not been investigated so far. So the aim of this study was to investigate the ozonation of the SPO wastewater and clarify the influence of different factors on the treatment efficiency.

Materials and methods

Apparatus and Reagents

The OREC™ L Series Ozonator (ozone generator) was used to produce up to 60 g h^{-1} ozone under pilot-scale conditions. The raw material for ozone generation was compressed oxygen. Ozone concentration was measured by an IKO-01 ozonometer. An ECOTEST-120 pH meter-ionomer was used to determine COD values. The MKS-500 Volumetric Karl Fisher Titrator was used to measure the mass fraction of water in the wastewater, which allowed for determination of the total organic carbon (TOC) concentration. The compositions of the studied samples were determined by chromatography using a Maestro7820 GC-MS (Agilent Technologies). The pH values were measured by a Sartorius PP-20 professional pH meter.

Petrochemical wastewater characteristics

The production of SPO is comprised of four main steps: ethylbenzene is oxidized to hydroperoxide ethylbenzene by atmospheric oxygen, epoxidation of propylene by hydroperoxide ethylbenzene to form propylene oxide and 1-phenylethanol, dehydration of 1-phenylethanol to obtain styrene, and hydrogenation of acetophenone into 1-phenylethanol. The wastewater from the production of SPO was characterized by extremely high organic loading and high alkalinity. The major components contained in the studied wastewater are barely degradable compounds, such as styrene, ethylbenzene, acetophenone, 1-phenylethanol, and other organic substances.

Experimental setup

Compressed oxygen flowed into the ozone generator, the feed rate of which was controlled by a flowmeter (Fig. 1). After passing through the ozonomer, the mixture of generated ozone and oxygen entered the heat-resistant glass reactor from bottom to top. Samples were oxidized by ozonation in the reactor, the volume of which was 100 ml. The electrode was submerged in the liquid layer to observe pH changes. A 0.1 mol L^{-1} KI solution with a saturated starch solution was used to destroy ozone from the reactor; therefore, iodine was displaced from potassium iodide.

Analysis

The experiments were performed at 28 °C in a reactor equipped with a porous glass plate for diffusion of the supplied ozone-oxygen mixture, a thermometer, and a sampler. The upper part of the reactor was reserved for destruction of the foam that formed due to bubbling of the ozone-oxygen mixture.

The initial values of COD, TOC and pH were 720000 mg O_2 L^{-1}, 55 wt% and 13.2, respectively. Since the initial wastewater from the SPO production was highly concentrated, the ozonation method may not achieve high efficiency due to the large quantities of ozone and time required. Therefore, we proposed to acidify this wastewater with concentrated sulfuric acid prior to ozonation. After acidification, the COD, TOC and pH levels were reduced to 95000 mg O_2 L^{-1}, 8 wt% and 3.0, respectively. This acidified wastewater was then the object of our studies of the influence of various factors on the ozonation process. In addition, a 0.2 mol L^{-1} acetophenone solution was used to identify the products of its oxidation by ozone.

The pH and COD values of the studied samples were determined. The composition of the organic products was determined by a chromatographic method.

Analysis methods

Method for chemical oxygen demand determination

COD was measured by a potentiometric method based on the bichromate oxidizability of the studied samples, using an Ecotest-120 pH meter-ionometer.
The method is based on direct potentiometric measurements in a boiling working solution that includes components of the oxidation–reduction

systems $Cr_2O_7^{2-}/Cr^{3+}$, Ce^{4+}/Ce^{3+}, Mn^{3+}/Mn^{2+}, and Ag^{2+}/Ag^{+}. This apparatus allows for the determination of COD values up to 1500 mg O_2 L^{-1}. If the COD values exceed this limit, the samples should be diluted.

Chromatographic method

A Maestro7820 GC-MS was used to perform the qualitative and quantitative chemical analysis of organic substances. The principle operation of the GC-MS is based on the separation of mixtures of substances on packed or capillary columns and their subsequent detection.

The GC-MS parameters were: a HP-INNOWax 19091N-133 (30 m × 0.25 mm, 0.25 microns) column; the column temperature was held at 80 °C for 1 min, after which it was raised from 80 to 250 °C at 5 °C min^{-1}, holding at 250 °C for 2 min; the injection temperature was 250 °C and the division ratio of the flow was 20:1; the temperature of the detector was 280 °C; the gas carrier was helium at 30 cm s^{-1}; the flow rate was constant at 0.9 ml min^{-1}.

Statistical analysis

All experiments were performed in triplicate. Graphical data were expressed as mean value ± standard deviation for the values obtained from three independent experiments.

Results and discussion

The influence of different factors on the wastewater ozonation

Our studied wastewater revealed a complex composition of organic compounds according to the results of the GC-MS analyses (Fig. 2). The studied wastewater primarily contained 1-phenylethanol, phenol, and acetophenone, which produced an unpleasant odor from the studied wastewater.

In order to determine the best catalysts, estimate their optimal concentrations, and study their effect on the efficiency of the wastewater ozonation, $MnSO_4.5H_2O$ and H_2O_2 were used at different concentrations. The ozone concentration, the ozone-oxygen mixture (OOM) volumetric flow rate, and ozonation duration were 20 mg L^{-1}, 400 L $(L \times h)^{-1}$, and 60 min, respectively. The analyses of COD conversion after the ozonation process are presented in Fig. 3.

Table 1. The composition of wastewater organic pollutants.

Components	The composition of WW* organic pollutants, wt%					
	The initial SPO WW	The studied WW	The effluent WW after O_3 process	The effluent WW after O_3/NH_3 process	The effluent WW after $O_3/MnSO_4.5H_2O$ process	The effluent WW after O_3/H_2O_2 process
Ethylbenzene	11.318	0.625	0.128	0.042	0	0
Styrene	2.625	0.305	0.183	0.118	0	0
Benzaldehyde	0.915	0	0.080	0.102	0.068	0
Propylene glycol	3.142	0.525	0.593	0.458	0.434	0.228
Acetophenone	5.068	1.185	0.558	0.215	0.162	0.020
1-Phenylethanol	11.509	1.846	0.802	0.559	0.326	0.186
Diisopropylbenzene	0.459	0	0	0	0	0
Benzyl alcohol	0.922	0	0	0	0	0
2-Phenylpropanol	1.082	0	0	0	0	0
Phenol	12.400	1.465	0.725	0.145	0	0
Benzoic acid	0.000	0.421	0.309	0.123	0.184	0.194
Unidentified components	0.814	0.160	0.108	0.080	0.062	0.059

* WW: wastewater.

The COD conversion was 50.2% in the case of non-catalytic wastewater ozonation, while the treatment efficiency ranged from 62.8% to 90.5% when catalysts were used. Therefore, it is evident that the use of catalysts to assist the ozonation can greatly enhance the efficiency of the treatment process. The highest COD conversion (90.5%) was observed at a H_2O_2 concentration of 0.075 wt%. In the meantime, the optimal concentration of $MnSO_4.5H_2O$ in this process was 0.1 wt%, achieving a COD conversion of 80.1%. However, for both catalysts, further increases in their concentrations beyond their optimal values did not enable an equivalent rise in treatment efficiency.

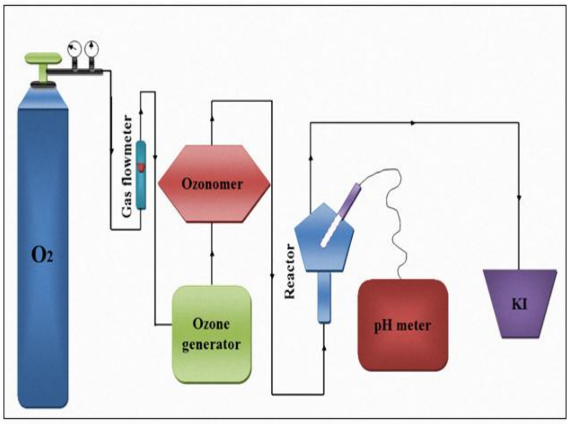

Fig. 1. Schematic of apparatus used for aqueous solution ozonation under laboratory conditions.

Some studies have indicated that manganese compounds can enhance the decay of ozone in aqueous solutions, which increases the ozonation efficiency (Einaga *et al.*, 2009; Einaga *et al.*, 2011; Zhao *et al.*, 2012; Dhandapani and Oyama, 1997; Oyama, 2000). In the case of using H_2O_2 as a catalyst, a high degree of treatment of wastewater is associated with an increase in the quantity of hydroxyl radicals (•OH-radicals) formed (Beltrán, 2004). Ozone principally participates in various complex reactions, leading to the formation of radicals such as •OH-radicals that are more powerful oxidants than ozone itself (Hoigne, 1998). Reaction between H_2O_2 and O_3 can increase the transition of ozone to •OH-radicals in aqueous solution. Hydrogen peroxide is a weak acid that partially dissociates into hydroperoxide ions (HO_2^-) when dissolved in water (Reaction 1). The reaction between ozone and HO_2^- to form •OH-radicals is faster than that with H_2O_2 (Reaction 2) (Hoigne, 1998).

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

$O_3 + HO_2^- \rightarrow {}^{\bullet}OH + O_2 + O_2^-$ (2)

Consequently, the greater the number of •OH-radicals formed in the reaction mixture, the better the ozonation process.

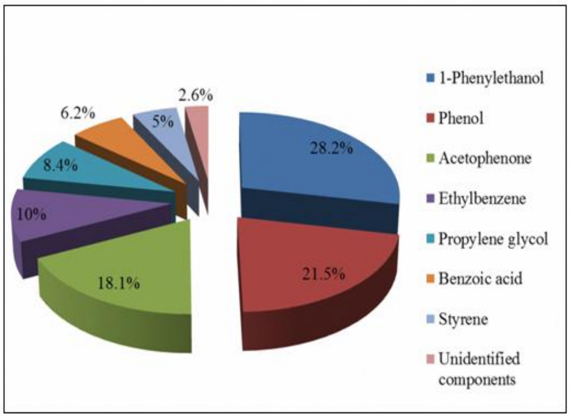

Fig. 2. The composition of the studied wastewater, wt%.

As mentioned above, our studied wastewater was the SPO wastewater after an acidification process. The pH of this wastewater was 3. The next step was clarifying the effect of the initial pH on the efficiency of the wastewater ozonation (Fig. 4). A concentrated ammonia solution was used to establish the initial pH values.

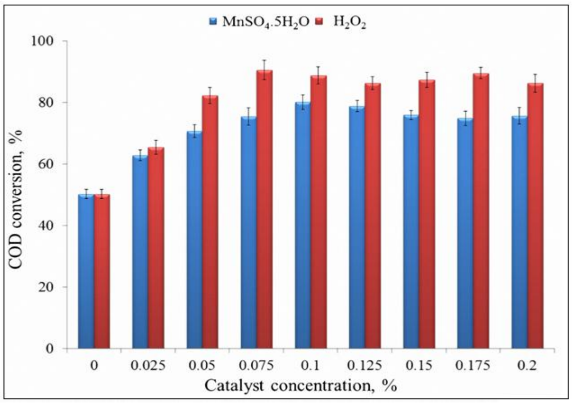

Fig. 3. The effect of catalyst concentration on COD conversion in the studied wastewater via the ozonation process.

It can be seen that the percent conversion of COD increased with increasing initial pH. In this case, NH_3 played a catalytic role in enhancing the studied wastewater treatment efficiency. This can be explained by the role of •OH-radicals during the ozonation process. During the treatment process, ozone decomposed partly into •OH-radicals. In an alkaline solution hydroxide ions act as an initiator for ozone decay (reaction 3).

$O_3 + OH^- \leftrightarrow HO_2^- + O_2$ (3)

The HO_2^- anions that formed in the reaction (3) easily reacted with ozone and formed $^{\bullet}OH$-radicals (reaction 4).

$$O_3 + HO_2^- \rightarrow {}^{\bullet}OH + O_2 + O_2^- \quad (4)$$

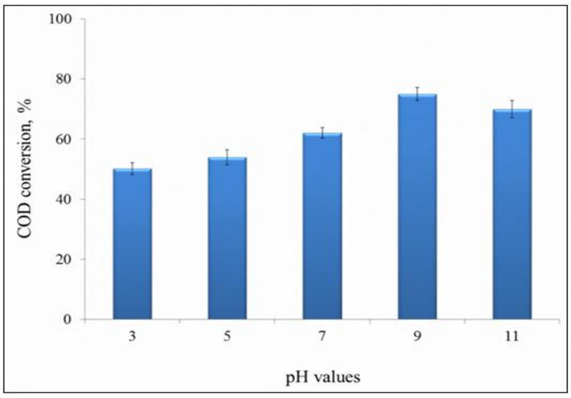

Fig. 4. The effect of pH on COD conversion in the studied wastewater via the ozonation process.

Thus, $^{\bullet}OH$-radical formation increased with increasing initial pH (Munter, 2001). The reaction between $^{\bullet}OH$-radicals and organic pollutants takes precedence under alkaline conditions, while low pH allowed direct reactions between ozone and organic compounds (Sumegová *et al.*, 2013). The hydroxyl radical is a stronger oxidant in comparison with ozone and can react rapidly with many hard-to-oxidize compounds (Glaze and Kang, 1988). Gunten *et al.* (2003) revealed that the rate constants of ozone reactions were greater than 500, while those for reactions with the participation of $^{\bullet}OH$-radicals were much higher (by 2-fold or even more) (Gunten *et al.*, 2003). This phenomenon was demonstrated in the obtained results, where the best cleaning was observed under alkaline conditions (pH = 9), where the COD conversion was 75% and the ammonia concentration was 4% (Fig. 4). In addition, our results also agree with the studies of Somensi *et al.* (2010) and Jagadevan *et al.* (2013) (Somensi *et al.*, 2010; Jagadevan *et al.*, 2013).

The COD conversion of the studied wastewater at pH 11.0 was less than that at pH 9.0. This may be related to the removal of $^{\bullet}OH$-radicals caused by the increase in hydroxide ions (Buxton *et al.*, 1988).

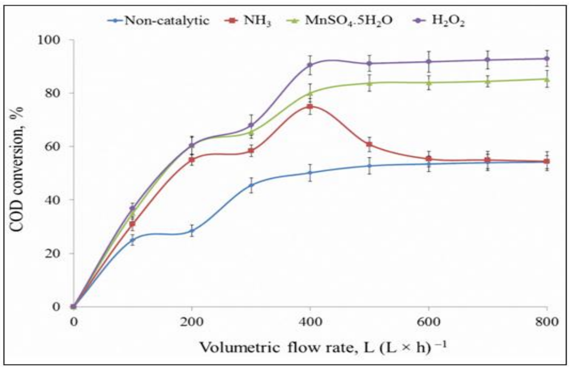

Fig. 5. Effect of OOM volumetric flow rate on COD conversion in the studied wastewater via an ozonation process.

Apart from the pH, OOM volumetric flow rate was also an important factor that influenced the efficiency of the studied wastewater ozonation. Different catalysts, such as $MnSO_4.5H_2O$, NH_3, and H_2O_2, were used separately at their optimal concentrations (Fig. 3). There was a general mechanism for all four cases, including non-catalytic ozonation. The interaction between ozone and water could be divided into two areas of OOM volumetric flow rate regime – diffusive and kinetic ones (Fig. 5).

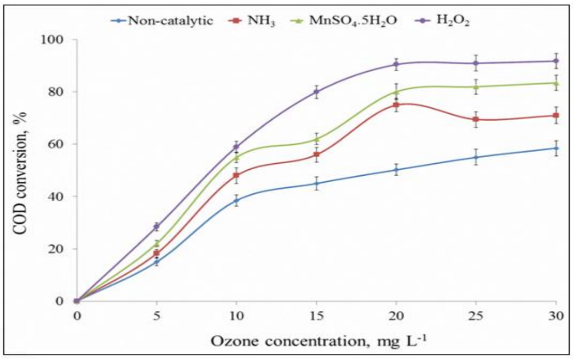

Fig. 6. Effect of ozone concentration on the COD conversion of the studied wastewater.

The diffusive area characterized the diffusive transition of ozone into aqueous solution. According to Henry's law, it can be seen that the amount of ozone that dissolves in water is directly proportional to the partial pressure of ozone in equilibrium with the water at a constant temperature (Rettich *et al.*, 2000). Therefore, the COD conversion increased with increasing OOM volumetric flow rate in the diffusive area. The area with a constant COD conversion in Fig. 5 corresponded to a kinetic regime, in which the transition of ozone to aqueous solution was limited. This meant that COD conversion of the reaction mixture was stable when the OOM volumetric flow rate was increased to more than 400 L (L × h)$^{-1}$. However, when using NH_3 as a catalyst, an OOM volumetric flow rate of more than 400 L (L × h)$^{-1}$ caused a decrease in COD conversion because NH_3 was displaced from the liquid layer in the form of fog.

Fig. 6 shows the effect of ozone concentration on the degree of wastewater treatment. Similarly, across the small range of ozone concentrations (0–20 mg L^{-1}), the COD conversion was directly proportional to the supplied ozone. This can be explained by the increase in dissolved ozone in the water with the increasing ozone concentration in the OOM. However, it should be noted that O_3 is limited in its ability to dissolve in water (Biń, 2006). Thus, when the ozone concentration was more than 20 mg L^{-1}, the quantity of ozone dissolved in water was constant, so the treatment efficiency did not increase in this case.

According to the results shown in Figs. 5 and 6, we can conclude that in terms of energy and resource efficiency it will be beneficial to treat the studied wastewater at an OOM volumetric flow rate of 400 L (L × h)$^{-1}$ and ozone concentration of 20 mg L^{-1}. The COD value in this case decreased from 95000 to 6650 mg O_2 L^{-1} after 60 min of ozonation. The effluent wastewater still needs to be further treated by biological methods in a bioreactor before discharging to the environment (Merayo *et al.*, 2013; Dao *et al.*, 2014). Our experiments showed that H_2O_2 and $MnSO_4.5H_2O$ were effective catalysts in the studied wastewater ozonation. In particular, the use of H_2O_2 combined with ozone allowed the COD treatment efficiency to be increased up to 93% (Fig. 5). Similar results were obtained in a study by Safarzadeh-Amiri (2001), which showed that the O_3/H_2O_2 process can enhance the efficiency to a significantly higher value (Safarzadeh-Amiri, 2001). In a study by Gallego *et al.* (2002) about SPO wastewater treatment by using, separately, wet oxidation, powdered activated carbon treatment and a wet air regeneration system, in spite of a high efficiency, these processes required high operating temperatures (200–300 °C) (Gallego *et al.*, 2002). In the meantime, the use of O_3/H_2O_2 not only achieved a high treatment efficiency but was also effective at laboratory temperatures (20–30 °C). Although the use of NH_3 as a catalyst could achieve relatively high COD conversion, it is a contaminant itself and in turn needs to be removed from the wastewater (Huang *et al.*, 2008). Also, as mentioned above, a high OOM volumetric flow rate displaced NH_3 from the reactor and resulted in a considerable decrease in treatment efficiency (Fig. 5).

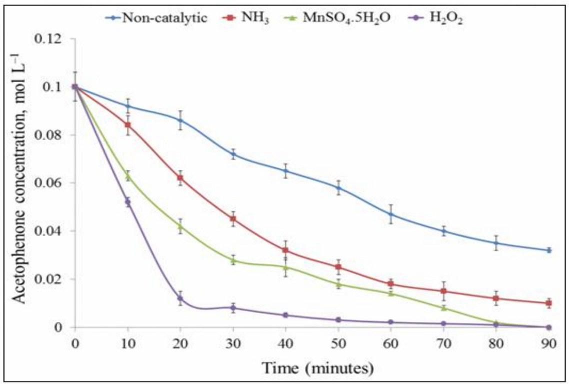

Fig. 7. Acetophenone concentrations at different times during ozonation.

The organic compositions of the wastewater samples, including the initial SPO wastewater, the studied wastewater, and the effluent wastewaters, were determined by GC-MS analyses (Table 1). It can be seen that the initial wastewater had a complex composition, including primarily ethylbenzene, acetophenone, 1-phenylethanol, and phenol, with concentrations of 11.318, 5.068, 11.509, and 12.400 wt %, respectively. After being acidified, the concentrations of some substances decreased significantly, and benzaldehyde, diisopropylbenzene, benzyl alcohol, and 2-phenylpropanol were completely removed. Using $MnSO_4.5H_2O$ or H_2O_2 as a catalyst allowed the acetophenone concentration to be decreased from 1.185 to 0.162 wt% or 0.020 wt%, respectively, and for phenol and styrene to be removed completely. However, propylene glycol is stable in the reaction with ozone. As mentioned above, the effluent wastewater still needs further treatment by biological methods (Merayo *et al.*, 2013; Miller, 1979). Among organic compounds, styrene and acetophenone are barely biodegraded, while propylene glycol can be utilized by many microorganisms. Therefore, the separate use of $MnSO_4.5H_2O$ or H_2O_2 as a catalyst in the ozonation not only could bring high treatment efficiency, but also supported the subsequent biological method.

However, in all experiments mentioned above, acetophenone still remained in the ozonated solution. In addition, acetophenone is difficult to degrade by biological methods. The next step in this study revealed the influence of catalysts and time on the decomposition efficiency of acetophenone in the studied wastewater.

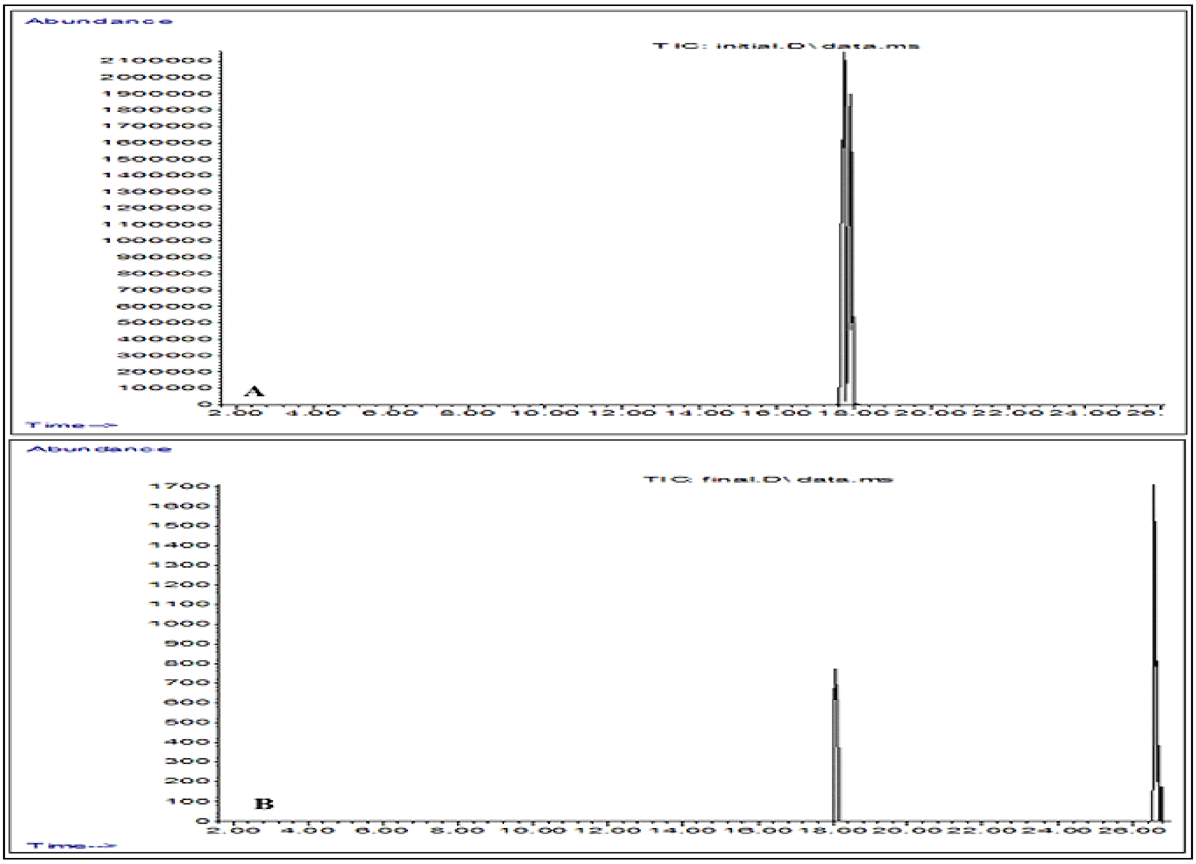

Fig. 8. GC-MS chromatograms of raw (A) and ozonated (B) acetophenone solution.

Acetophenone removal by catalytic ozonation

Despite the high COD conversion, the odor of acetophenone still remained after the ozonation process. Therefore, the wastewater was ozonated for an increased time of 90 min. The acetophenone concentrations of the studied wastewater were determined after every 10 min by GC-MS analyses. The Fig. 7 indicates the effect of the nature of the catalyst on the removal of acetophenone from the studied wastewater over time.

The experiments were performed at an optimal OOM volumetric flow rate of 400 L (L × h)$^{-1}$ (according to Fig. 5), optimal concentrations of ozone ($[O_3]$ = 20 mg L^{-1}, according to Fig. 6) and catalysts ($[MnSO_4.5H_2O]$ = 0.1%, $[H_2O_2]$ = 0.075%, according to Fig. 3, $[NH_3]$ = 4%, according to Fig. 4).

It can be seen that the efficiency of acetophenone removal from the studied wastewater increased in the order non-catalytic and catalytic ozonation ($NH_3 < MnSO_4.5H_2O < H_2O_2$), as a result of which the acetophenone concentration was reduced from 0.1 to 0.032, 0.01, 0, and 0 mol L^{-1}, respectively, after 90 min of ozonation. The obtained results shown in Fig. 7 reconfirmed that H_2O_2 and $MnSO_4.5H_2O$ are the most effective catalysts among the studied ones and could increase the efficiency of acetophenone removal up to 100%. However, extending the length of the ozonation process proved ineffective both for the non-catalytic reaction and the catalytic one using NH_3.

In the next step we identified the products of acetophenone ozonation. A 0.2 mol L^{-1} acetophenone solution was analyzed by GC-MS after being oxidized by ozone in the reactor for 15 min.

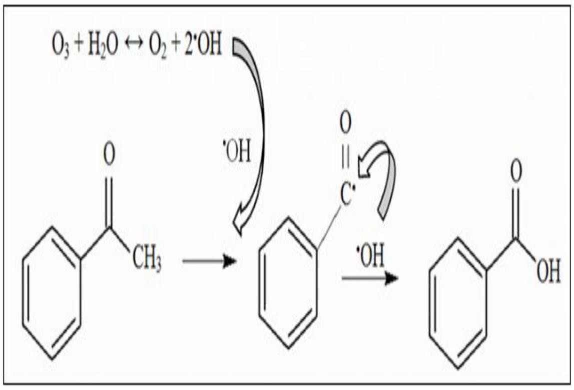

Fig. 9. Mechanism of oxidation of acetophenone to benzoic acid by ozone.

The above chromatograms both indicated an absorption peak with a retention time of 18.2 min, which was identified as being acetophenone. For the case of the obtained reaction mixture (Fig. 8B) the benzoic acid peak was found with a retention time of 27 min. According to the literature the products of the ozonation of organic compounds are typically organic acids such as benzoic acid, formic acid, etc (Sumegová *et al.*, 2013).

The mechanism of oxidation of acetophenone to benzoic acid by ozone is represented in Fig. 9.

As described above, in order to study pH changes in the reaction mixtures during the ozonation process, a pH-meter electrode was submerged in the liquid phase of the reactor. An abnormal change in pH was observed in the first minutes of the acetophenone ozonation process. Generally, ozonation decreases pH values throughout the process due to the formation of acids (Sumegová *et al.*, 2013). In contrast to this, in our experiments, after blowing ozone into the reactor, pH values in the first 2 minutes of the reaction mixture increased dramatically, from neutral to high alkaline values (pH ≈ 14) (Fig. 10).

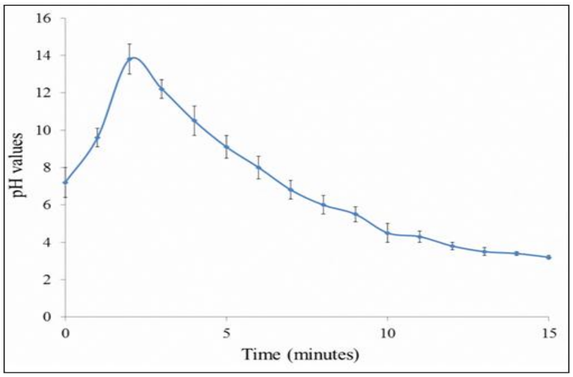

Fig. 10. The abnormal pH change during the acetophenone ozonation process (acetophenone concentration 0.2 mol L^{-1}, temperature 28 °C, $[O_3]$ = 20 mg L^{-1}, OOM volumetric flow rate 400 L $(L \times h)^{-1}$).

This can be explained by the formation of ·OH-radicals due to the reaction between ozone and water (Kavanaugh *et al.*, 2004). Along with their strong oxidizing properties, ·OH-radicals indicate alkalinity as well, and can increase the pH of reaction mixtures (Nilvebrant and Jansson, 2005). After reaching a maximum level, the pH value began to decrease due to the formation of acids that were products of organic compound oxidation. This interesting phenomenon led to the ability to raise the degree of treatment by prolonging the time during which the maximum pH as well as the maximum quantity of ·OH-radicals were observed.

We performed a series of experiments with various concentrations (from 0.05 to 0.5 mol L^{-1}) of different organic substances such as acetophenone, styrene, phenol, and 1-phenylethanol. The results showed that the abnormal phenomenon of pH increase could be obtained only when the hydrocarbon concentration was less than 0.3 mol L^{-1}.

Conclusions

In this work, we studied the influence of different factors on the efficiency of ozonation of wastewater from the SPO production, such as the presence, nature and concentration of different catalysts (H_2O_2, $MnSO_4.5H_2O$, and NH_3), the initial pH of all of the solutions, the volumetric flow rate of the ozone-oxygen mixture, and the ozone concentration. We determined that the optimal values of pH, ozone concentration, and volumetric flow rate of the ozone-oxygen mixture were 9, 20 mg L^{-1}, and 400 L $(L \times h)^{-1}$, respectively.

Among the used catalysts, H_2O_2 and $MnSO_4.5H_2O$ showed a strong ability to expedite the ozone treatment process; their optimal concentrations were 0.075 and 0.1 wt%, respectively. Hydrogen peroxide showed the greatest ability to remove organic compounds (93%) and acetophenone (98%) from the studied wastewater after 60 min of ozonation. Extending the ozonation process to 90 min allowed for the complete removal of acetophenone from the studied wastewater in the case of using H_2O_2 or $MnSO_4.5H_2O$.

GC-MS analyses of the acetophenone solution after ozonation for 15 min showed the presence of benzoic acid. An abnormal increase in pH during the first 2 min of the ozonation process in an aqueous solution occurred at low hydrocarbon concentrations. The pH increased sharply due to the formation of $^{\cdot}$OH-radicals in the reaction between ozone and water. Extending the time during which the maximum number of $^{\cdot}$OH-radicals was observed and its value for achieving the highest treatment efficiency will be the subject of a further study.

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