Effect of ozonation combined with heterogeneous catalysts and ultraviolet radiation on recycling of gas-station wastewater

Eman A. Emam

Department of Refining and Petrochemical Engineering, Faculty of Petroleum and Mining Engineering, Suez Canal University, 34721, Salah Nasem St., Suez, Egypt

Received 5 May 2011; accepted 27 July 2011

Abstract Ozonation is extensively applied in the treatment of drinking water and wastewater due to the powerful oxidation potential of ozone. Heterogeneous catalytic ozonation (HCO) of wastewater proceeds through hydroxyl radicals as the oxidation species. The effect of ozonation alone and combined with catalysts in the presence and absence of UV-radiation was investigated to reuse the biologically pretreated gas-station wastewater instead of fresh water. Two types of catalysts: titanium dioxide (TiO₂) and activated carbon (AC) were studied. The concentration of catalyst, dark adsorption, reaction time and the improvement of biodegradability were studied. The combination of catalysts and ozonation reveals a significant improvement in the removal of contaminants present in wastewater by using the ozonation, adsorption or photocatalysis systems. Maximum dissolved organic carbon (DOC) removal of 91% was achieved by the combination of ozone, TiO₂ and the UV-radiation system. But, an increase in biodegradability from 0.12 to 0.33 was realised with ozone and the TiO₂ system. Furthermore, the biodegradability was increased with increasing catalyst concentration combined with ozone up to 1 g/L with TiO₂ and 0.5 g/L with AC.

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1. Introduction

Gas-stations usually consume large volumes of water in many activities such as car washing, floor cleaning, toilet, cafeteria use, etc. Many particles and chemicals are found in the wash water. The concentration and severity of these particulates are usually extrapolated or not considered [1]. Many contaminants of gas-station wastewater have an impact on the environment. Several treatment methods have been employed for the reuse of gas-station wastewater [1,2]. The conventional treatment processes do not allow complete removal of detergents and dissolved solids or heavy metals. Therefore, additional treatment steps are required to eliminate refractory and harmful contaminants to the environment and also to reduce the consumption of fresh water. Because of the large...
variety of chemicals applied in gas-station, the organic content of wastewater is normally measured using integral parameters such as biochemical oxygen demand (BOD), chemical oxygen demand (COD) and dissolved organic carbon (DOC) or hydrocarbon content.

Ozonation is a green processes widely used to destroy or degrade many toxic organic compounds, in water and wastewater with the resulting formation of more biodegradable molecules. Ozone reacts through a direct mechanism that involves the O₃ molecule and/or an indirect mechanism that involves hydroxyl radicals (OH·). It has been shown that ozone system achieves limited mineralisation of organics in drinking water and little COD removal in wastewaters. Consequently, ozone-based advanced oxidation processes were employed to enhance ozone reactivity. Catalytic systems such as O₃/H₂O₂, O₃/UV, and O₃/catalyst have been used for the removal of various wastewater pollutants [3–5]. Mechanisms of OH· production from ozone combined with hydroxide ion, hydrogen peroxide and UV-radiation are well established but to a lesser extent than those of heterogeneous catalytic ozonation [6,7].

The combination of ozone and UV-radiation (O₃/UV) is an effective catalytic system for oxidation and destruction of toxic and refractory organics in water; the process is initiated by photolysis of ozone. Ultraviolet lamps should have their maximum radiation output at 254 nm for an efficient ozone photolysis [8]. A two step mechanism has been proposed involving light-induced homolysis of O₃ and subsequent production of OH· radicals by the reaction of O₃ with water [9,10].

\[
\text{O}_3 + hv \rightarrow \text{O}_2 + \text{O}
\]

(1)

\[
\text{O} + \text{H}_2\text{O} \rightarrow 2\text{OH}
\]

(2)

The use of ozone in combination with heterogeneous catalysts [11,12] has been recently investigated in liquid phase reactions with aniline [13], phenol [14], formic acid [15], and cyanide ions [16]. In all cases a significant improvement of the oxidation process performance has been reported as the mineralisation rate of organic and inorganic substances is greatly enhanced.

Activated carbon (AC) has high surface area and possesses good porous texture allowing the high adsorption capacity of some substances, which allow the efficient use of AC in the removal of aqueous and/or gaseous pollutants. In addition, the use of activated carbon can accelerate the decomposition rate of O₃ and result in higher concentration of active radicals [17,18]. Based on these remarks, the combination of O₃ and AC has been used in wastewater treatment.

Titanium dioxide (TiO₂) is extensively used as photocatalyst. To improve the performance of the photocatalytic system is to change the reaction ambient by adding strong a oxidant species such as hydrogen peroxide [19] also in the presence of Fe(II) ions [20], or ozone. Furthermore, TiO₂ was studied as an adsorbent to remove contaminants from wastewater without UV-radiation in order to access the effect of dark adsorption.

The aim of this study is the efficient removal of refractory contaminants in biologically pre-treated gas-station wastewater to minimise the use of fresh water through the recycling process. The influence of ozone alone and/or combined with ultraviolet (UV) radiation and catalysts was investigated to compare the different studied systems: ozone (O₃ alone), ozone/titanium dioxide (O₃/TiO₂), ozone/activated carbon (O₃/AC), UV/O₃, UV/TiO₂, UV/O₃/TiO₂ and UV/O₃/AC. The influence of the concentration of catalyst, dark adsorption, reaction time and the improvement of biodegradability was investigated.

2. Experimental

2.1. Wastewater characteristics

Biologically pre-treated wastewater was collected from a gas-station. Wastewater was stored at 20 ± 1 °C. The properties of the investigated wastewater are listed in Table 1.

2.2. Materials

A commercial activated carbon from NORIT Nederland B.V. type NRS CARBON EA 0.5–1.5 was used with: 350 kg/m³ apparent density, 13 wt% ash content, 10 wt% moisture content (as packed) and min. 850 Iodine number. All analyses are based on NORIT Standard Test Methods (NSTM).

A commercially titanium dioxide catalyst (Degussa P25) was used; characterised by: 50 ± 15 m²/g, specific surface area, 20–30 nm, particle size and crystal structure shows 70% anatase and 30% rutile.

2.3. Experimental set-up

A 1.8 L glass reactor was used (1) as showed in Fig. 1. The reactor was operated in the batch mode. A magnetic stirrer (3) was used to ensure well mixing and prevent gas bubbles coalescence. A light source (4) was placed in the centre of the reactor composed of a medium pressure mercury vapour lamp (UV-H1022, BLV Licht- und Vakuumtechnik, Germany) housed in a double quartz sleeve with a cooling jacket. The lamp was constantly cooled by circulating distilled water through the cooler (5) to keep a constant temperature and protect the lamp from overheating.

Ozone was supplied by an Ozomat ozone generator (Ozomat COM/R, Anseros, Tübingen, Germany) from dry oxygen used as the feed with a maximum ozone concentration of 150 g/m³. Online analysers were used to measure the ingoing and outgoing ozone concentration (Ozomat GM, Fa. Anseros, Tübingen, Germany). The oxygen–ozone mixture was supplied at the end bottom of the reactor through a microporous distributor which permits for a good gas distribution (6). Teflon tubing was used for the ozone gas lines. Ozone consumption was determined as the difference between the initial and residual ozone concentration in the gas phase. The operating conditions for the experiments are summarised in Table 2.

All experiments were carried out at an initial pH of 7.2 (the pH of wastewater) (see Table 1). For all the experiments carried out with UV-radiation, the light was immediately turned on.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>–</td>
<td>7.2</td>
</tr>
<tr>
<td>DOC</td>
<td>mg/L</td>
<td>45</td>
</tr>
<tr>
<td>COD</td>
<td>mg/L</td>
<td>112</td>
</tr>
<tr>
<td>BOD₅</td>
<td>mg/L</td>
<td>14</td>
</tr>
<tr>
<td>Colour</td>
<td>–</td>
<td>Light yellow</td>
</tr>
</tbody>
</table>
on defining the start of the reaction, i.e. \( t = 0 \), whilst, for the UV/O₃/TiO₂ system, the system was maintained in the dark for 15 min, before turning on the lamp, in order to reach steady state conditions. In experiments where catalyst was used, the catalyst was fed to the reactor with or without ozone (in adsorption tests). The samples were taken from the sample port (2) and filtered through 0.45 μm cellulose nitrate filter paper and then analysed for the concentrations of DOC, COD and BOD₅.

2.4 Analyses

DOC was detected by a Shimadzu Analyzer TOC 5000. COD and BOD₅ were analysed according to the German standards of DIN 38 409 – H 41 and DIN 38 409 – H 51.

3. Results and discussion

3.1 Adsorption tests

In many cases, contaminants of industrial processes wastewater are not readily biodegradable, but they can be effectively removed from wastewater by means of adsorption. Adsorption tests were conducted in batch experiments in order to determine the adsorption effect of the catalysts on DOC removal from gas-station wastewater. The adsorption measurements for the DOC removal were accomplished through replacing ozone by nitrogen during the all adsorption time. The study was carried out with 0.3 g/L catalyst. The adsorption time was 60 min. Also the removal of DOC by using the activated carbon (AC) and TiO₂ was studied. The AC shows a better efficiency by achieving a removal 17% of DOC and compared with only 8% for TiO₂. This may be attributed to the expected higher surface area of the activated carbon compared with that of titanium dioxide (Degussa P25 have only 50 m²/g).

3.2 DOC removal using catalytic ozonation

For the study the effect of catalytic ozonation on DOC removal from gas-station wastewater, three experiments were performed with O₃ alone, O₃/TiO₂ and O₃/AC with catalyst and ozone concentrations of 0.3 g/L and 15 mg/L, respectively. The results of the DOC removal are shown in Fig. 2. The removal of DOC increased with increasing the ozonation reaction time for both O₃ alone and the catalytic ozonation systems. The degradation of DOC was improved with O₃/TiO₂ and O₃/AC systems. The degradation of DOC was 47% and 35% with O₃/AC and O₃/TiO₂ systems, respectively. This difference between the catalytic ozonation systems may be attributed by the high DOC adsorption characteristics of AC than TiO₂. The improvement in DOC removal following the addition of catalysts can be explained by the combination of decomposition of ozone into highly oxidising radicals, catalysed by catalyst surface, and participation in chemical reactions with catalyst surface functional groups. Also, it was concluded that, the stability of ozone is reduced by the presence of activated carbon in the system, [21]. It is well known that the efficiency of the catalytic ozonation depends to a great extent both on the type of catalyst and its surface properties and the pH of the solution [22].

3.3 Effect of catalytic ozonation on the biodegradability enhancement

Oxidation processes for water treatment have showed their worthiness in the field of contaminants elimination. On the other hand, total mineralisation through oxidation processes is very expensive and the biological treatment is really cheap and reliable. However, there are substances that are unable to deal with the biological treatment. So, a combination of both kinds of processes means a cheaper option for total organics degradation from wastewater. This is the general idea that makes some investigators apply a combination of a chemical oxidation process followed by a biological one [23].

Table 2 The operating experimental conditions for ozonation system.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input ozone concentration</td>
<td>mg/L</td>
<td>15</td>
</tr>
<tr>
<td>Reaction volume</td>
<td>L</td>
<td>1.6</td>
</tr>
<tr>
<td>pH</td>
<td>–</td>
<td>7.2</td>
</tr>
<tr>
<td>Catalyst concentration</td>
<td>g/L</td>
<td>0–3</td>
</tr>
<tr>
<td>Temperature</td>
<td>°C</td>
<td>20 ± 2</td>
</tr>
</tbody>
</table>

Figure 2 Effect of catalytic ozonation on the removal of DOC at O₃ concentration = 15 mg/L and catalyst concentration = 0.3 g/L.
The removal of COD by O₃ alone, O₃/TiO₂ and O₃/AC systems are shown in Fig. 3 with about 30%, 38% and 50% of the COD being degraded after 60 min, respectively. These results proved that the activated carbon combined with ozone is the best option in removing COD.

The effects of ozonation time and catalyst concentration on the biodegradability enhancement are shown in Figs. 4 and 5. Biodegradability is defined as the ratio of BOD₅ to COD (as a reference, this parameter for municipal wastewater is around 0.4) [24]. It can be noted from Fig. 4 that, wastewater is not biodegradable, because the initial biodegradability was 0.12. When oxidation process is applied, biodegradability increases slowly to about 0.19 with the O₃ alone system. The O₃/TiO₂ system has substantially improved biodegradability by nearly two times as compared to the O₃ alone after only 40 min of the reaction time. On the other hand, the addition of AC showed only slight improvement in biodegradability as compared to O₃ alone. A combination of O₃/TiO₂ system with a subsequent biological treatment may be an economic way for the treatment of this wastewater.

From Fig. 5, as catalyst concentration increased, the BOD₅/COD ratio increased significantly by about three and two times of the initial biodegradability with O₃/TiO₂ and O₃/AC systems respectively. Catalysts concentrations higher than 1 and 0.5 g/L of TiO₂ and AC, respectively did not improve the biodegradability.

### 3.4. Effect of combination of catalytic ozonation and UV-radiation on the removal of DOC

Fig. 6 shows the degradation of DOC versus reaction time for experiments carried out by the following systems: (i) UV-radiation and ozone without catalyst; (ii) UV-radiation in the presence of TiO₂; (iii) UV-radiation in the presence of TiO₂ and ozone, (iv) UV-radiation in the presence of AC and ozone. It can be noted that, the DOC degradation increases with the reaction time. The highest degradation of DOC takes place in the presence of ozone, UV-radiation and catalyst. The result of UV/O₃/TiO₂ system was slightly improved than UV/O₃/AC system with about 91% and 88% of DOC removal, respectively.

The increase of DOC degradation with UV/O₃/AC system than ozonation may be attributed to overall reactions through: (i) adsorption of the contaminant on the AC, (ii) oxidation by free radical reactions, which AC can promote the generation of free radicals from ozone in aqueous solution, (iii) ozone photoinactivity by the combination of ozone and UV-radiation, which increasing the decomposition of ozone to hydroxyl radicals.

It is well known that TiO₂ is widely used as photocatalyst. By using of UV-radiation with TiO₂ as the photocatalytic system, electron-hole pairs are generated after absorption of radiation by the semiconductor and they can be trapped by a
particular species. Hydroxyl groups act as traps for the holes, forming oxidant hydroxyl radicals; oxygen molecules adsorbed on TiO₂ surface, can trap photogenerated electrons. O₂ is transformed to $\text{O}^\cdot_2^-$ that produces OH₂ and OH⁻ species:

$$\text{TiO}_2 + h\nu \rightarrow \text{TiO}_2 + e^- + h^+ \quad (3)$$

$$\text{OH}^- + h^+ \rightarrow \text{OH} \quad (4)$$

$$\text{O}_2 \rightarrow \text{O}_2(\text{ads}) \quad (5)$$

$$\frac{1}{2}\text{O}_2 + 2\text{H}_2\text{O} \rightarrow \text{OH}_2 + 2\text{OH}^- \quad (6)$$

Where HO₂ generated produce the hydroxyl radical according to reactions:

$$2\text{HO}_2 \rightarrow \text{O}_2 + \text{H}_2\text{O}_2 \quad (8)$$

$$\text{H}_2\text{O}_2 + \text{O}_2^- \rightarrow \text{OH}^- + \text{OH} + \text{O}_2 \quad (9)$$

When ozone is present in the photo-reaction (see reactions (1) and (2)) and catalytic suspension, in addition to the reactions (8)–(11), it must be considered the role of O₃ as electron trap.

$$\text{O}_3 + \text{OH}^- \rightarrow \text{O}_2^- + \text{HO}_2 \quad (10)$$

$$\text{O}_3 + \text{OH}^- \rightarrow \text{O}_2 + 2\text{HO} \quad (11)$$

In the presence of TiO₂ and UV-radiation, ozone acts as a very strong electrophilic agent forming O₅⁻ ozonide radicals [16] that lead to hydroxyl radicals:

$$\text{O}_3(\text{ads}) + e^- \rightarrow \text{O}_5^- \quad (12)$$

$$\text{O}_5^- + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{OH} + \text{O}_2 \quad (13)$$

Therefore, when the TiO₂ is irradiated in the presence of ozone, a greater amount of hydroxyl radicals is formed. This fact can justify the significant positive effect of ozone oxidation combined with photocatalysis on the removal of DOC.

### 3.5. Effect of combination of catalytic ozonation and UV-radiation on the biodegradability enhancement

Fig. 7 shows the effect of catalytic ozonation combined with UV-radiation on the biodegradability of gas-station wastewater. At the beginning of the experiment, biodegradability increased with increasing the time up to 20 min for UV/O₃ and UV/O₃/TiO₂ systems and 30 min for UV/O₃/AC system. The biodegradability was achieved 0.22 and 0.28 with UV/O₃ and UV/O₃/TiO₂ systems, respectively, whereas, the highest value was obtained with UV/O₃/AC system of about 0.31. The increase of the biodegradability with UV/O₃/AC system may be attributed to overall reactions through adsorption activity of AC and oxidation reaction by hydroxyl radicals, which are generated from the decomposition of ozone by the photocatalytic activity with UV-radiation and the adsorption of AC may increase the decomposition of ozone to hydroxyl radicals. As a result, these reactions produce compounds, which are not easily biodegradable, as well as the simple biodegradable compounds present in wastewater. It was explained that, the relative proportions of these organic compounds determine the tendency of wastewater toward changes in its biodegradability [25].

### 4. Conclusions

Heterogeneous catalytic ozonation (HCO) systems have proven to be more effective in removing DOC in biologically pre-treated gas-station wastewater. Two different catalysts (AC and TiO₂) and ozone with and without UV-radiation have been studied. The combination of ozone and catalysts was very effective in removing DOC, COD and increasing the biodegradability of wastewater compared with ozone alone and/or ozone with UV-radiation. UV/O₃/TiO₂ system was able to remove 91% of DOC whereas; UV/O₃/AC system removed 88%. The highest biodegradability (BOD₅/COD ratio) was achieved with O₃/TiO₂ system with about 0.39 at 1 g/L of catalyst concentration. It can be concluded that, HCO seems to be promising technology for the treatment of refractory wastewaters.

### References