Gas-station Wastewater Treatment using Catalytic and non-Catalytic Ozonation

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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 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 (TiO\textsubscript{2}) 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 DOC (Dissolved Organic Carbon) removal of 91\% was achieved by the combination of ozone, TiO\textsubscript{2} and UV-radiation system. But, an increase in biodegradability from 0.12 to 0.33 was realized with ozone and TiO\textsubscript{2} system. Furthermore, the biodegradability was increased with increasing catalyst concentration combined with ozone up to 1 g/L with TiO\textsubscript{2} and 0.5 g/L with AC.

Keywords: Heterogeneous catalytic ozonation; titanium dioxide; activated carbon; adsorption; UV-radiation; improved biodegradability
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 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 [1-3]. 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 direct mechanism that involves O_3 molecule and/or indirect mechanism that involves hydroxyl radicals \( \cdot OH \). 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 \( O_3/\text{H}_2\text{O}_2 \), \( O_3/\text{UV} \), and \( O_3/\text{catalyst} \) (such as \( O_3/\text{Fe}^{2+} \)) have been used for the removal of various water pollutants [4-7]. Mechanisms of \( \cdot OH \) production from ozone combined with hydroxide ion, hydrogen peroxide and UV-radiation are well established but at a lesser extent those of heterogeneous catalytic ozonation [7-9].

The combination of ozone and UV-radiation (\( O_3/\text{UV} \)) 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 [10]. A two step mechanism has been proposed involving light-induced homolysis of O_3 and subsequent production of \( \cdot OH \) radicals by the reaction of \( O \) with water [11-13].

\[
O_3 + hv \rightarrow O_2 + O \quad (1)
\]

\[
O + H_2O \rightarrow 2OH \quad (2)
\]

The use of ozone in combination with heterogeneous catalysts [14,15] has been recently investigated in liquid phase reactions with aniline [16], phenol [17], formic acid [18], organic compounds [13], ammonia [7], and cyanide ions [19].
In all cases a significant improvement of oxidation process performance has been reported as the mineralization 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 O$_3$ and result in higher concentration of active radicals [20,21]. Based on these remarks, the combination of O$_3$ and AC has been used in wastewater treatment.

Titanium dioxide (TiO$_2$) is extensively used as photocatalyst. To improve the performance of the photocatalytic system is to change the reaction ambient by adding strong oxidant species as hydrogen peroxide [22] also in the presence of Fe(II) ions [23], or ozone. Furthermore, TiO$_2$ 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 recycling process. The influence of ozone alone and/or combined with ultraviolet (UV) radiation and catalysts were investigated to compare the different studied systems: ozone (O$_3$ alone), ozone/titanium dioxide (O$_3$/TiO$_2$), ozone/activated carbon (O$_3$/AC), UV/O$_3$, UV/TiO$_2$, UV/O$_3$/TiO$_2$ and UV/O$_3$/AC. The influence of the concentration of catalyst, dark adsorption, reaction time and the improvement of biodegradability were investigated.

2. Experimental

2.1. Wastewater characteristics

Biologically pre-treated wastewater was collected from a gas-station. The 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/m$^3$ 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 m$^2$/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 center of the reactor composed of a medium pressure mercury vapor lamp (450 W, 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/m$^3$. 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 the wastewater) (see Table 1). For all the experiments carried out with UV-radiation, the light was immediately turned on defining the start of the reaction, i.e. t = 0. In whilst, for the UV/O$_3$/TiO$_2$ 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 BOD$_5$.

Table 1: Characteristics parameters of biologically pre-treated gas-station wastewater

<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>BOD$_5$</td>
<td>mg/L</td>
<td>14</td>
</tr>
<tr>
<td>Color</td>
<td>-</td>
<td>Light yellow</td>
</tr>
</tbody>
</table>
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>

2.4. Analyses

DOC was detected by a Shimadzu Analyzer TOC 5000. COD was used as a measure of the oxygen equivalent of the organic matter content of a sample susceptible to oxidation by the strong chemical oxidant potassium dichromate in an acidic medium (H₂SO₄). Silver sulfate (Ag₂SO₄) was added as a catalyst at 148 °C during a 2 hr period according to the German standard method DIN 38 409-H 41. BOD relates to the amount of biodegradable organic matter in a water sample and mirrors the consumption of oxygen by microorganisms during the biological degradation of organic matter. BOD₅ was measured according to the German standard method DIN 38 409-H51.

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 the 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 O$_3$ alone and the catalytic ozonation systems. The degradation of DOC was improved with O$_3$/TiO$_2$ and O$_3$/AC systems. The degradation of DOC was 47% and 35% with O$_3$/AC and O$_3$/TiO$_2$ systems, respectively. This difference between the catalytic ozonation systems may be attributed by the high DOC adsorption characteristics of AC than TiO$_2$. The improvement in DOC removal following the addition of catalysts can be explained by the combination of a decomposition of ozone into highly non-selective oxidizing radicals, which react with almost organic molecules, catalysed by catalyst surface, and participation in chemical reactions with catalyst surface functional groups. Also, it has been demonstrated that electrons of the graphitic layers and basic surface groups of the activated carbon are the main factors responsible for the decomposition of ozone into $\cdot$OH radicals and the stability of ozone is reduced by the presence of activated carbon in the system [24]. 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 [25].

### 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 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 a wastewater. This is the general idea that makes some investigators apply a combination of a chemical oxidation process followed by a biological one [26].

The removal of COD by O$_3$ alone, O$_3$/TiO$_2$ and O$_3$/AC systems are showed 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 BOD$_5$ to COD (as a reference, this parameter for municipal wastewater is around 0.4) [27]. It can be noted from Fig. 4 that, the wastewater is not biodegradable, because the initial biodegradability was 0.12. When oxidation process is applied, biodegradability increases slowly to about 0.19 with O$_3$ alone system. The O$_3$/TiO$_2$ system has substantially improved biodegradability by nearly 2 times as compared to the O$_3$ 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 O$_3$ alone. A combination of O$_3$/TiO$_2$ 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 BOD$_5$/COD ratio increased significantly by about 3 and 2 times of the initial biodegradability with O$_3$/TiO$_2$ and O$_3$/AC systems respectively. Catalysts concentrations higher than 1 and 0.5 g/L of TiO$_2$ 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 TiO$_2$; (iii) UV-radiation in the presence of TiO$_2$ 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/O$_3$/TiO$_2$ system was slightly improved than UV/O$_3$/AC system with about 91% and 88% of DOC removal, respectively.

The increase of DOC degradation with UV/O$_3$/AC system than ozonation may 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 [24, 28], (iii) ozone photoactivity by the combination of ozone and UV-radiation, which increasing the decomposition of ozone to hydroxyl radicals.

It is well known that TiO$_2$ is widely used as photocatalyst. By using of UV-radiation with TiO$_2$ as the photocatalytic system, electron–hole pairs are generated after absorption of radiation by the semiconductor and they can be trapped by particular species. Hydroxyl groups act as traps for the holes, forming oxidant hydroxyl radicals; oxygen molecules adsorbed on TiO$_2$ surface, can trap photogenerated electrons. O$_2$ is transformed to $O_2^-$ that produces $OH_2^-$ and $OH^-$ species:

$$TiO_2 + hv \rightarrow TiO_2 + e^- + h^+ \quad (3)$$

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

$$O_2 \rightarrow O_{2(ads)} \quad (5)$$

$$O_{2(ads)} + e^- \rightarrow O_2^- \quad (6)$$

$$\frac{1}{2}O_2^- + 2H_2O \rightarrow OH_2 + 2OH^- \quad (7)$$

Where $HO_2^-$ generated produce the hydroxyl radical according to reactions:
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 $O_3$ as electron trap.

$$O_3 + OH^- \rightarrow O_2^- + HO_2$$  \hspace{1cm} (10)  

$$O_3 + OH_2 \rightarrow O_2 + 2HO$$  \hspace{1cm} (11)

In the presence of TiO$_2$ and UV-radiation, ozone acts as a very strong electrophilic agent forming $O_3^-$ ozonide radicals [19] that lead to hydroxyl radicals:

$$O_3(ads) + e^- \rightarrow O_3^-$$ \hspace{1cm} (12)

$$O_3^- + H_2O \rightarrow OH^- + OH^+ + O_2$$ \hspace{1cm} (13)

Therefore, when the TiO$_2$ 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 a gas-station wastewater. At the beginning of the experiment, biodegradability increased with increasing the time up to 20 min for UV/O$_3$ and UV/O$_3$/TiO$_2$ systems and 30 min for UV/O$_3$/AC system. The biodegradability was achieved 0.22 and 0.28 with UV/O$_3$ and UV/O$_3$/TiO$_2$ systems, respectively. Whereas, the highest value was obtained with UV/O$_3$/AC system of about 0.31. The increase of the biodegradability with UV/O$_3$/AC system may be attributed to overall reactions through adsorption activity of AC and oxidation reaction by hydroxyl radicals, which generate from decomposition of ozone by the photoactivity with UV-radiation and the adsorption of AC may be increase the decomposition of ozone to hydroxyl radicals.

As a result, these reactions produce compounds, which are not easily aerobically biodegradable, as well as the simple biodegradable compounds presence in the wastewater. It was explained that, the relative proportions of these organic compounds determine the tendency of the wastewater towards changes in its biodegradability [29].
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 TiO$_2$) and ozone with and without UV-radiation have been studied. Combination of ozone and catalysts was very effective in removing DOC, COD and increasing the biodegradability of the wastewater compared with ozone alone and/or ozone with UV-radiation. UV/O$_3$/TiO$_2$ system was able to remove 91% of DOC whereas; UV/O$_3$/AC system removed 88%. A highest biodegradability (BOD$_5$/COD ratio) was achieved with O$_3$/TiO$_2$ system with about 0.39 at 1 g/L of catalyst concentration. It can be concluded that, HCO seems as a promising technology for the treatment of refractory wastewaters.

5. References

Figure 1: Reactor set-up
(1) Glass reactor, (2) sample port, (3) magnetic stirrer, (4) light source, (5) cooler (input/output) and (6) microporous gas distribution

Figure 2: Effect of catalytic ozonation on the removal of DOC at $O_3$ concentration = 15 mg/L and catalyst concentration = 0.3 g/L.
Figure 3: Effect of catalytic ozonation on the removal of COD at \(O_3\) concentration = 15 mg/L and catalyst concentration = 0.3 g/L.

Figure 4: Effect of catalytic ozonation on the biodegradability at \(O_3\) concentration = 15 mg/L and catalyst concentration = 0.3 g/L.
Figure 5: Effect of catalyst concentration on the biodegradability at $O_3$ concentration = 15 mg/L time.

Figure 6: Effect of catalytic ozonation combined with UV-radiation on the removal of DOC at $O_3$ concentration = 15 mg/L and catalyst concentration = 0.3 g/L.
Figure 7: Effect of catalytic ozonation combined with UV-radiation on the biodegradability at $O_3$ concentration = 15 mg/L and catalyst concentration = 0.3 g/L.