Treatment of wastewater containing o-phenylenediamine by ozone in a rotor-stator reactor

Moses Arowo, Yingwen Li, Guangwen Chu, Baochang Sun, Jianfeng Chen and Lei Shao

ABSTRACT

This work employed a novel rotor-stator reactor (RSR) to intensify the degradation process of o-phenylenediamine (o-PDA) by ozone. The effects of different operating parameters including initial pH, temperature, rotation speed, liquid volumetric flow rate and inlet ozone concentration on the removal efficiency of o-PDA were investigated in an attempt to establish the optimum conditions. The removal efficiency was evaluated in terms of degradation ratio and chemical oxygen demand (COD) reduction ratio of the o-PDA wastewater. Results indicate that the removal efficiency decreased with increasing liquid volumetric flow rate but increased with an increase in pH and inlet ozone concentration. Also, the removal efficiency increased up to a certain level with an increase in rotation speed and temperature. Additionally, a comparison experiment was carried out in a stirred tank reactor (STR), and the results show that the degradation and COD reduction ratios reached a maximum of 94.6% and 61.2% in the RSR as compared to 45.3% and 28.6% in the STR, respectively. This work demonstrates that ozone oxidation carried out in RSR may be a promising alternative for pre-treatment of o-PDA wastewater.

Key words | advanced oxidation, degradation, o-phenylenediamine, ozone, rotor-stator reactor

INTRODUCTION

O-Phenylenediamine (o-PDA), also referred to as either 1,2-diaminobenzene or 1,2-phenylenediamine, is an important aromatic amine with widespread applications in the chemical industry including the synthesis of dyes (Sorensen et al. 2001), pharmaceuticals and polymeric materials (Wang et al. 2008) and as a redox mediator for laccase (Palys et al. 2007). However, it is also classified by the Environmental Union as a highly toxic and significant environmental pollutant which is harmful in cases of contact with the eye or skin, inhalation and ingestion (Ejhieh & Salimi 2010) and, in extreme levels, may lead to mutagenic and carcinogenic conditions (Erdemir et al. 2009). Large concentrations of o-PDA is usually present in wastewater effluents originating from its preparation process, thus posing a serious challenge to the environment due to its resistance to bacterial degradation and highly toxic effect. Therefore, it is necessary to remove o-PDA or transform it into less harmful byproducts prior to discharge of the effluents into the environment.

Attempts made in recent years to pre-treat o-PDA wastewaters include oxidation with hydrogen peroxide catalyzed by cytochrome c encapsulated in reversed micelles (Ono et al. 2001), oxidation with hydrogen peroxide catalyzed by horseradish peroxidase (Liu et al. 2006) and solar photocatalytic degradation by heterogeneous CuO/X zeolite catalyst (Ejhieh & Salimi 2011). Nevertheless, all of these methods are associated with several limitations, such as complex operation procedures, low efficiency, low throughput capacity and intermittent operation. Therefore, there is a need to develop a high throughput, simple and efficient technique that can degrade o-PDA in wastewaters.

Oxidation by ozone is supposed to be an efficient technique for pre-treatment of o-PDA in wastewater effluents. Ozonation is an advanced oxidation process that has been extensively applied in recent years to treat wastewater effluents containing concentrated refractory organics, owing to the high oxidation potential of ozone ($E_0 = +2.08$ V) and, thus, its ability to break down the structure of most organics (Park & Jin 2005; Leitner & Roshani 2010; Sun et al. 2014). The ozonation process can also generate hydroxyl radical (·OH), the second most powerful oxidant after fluorine with.

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a redox potential of $+2.72$ and $+1.89$ V at pH 0 and 14, respectively, versus the standard hydrogen electrode (Saien & Khezrianjoo 2008), which can significantly enhance the degradation process of the contaminants (Hoigné 1988). However, owing to the rapid consumption of ozone, mass transfer between ozone and the wastewater stream is the rate limiting step in ozone oxidation processes (Chedeville et al. 2009). Thus, there is a need to build a system that can considerably intensify the mass transfer and consequently enhance the degradation process of the contaminants.

The possible application of a novel device: rotor-stator reactor (RSR), which was first developed by Song et al. (2006), to intensify the ozonation process of o-PDA is described herein. RSR can considerably enhance micromixing and mass transfer effects owing to a greatly increased gas-liquid interfacial area and rapid surface renewal rate of the gas-liquid interface, which may be ascribed to thin liquid films and tiny liquid droplets formed due to the huge centrifugal force created by the rotating rotor and the intense turbulence of the gas and liquid streams. In fact, the micromixing time of RSR has been studied and calculated to be approximately $10^{-5}$ s (Chu et al. 2007). Besides, RSR has successfully been employed in several applications including the preparation of nano CaCO$_3$ (Chu et al. 2005), ammonia absorption into water (Li et al. 2015) and the preparation of CeO$_2$ nano support (Wang et al. 2015).

This study employed an RSR to intensify the degradation process of o-PDA by ozone. The effects of various operating parameters on the removal efficiency of o-PDA were investigated in an attempt to optimize the operating conditions. Also, the removal efficiencies of o-PDA in the RSR and a conventional stirred tank reactor (STR) were compared to assess the efficiency of the two different reactors.

**EXPERIMENTAL SECTION**

**Structure and characteristics of RSR**

The structure and characteristics of RSR are shown in Figure 1. It mainly comprises a series of concentric rotor-rings and stator-rings alternately configured in a radial direction. The rotor comprises rotor-rings fixed concentrically on the motor-driven rotor seat while the stator is made up of stator-rings formed by pins mounted concentrically on the cover cap. The stator-rings and rotor-rings have open slots and holes, respectively, which form radial channels for the gas and liquid streams. Liquid flows radially outwards through the slots and holes under the action of centrifugal force generated by the rotation of the rotor. The specifications of the RSR are shown in Table 1.

**MATERIALS AND PROCEDURES**

Figure 2 illustrates a schematic diagram of the experimental setup used in this study. It mainly includes the RSR, oxygen gas cylinder, ozone generator, two liquid tanks, a peristaltic pump and flow meters. Ozone was produced from pure oxygen using an ozone generator (Tonglin Science and Technology Co. Ltd, China). The ozone concentrations in the inlet and outlet gas streams were monitored and measured using ozone analyzer (Double UV Light Ozone Meter, Limicen Ozone R & D Center, China). A simulated wastewater containing o-PDA of an initial concentration of 50 mg/L was prepared by dissolving o-PDA (purity 99.8%) into de-ionized water and adjusting its pH to a desired value using either sodium hydroxide (NaOH) or sulfuric acid (H$_2$SO$_4$), purity
95–97%), both purchased from Beijing Chemical Works, China. The wastewater was pumped into the RSR through the liquid inlet and sprayed uniformly via a nozzle to the innermost layer of the rotor where it flowed radially outwards through the rotor and stator under the action of centrifugal force generated by the rotation of the rotor. At the same time, the ozone-containing gas stream was fed into the RSR through the gas inlet and flowed inwardly through the holes and slots. The gas and liquid streams contacted counter-currently inside the RSR and mixed rapidly, leading to enhanced absorption of ozone into the wastewater and its subsequent degradation of o-PDA. Finally, the gas and liquid streams left the RSR via the gas outlet and liquid outlet, respectively. Effluent liquid samples were collected and immediately analyzed when the ozone concentration in the gas outlet stream reached a steady state.

The RSR system was operated in a continuous mode without recycle, and the liquid residence time in the RSR was approximately less than 3 seconds. During all the experiments, the operating parameters including the initial pH, rotation speed of the rotor, liquid volumetric flow rate, temperature and the inlet ozone concentration were adjusted to a desired value while varying only one parameter at a time in each run.

### Analyses

The removal efficiency of o-PDA was evaluated in terms of degradation ratio and chemical oxygen demand (COD) reduction ratio. The degradation ratio was calculated based on the concentrations of o-PDA before and after ozonation as measured by a UV-Vis spectrophotometer (UV2600, Shimadzu, Japan) at 416 nm, while the COD of the untreated and treated wastewater was determined using a COD analyzer (5B-3A, Lian-hua Tech. Co., Ltd,

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Specifications of the RSR</th>
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<tbody>
<tr>
<td>Item</td>
<td>Unit</td>
</tr>
<tr>
<td>Number of rotor-rings</td>
<td>–</td>
</tr>
<tr>
<td>Number of stator-rings</td>
<td>–</td>
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<tr>
<td>Inner diameters of rotor-rings</td>
<td>mm</td>
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<td>Inner diameters of stator-rings</td>
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<td>Inner diameter of the RSR</td>
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<td>Outer diameter of RSR</td>
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<td>Length of RSR</td>
<td>mm</td>
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<td>Reactor internal volume</td>
<td>m³</td>
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![Figure 2](https://iwaponline.com/wst/article-pdf/73/6/1357/462832/wst073061357.pdf)
China) according to the Chinese standard (HJ/T 399–2007). The degradation ratio signifies the decomposition percentage of o-PDA while the COD reduction ratio indicates the removal degree of organic contaminants. Equations (1) and (2) define the degradation ratio and COD reduction ratio, respectively.

\[
\text{Degradation ratio (\%) } = \frac{C_o - C_f}{C_o} \times 100
\]

(1)

\[
\text{COD reduction ratio (\%) } = \frac{COD_o - COD_f}{COD_o} \times 100
\]

(2)

where \(C_o\) and \(C_f\) are the concentrations of o-PDA before and after ozonation, respectively, while \(COD_o\) and \(COD_f\) represent the COD of wastewater before and after ozonation, respectively. The COD of the untreated wastewater was 101.6 mg/L.

**RESULTS AND DISCUSSION**

**Effect of initial pH**

The effect of pH on the removal efficiency of o-PDA is shown in Figure 3. The degradation ratio sharply increased from 64.3 to 95.1% with an increase in pH from 2 to 8 and, thereafter, slightly increased with further rise in pH. The COD reduction ratio, however, steadily increased all the time with an increase in pH probably because an alkaline environment favored further degradation of the resulting intermediates. Higher pH favored the decomposition of ozone to generate large amounts of hydroxyl radicals which enhanced the degradation of o-PDA. This observation is in agreement with the literature which also reports that direct ozonation is the dominating pathway at lower pH while both direct and indirect ozonation can synergistically take place at higher pH (Titus et al. 2004). In this study, the optimal pH was determined as 6.5, and this is also advantageous since it is the natural pH of o-PDA wastewater.

**Effect of rotation speed**

The effect of rotation speed on the removal efficiency of o-PDA is illustrated in Figure 4. Both degradation and COD reduction ratios increased from 79.2% and 47.8% to 94.6% and 61.2%, respectively, with an increase in rotation speed from 400 to 1,000 rpm beyond which both slightly decreased. Higher rotation speed generates stronger centrifugal force which causes liquid to split into smaller droplets and thinner films, leading to increased gas–liquid interfacial area and faster gas–liquid interface renewal rate. All of these led to enhanced ozone mass transfer into the o-PDA solution and, hence, the observed increase in the removal efficiency. Nonetheless, extremely high rotation speed can reduce the residence time of liquid in RSR and, thus, minimize the contact time between gas and liquid, which is unfavorable for mass transfer between gas and liquid. The effect of this phenomenon at a rotation speed greater than 1,000 rpm overrode the aforementioned benefits of higher rotation speed in this study, hence, resulting in the slight decline in the removal efficiency of o-PDA at rotation speed beyond 1,000 rpm. These results reflect the pattern of the variation of ozone–liquid volumetric mass transfer coefficient. 

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**Figure 3** | Effect of initial pH on removal efficiency of o-PDA (\(T = 25^\circ\text{C}\); inlet ozone concentration = 61.3 mg/L; liquid volumetric flow rate = 18 L/h; rotation speed = 1,000 rpm).

**Figure 4** | Effect of rotation speed on \(k_L\) and removal efficiency of o-PDA (\(T = 25^\circ\text{C}\); inlet ozone concentration = 61.3 mg/L; liquid volumetric flow rate = 18 L/h; pH = 6.5).
transfer coefficient \((k_{L,a})\) with rotation speed. Owing to the low solubility of ozone in water, the gas-phase mass transfer resistance was neglected in this study, and only the liquid-phase resistance was considered. \(k_{L,a}\) was calculated using Equation (3), which is a modification of the formula proposed by Lin et al. (2010). It is evident from Figure 4 that \(k_{L,a}\) increased from 1.16 to 4.1 min\(^{-1}\) with rise in rotation speed from 400 to 1,000 rpm and, thereafter, declined slightly with further increase in rotation speed.

\[
k_{L,a} = \frac{Q_L}{\pi (R_o^2 - R_i^2)L} \ln \left( \frac{C_i}{C_o} \right)
\]  

where \(Q_L\) represents liquid volumetric flow rate (L/min), \(L = \) Length of RSR (m), \(R_i\) and \(R_o\) represent inner and outer radius of RSR (m), respectively. \(C_i\) and \(C_o\) represent inlet and outlet ozone concentrations (mg/L), respectively.

**Effect of liquid volumetric flow rate**

Figure 5 shows the variation of removal efficiency of \(o\)-PDA with liquid volumetric flow rate. The removal efficiency decreased with an increasing liquid volumetric flow rate. An increase in liquid volumetric flow rate leads to lower gas–liquid ratio, resulting in reduced ozone mass transfer into the liquid. In addition, higher liquid volumetric flow rate causes larger liquid droplets size and shorter residence time of the liquid in the reactor (Sun et al. 2015). All of these are unfavorable for mass transfer between ozone and the liquid, and consequently led to the decline in the removal efficiency of \(o\)-PDA.

**Effect of temperature**

The variation of removal efficiency of \(o\)-PDA with temperature is shown in Figure 6. The removal efficiency increased with an increase in temperature, reaching up to a maximum of 98.8% and 80.7% in terms of degradation and COD reduction ratios, respectively, at 35°C and, thereafter, decreased with further rise in temperature. Although higher temperature can increase the decomposition rate of ozone and \(o\)-PDA reaction rate and, thereby, enhance the degradation of \(o\)-PDA, it can also reduce the solubility of ozone in the solution and, hence, limit the ozone mass transfer rate into the \(o\)-PDA solution and, consequently, reduce the degradation process. In this study, the effects of the latter factor predominated at higher temperatures beyond 35°C, resulting in the decline in the removal efficiency \(o\)-PDA.

**Effect of inlet ozone concentration**

Figure 7 illustrates the effect of inlet ozone concentration on the removal efficiency of \(o\)-PDA. The removal efficiency increased from 61.0% and 40.0% to 94.6% and 61.2% in terms of degradation and COD reduction ratios, respectively, with an increase in inlet ozone concentration from 38.3 to 61.3 mg/L and, thereafter, remained relatively stable with further increase in inlet ozone concentration. Since mass transfer rate of ozone into the solution is the limiting step, it is supposed that higher inlet ozone concentration can create a greater driving force and, thereby, increase ozone mass transfer rate into the solution and, consequently, increase the removal efficiency of \(o\)-PDA. When the inlet
The ozone concentration was more than 61.3 mg/L, the absorption efficiency of ozone tended to maximum and, thus, the removal efficiency of o-PDA remained fairly unchanged.

Comparison experiment

A flask containing 1 L of the o-PDA aqueous solution under strong magnetic stirring at 1,500 rpm was used to simulate the STR experiment. The ozone-containing gas stream was introduced into the STR through an aeration stone measuring 25 mm and 30 mm in diameter and length, respectively. The ozonation time in the STR system was set to 2 min, after which the treated wastewater samples were immediately taken for analysis. The 2 min duration was to ensure that the applied amount of ozone per unit volume o-PDA solution in the STR system was approximately equal to that in the RSR system. Other operating conditions were the same as the operating conditions in the RSR experiment, which were set as follows: T = 25 °C, inlet ozone concentration = 61.3 mg/L and pH = 6.5.

The comparison experiment results, as shown in Figure 8, reveal that the degradation and COD reduction ratios attained in the RSR were 109.0% and 114.0%, respectively, higher than those achieved in the STR. This suggests that the RSR greatly intensified the ozonation process of o-PDA, indicating that it is a more efficient gas–liquid mass transfer device as compared to the STR.

The ozonation process of organic pollutants in wastewater involves mass transfer with chemical reactions and, thus, the rates of the chemical reaction and mass transfer in the gas–liquid system are of great significance as they affect the Hatta number (Ha) of the reaction, which, consequently, determines the choice of the gas–liquid mass transfer device. Since the reaction of ozone with o-PDA follows the second order kinetics, the Hatta number can be expressed as shown in Equation (4) according to the literature (Amr & Aziz 2012).

$$Ha = \frac{\sqrt{k \times [o-PDA] \times DO_3}}{k_L}$$  

(4)

where k is the rate constant of the reaction between ozone and o-PDA (L/mol s), [o-PDA] is the concentration of o-PDA in the bulk liquid (mol/L), DO_3 is the ozone diffusivity in water (m²/s) and k_L is the mass transfer coefficient (m/s).

When the Ha < 0.3, the reaction is in the slow kinetic regime and occurs wholly in the bulk liquid, thus, a device with a large liquid volume such as the STR would greatly favor the reaction, while if Ha > 0.3, the reaction is in the fast kinetic regime and occurs entirely in the liquid film and, therefore, a device with a large interfacial area would greatly favor the reaction.

In this study, the Hatta number was calculated to be 25.5, using $k = 1.6 \times 10^3$ L/mol s with $D_{O_3}$ and $k_L$ at $1.4 \times 10^{-9}$ m²/s and $4.0 \times 10^{-5}$ m/s, respectively (Beltrán 2005). Therefore, RSR is feasible for this kind of reaction as it can considerably intensify mass transfer and reaction rates owing to the existence of a huge interfacial area.

**CONCLUSIONS**

The treatment of o-PDA by ozone in an RSR under different operating conditions was investigated in this study. Results indicate that the removal efficiency of o-PDA decreased with increasing liquid volumetric flow rate but increased...
with an increase in pH and inlet ozone concentration. Also, the removal efficiency increased up to a certain level with an increase in rotation speed and temperature. The optimal conditions were determined as pH 8 and rotation speed of 1,000 rpm. The comparison experimental results reveal that the degradation and COD reduction ratios achieved in the RSR were 109.0% and 114.0%, respectively, higher than those attained in the STR. This indicates that the RSR greatly intensified the ozonation process of o-PDA, indicating that it is a more efficient gas-liquid mass transfer device as compared to the STR. This work demonstrates that ozone oxidation carried out in RSR may be a promising alternative for pre-treatment of o-PDA wastewater.

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