Technical Note

Ozonation of azo dye Acid Red 14 in a microporous tube-in-tube microchannel reactor: Decolorization and mechanism

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Highlights

- First use of a high-throughput microreactor to enhance ozonation of dye effluent.
- Ozone–liquid volumetric mass transfer coefficient in the microreactor was studied.
- Effects of design and operating parameters were studied to optimize the conditions.
- The formation of six intermediates during ozonation was detected by GC/MS.
- The probable degradation mechanism of AR 14 in aqueous solution was proposed.

Abstract

The ozonation of synthetic wastewater containing azo dye Acid Red 14 (AR 14) was investigated in a high-throughput microporous tube-in-tube microchannel reactor. The effects of design and operating parameters such as micropore size, annular channel width, liquid volumetric flow rate, ozone-containing gas volumetric flow rate, initial pH of the solution and initial AR 14 concentration on decolorization efficiency and ozone utilization efficiency were studied with the aim to optimize the operation conditions. An increase of the ozone-containing gas or liquid flow rate could greatly intensify the gas–liquid mass transfer. Reducing the micropore size and the annular channel width led to a higher mass transfer rate and was beneficial to decolorization. Decolorization efficiency increased with an increasing ozone-containing gas volumetric flow rate, as well as a decreasing liquid volumetric flow rate and initial AR 14 concentration. The optimum initial pH for AR 14 ozonation was determined as 9.0. The degradation kinetics was observed to be a pseudo-first-order reaction with respect to AR 14 concentration. The difference between the decolorization and COD removal efficiency indicated that many intermediates existed in AR 14 ozonation. The formation of six organic intermediates during ozonation was detected by GC/MS, while the concentration of nitrate and sulfate ions was determined by ion chromatography. The possible degradation mechanism of AR 14 in aqueous solution was proposed.

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1. Introduction

Textile industries have shown a significant increase in the use of synthetic complex organic dyes as the coloring materials. The annual world production of dyestuffs amounts to more than 0.7 Mt (Spadaro et al., 1994; Talarposhti et al., 2001). Thus, dyeing and finishing processes produce large volumes of discharge effluent, which is considered to be one of the major industrial polluters. Azo dyes with at least one azo group (–N=N–) attached to substituted benzene or naphthalene rings are the most widely used commercial dyes in textile coloration (Wu and Wang, 2001). These dyes are resistant to biodegradation due to their refractory nature (Liakou et al., 1997). Strongly colored wastewater not only causes aesthetic problem, but there are also environmental concerns about the possible carcinogenicity and toxicity to aquatic life (Banat et al., 1996; Pinheiro et al., 2004; Patel and Suresh, 2006; Lin et al., 2008; Wu et al., 2008).

Ozonation is a very effective technology in treating wastewater containing recalcitrant compounds and considered as one of the most attractive alternatives for solving the problem of color in textile effluents. (Chu and Ma, 1998; Peyton and Glaze, 1988; Beltran-Heredia et al., 2001; Koch et al., 2002; Chu and Ching, 2003; Zhao et al., 2004). The ozonation process depends not only...
on the kinetic reactions but also on the transfer between phases (López-López et al., 2007). It has been reported that the rate-limiting step in the ozonation of dye-containing wastewater is the mass transfer of ozone from the gas phase to the liquid phase owing to its low solubility in water, leading to low efficiency and high cost of ozonation process (Saunders et al., 1983; Carriere et al., 1993; Tzitzi et al., 1994; Shu and Huang, 1995; Lin and Liu, 2003). The mass transfer rate of ozone depends on the mixing characteristics of the gas–liquid contactor used, the kinetics of ozone decay in the water and the number and size of the ozone bubbles produced (Shin et al., 1999; Rosal et al., 2006; Chu et al., 2007). Therefore, the ozonation performance can be enhanced by increasing the gas–liquid mass transfer rate of ozone. Consequently, innovation of an ozone-contacting device with better mass transfer efficiency is desirable.

As one of the most important means to intensify mass transfer, microscale devices such as micromixers and microreactors have attracted increasing attention in both laboratories and commercial areas in recent years. The characteristic dimension of micron scale, the extremely large surface-to-volume ratio, and the short transport path in microchannels enhance heat and mass transfer dramatically as compared to conventional gas–liquid contactors and reactors, thereby providing many potential opportunities in chemical process development and intensification (Jahnisch et al., 2004). Comparison of mass transfer performance among different gas–liquid contactors reveals that the liquid side volumetric mass transfer coefficients and interfacial areas of the gas–liquid microchannel reactor can exceed those of laboratory bubble columns and other conventional industrial gas–liquid contactors by at least one or two orders of magnitude, thus gas–liquid mass transfer rates are greatly increased (Jahnisch et al., 2000; Hessel et al., 2005). However, due to the structure limitation, the maximum throughputs of most reported microdevices are usually at μL or mL min⁻¹ scale for liquid and at mL min⁻¹ scale for gas, which are much smaller than those of conventional devices, and this is hard to meet the demand of industrial applications for high throughput.

In our laboratory, a high-throughput microporous tube-in-tube microchannel reactor (MTMCR) with better mass transfer efficiency has been designed and developed as a novel gas–liquid contactor. In the reactor, two coaxial tubes form an annular microchannel, and micropores in the annular wall of one end of the inner tube are employed as the dispersion media. The gas in the inner tube is flowed outward radially through the annular micropores is dispersed into a great number of separate gas microstreams, followed by violent impinging cross-currently with the axial flow of the liquid in the channel between the inner and outer tubes, thereby it will exhibit enhanced gas–liquid mass transfer efficiency and combined action of many T-type microchannels which can realize the large throughput capacity (Wang et al., 2009; Chen et al., 2011).

The aim of the present work is to study the ozonation of azo dye Acid Red 14 (AR 14) solution in a MTMCR. Gas–liquid mass transfer characteristics in the MTMCR based on ozone-liquid volumetric mass transfer coefficient were evaluated. The influences of different parameters such as micropore size, annular channel width, liquid volumetric flow rate, ozone-containing gas volumetric flow rate, initial pH of the solution and initial AR 14 concentration on the ozonation were investigated in order to optimize the operating conditions. The effects of these operating parameters on decolorization efficiency and ozone utilization efficiency were analyzed. Decolorization and ozone utilization are the important indexes to evaluate the decolorization performance of textile effluents by ozone as ozone utilization determines the economical advantage. Also, on the basis of GC/MS analysis, a tentative analysis on the mechanism of AR 14 dye decomposition in aqueous solution is postulated.

2. Experimental

2.1. Reagents

AR 14 (Color Index 14720), a commercial dye with a chemical formula of C₁⁷₆H₁₂₆N₂O₇S₂ and molecular weight of 502.42, was purchased from Tianjing Dyestuff Chemical Factory (China) and used without further purification. The chemical structure of AR 14 is shown in Supplementary Material (SM), Fig. SM-1. The dye solution was prepared by dissolving AR 14 in deionized water, and the natural pH of the dye solution with 200 mg L⁻¹ AR 14 was 6.3. The initial pH of the dye solutions were adjusted using 1 M H₂SO₄ (AR, 98%, Beijing Chemical Works, China) and 1 M NaOH (AR, Beijing Chemical Works, China).

2.2. Apparatus and experimental procedures

Schematic diagram of the structure and principle of the MTMCR can be found in other articles (Wang et al., 2009; Chen et al., 2011). The inner tubes with different pore sizes of 5–200 μm were employed in this study. The annular channel widths, i.e. the distance between the inner and outer tubes, were 250–1500 μm. The experimental setup is shown in Fig. 1. Ozone was produced from pure oxygen by an ozone generator (GF-G10, Shanmeishuimei Environmental Technologies, Beijing, China). The oxygen flow rate into the generator was controlled using a gas flow meter. The ozone-oxygen mixture stream from the ozone generator was introduced into the inner tube and flowed radially through the micropores into the channel, while AR 14 solution was axially introduced into the channel from a liquid tank by using a peristaltic pump. The mass ratios of AR 14 to O₃ used for the experiments were from 0.23 to 5.12. After the cross-current impingement of the dye solution with gas and the reaction of AR 14 with ozone in the MTMCR, the two-phase mixture flowed into a sealed phase separator for gas and liquid separation and the gas subsequently flowed into two absorption bottles filled with 2% (w/v) KI solution for ozone absorption. Liquid samples were collected at sampling point between the MTMCR and the separator. The ozone concentrations in the gas streams at the MTMCR inlet and outlet were measured using an ozone analyzer (Double UV Light Ozone Meter, Limicen Ozone R&D Center, Guangzhou, China). The experiments were carried out in a thermostatic bath to maintain a desired temperature (25 ± 0.5 °C).

During all the experiments, the initial dye concentration, initial pH, liquid and ozone-containing gas volumetric flow rate were adjusted to a desired value, varying only one parameter in each run. The ozone concentration in the inlet gas stream was monitored by the ozone analyzer, and the gas stream was not fed into the MTMCR until a desired ozone concentration was achieved. 30 mL of each liquid sample was collected at the outlet of the MTMCR when a steady ozone concentration in the outlet gas stream was reached, and the absorbance of the sample was measured at AR 14’s maximum absorption wavelength of 515 nm. Every experiment was replicated three times or more.

2.3. Analytical methods

The UV–Vis optical spectra of a sample were recorded from 200 to 800 nm using UV2501PC UV–Vis Spectrophotometer (Shimadzu, Japan). The AR 14 concentration and decolorization capacity by ozonation were determined by measuring the absorbance at 515 nm. The decolorization efficiency was determined in terms of the initial AR 14 concentration and AR 14 concentration after ozonation, while the ozone utilization efficiency was calculated based on the inlet and outlet ozone concentration in the gas stream.
The liquid-phase ozone concentration was measured using a dissolved ozone measurement system (Q45H/64, ATI, America). The COD of AR 14 solution before and after ozonation was measured using a COD analyzer (DR5000, HACH, America).

The intermediate products of AR 14 decomposition were detected by GC/MS (QP2010, Shimadzu, Japan). The GC was equipped with a GsBP-XLB (General Separation Technologies, USA) fused-silica capillary column (30 m × 0.25 mm × 0.25 μm). 200 mL of the liquid samples with the intermediates were collected and then extracted by solid phase extraction tubes (Huang and Shu, 1995). 1 μL of the solution was chromatographed under the following conditions: injection temperature was 250°C; the initial column oven temperature was held constant at 80°C for 1 min and then increased to 250°C at the rate of 10°C min⁻¹. The carrier gas was helium and the pressure in the column head was 100 kPa. The MS source temperature was 200°C. The products were identified by comparing the obtained mass spectra with those stored in NIST147 library.

The concentration of nitrate and sulfate ions was measured by an ion chromatograph (IC, ICS-900, Dionex, America). 20 μL of the sample was pre-filtered by passing through a 0.22 μm membrane filter and injected into a separating column (IonPac AS23, 250 mm × 4.0 mm) for analysis. The eluent was a mixture of Na₂CO₃ (4.5 mM) and NaHCO₃ (0.8 mM) with a flow rate of 1.0 mL min⁻¹.

3. Results and discussion

3.1. Ozone-liquid volumetric mass transfer coefficient (kLa)

For the adsorption of ozone into water, the gas-phase resistance of mass transfer is negligible since ozone is slightly soluble in water. Because the self-decomposition constant (kd) of ozone is much lower than kLa, the influence of kd was not taken into account in the derivation of kLa. Consequently, kLa of the MTMCR can be evaluated by the following equation (Chen et al., 2011):

\[
k_{La} = \frac{Q_i}{\pi (R_i^2 - R_o^2)} L \ln \left( \frac{C_{O_3,i} - C_{O_3,o}}{C_{O_3,i} - C_{O_3,o}} \right)
\]

where \(Q_i\) is the liquid volumetric flow rate (L h⁻¹), \(L\) is the length of the microchannel of the MTMCR (m), \(R_i\) and \(R_o\) are the radius of the inner and outer tubes of the MTMCR (m), respectively. \(C_{O_3,i}\) and \(C_{O_3,o}\) are the concentrations of dissolved ozone in the inlet and outlet liquid phase (mg L⁻¹), respectively. \(C^\circ\) is the concentration of saturated ozone in water (mg L⁻¹).

Fig. 2 shows the measured \(k_{La}\) in the MTMCR as a function of \(Q_G\) and \(Q_i\) in O₃–H₂O adsorption process. It can be clearly seen that \(k_{La}\) increased significantly with the increase of \(Q_i\) at a fixed \(Q_G\). This is due to the fact that increasing \(Q_i\) would result in a more violent turbulence and the formation of thinner liquid boundary layer, thereby leading to the reduction of mass transfer resistance and the increase of \(k_{La}\). When \(Q_G\) increased at a constant \(Q_i\), an increase of \(k_{La}\) was also observed as a result of the increase of gas holdup and turbulence of the system.

3.2. Influence of parameters

Fig. 3a displays the effect of the micropore size on the decolorization efficiency and ozone utilization efficiency. As the pore size increased from 5 to 200 μm, the decolorization efficiency decreased from 83% to 64%, and the ozone utilization efficiency decreased from 18% to 14%. This is because the bubble size of gas phase as dispersed phase is mainly determined by the micropore size. The smaller is the micropore size, the smaller and the more are the formed gas bubbles. Accordingly, the larger interfacial area is generated and the mass transfer between ozone and the dye solution is enhanced.
Fig. 3b shows the change of the decolorization efficiency and ozone utilization efficiency with different annular channel widths, another important structure parameter of the MTMCR. It can be seen that the decolorization efficiency and ozone utilization efficiency were significantly influenced by the annular channel width. When the annular channel width decreased from 1500 to 250 µm, the decolorization efficiency and ozone utilization efficiency increased from 58% to 92% and from 14% to 41%, respectively. This is possibly due to the decreased thickness of liquid film. In addition, at a constant liquid volumetric flow rate, the liquid velocity increases when the annular channel width decreases, thereby resulting in a stronger turbulence and a better gas–liquid mass transfer effect.

Fig. 3c depicts the effect of liquid volumetric flow rate on the decolorization efficiency and ozone utilization efficiency. The decolorization efficiency decreased but ozone utilization efficiency increased with an increase in the liquid volumetric flow rate from 6 to 30 L h\(^{-1}\). A higher liquid volumetric flow rate induces a higher injection velocity and running velocity in the microchannel, which is beneficial to the formation of a thinner liquid boundary and the
corresponding reduction of mass resistance as a result of a more violent turbulence. However, contact time between ozone and dye solution is shorter and ozone dose per volume of dye solution is lower at a higher liquid volumetric flow rate, which are unfavorable factors for decolorization. In this study, the latter factors predominated over the former factors, resulting in the decrease of decolorization efficiency of AR 14 with increasing liquid volumetric flow rate.

The decolorization efficiency increased with an increasing ozone-containing gas volumetric flow rate (Fig. 3d). The increase of the ozone-containing gas volumetric flow rate results in the increase of the gas holdup and the turbulence of the system. In addition, the gas–liquid mass-transfer resistance decreases with an increasing gas volumetric flow rate, resulting in an increase in volumetric mass transfer coefficient and ozone mass transfer, and correspondingly an increasing O$_3$ concentration in the liquid phase. Both of these factors favor an increase of decolorization efficiency. However, it was observed that only a marginal effect in the decolorization efficiency was obtained when the ozone-containing gas volumetric flow rate increased over 50 L h$^{-1}$. It was also observed that ozone utilization efficiency decreased with increased ozone-containing gas volumetric flow rate, the highest ozone utilization efficiency being obtained for the lowest ozone-containing gas volumetric flow rate. Therefore, it was not necessary to try to increase the ozone concentration to a saturation level in AR 14 decolorization.

The pH of the solution plays an important role in the degradation of AR 14. The effects of initial pH from 2 to 12 on the decolorization efficiency and ozone utilization efficiency are shown in Fig. 3e. The decolorization efficiency increased from 64% to 87% with the increase of initial pH of the dye solution from 2 to 9, and a further increase of initial pH from 9 to 12 led to a slight decrease of the decolorization efficiency from 87% to 82%. This is due to the following reasons: hydroxyl radicals with a high oxidizing potential are formed from ozone decomposition at high pH values and the reaction of hydroxyl radicals with the dye might be easier under alkaline than under acidic conditions, resulting in the increase of decolorization efficiency. But at pH > 9, the reaction among the same radicals predominates over the reaction among radicals and AR 14 due to the fact that the concentration of hydroxyl radicals is greater than ozone concentration. As a result of the combined action of the hydroxyl radicals and ozone, the highest decolorization efficiency was obtained at the initial pH of 9 during these experiments. The ozone utilization efficiency increased with the increase of initial pH all the time, probably because an alkaline environment was favorable for ozone decomposition.

It can be seen from Fig. 3f that decolorization efficiency decreased and ozone utilization efficiency increased with an increasing initial AR 14 concentration. When the initial AR 14 concentration increased from 50 to 800 mg L$^{-1}$, the decolorization efficiency decreased from 98% to 67% and the ozone utilization efficiency increased from 42% to 86%. The results can be explained by the following two reasons. Firstly, the number of hydroxyl radicals generated in the dye solution remained almost steady with a varying AR 14 concentration. Therefore, a lower initial dye concentration resulted in a better decolorization efficiency. Secondly, the oxidation by-products increased accordingly when the initial AR 14 concentration increased. Competition between the by-products and AR 14 for hydroxyl radicals became intense, which led to the decrease of the removal efficiency of apparent color and enhanced ozone utilization efficiency.

3.3. Reaction kinetics

It is reported that dye ozonation is a first-order kinetics reaction with respect to ozone and dye concentration (Langlais et al., 1990; Shu and Huang, 1995). Thus, the ozonation rate increases with both dye concentration and ozone concentration. In this study, the ozone injecting concentration is fixed. Therefore, the degradation kinetics can be treated as a pseudo-first-order reaction with respect to the dye concentration. The study was carried out at the initial AR 14 concentration of 200 mg L$^{-1}$. The correlation between ln(C/C$_0$) and the reaction time was linear as shown in Fig. SM-2. The pseudo-first-order rate constant for the degradation of AR 14 was 0.23 min$^{-1}$.

3.4. COD reduction

The COD of the AR 14 solution was measured before and after the decolorization of the solution in the MTMCR at different liquid volumetric flow rate (Fig. SM-3). It was found that the COD removal and decolorization efficiency of AR 14 solution decreased from 45% to 17% and from 98% to 92%, respectively, with an increasing liquid volumetric flow rate from 9 to 24 L h$^{-1}$. The low COD removal efficiency and high decolorization efficiency indicated that most of the AR 14 was degraded into organic intermediate compounds in the ozonation. It was reported that these compounds can be easily biodegraded in post-treatment like activated sludge processes (Guelli et al., 2010).

3.5. Degradation pathway

In this part of the study, samples were taken from the MTMCR after decolorization to identify the intermediates produced in the ozonation degradation of the AR 14 through GC/MS analysis. The GC/MS chromatograms of the sample is displayed in Fig. 4, and the peaks were identified by MS analysis. The typical intermediate compounds were determined in terms of the mass spectra and are displayed in Table 1.

It was reported that the production of hydroxyl radicals starts when the pH exceeds 5 and the hydroxyl radicals are the primary reactive species in ozonation at the pH values in excess of 6 (Hoigne and Bader, 1976; Rice, 1997). It was thus assumed that the hydroxyl radicals were the major reactive species in this study. A tentative pathway for the degradation of AR 14 dye was postulated accordingly and the mechanism is presented in Fig. 5.

Because the contact time between ozone and dye solution in the MTMCR was very short (about 0.3 s) and a relatively high decolorization efficiency was reached in this study, it was obvious that cleavage of the chromophoric azo (–N–N–) bonds was fast and thorough. In the very first step of AR 14 degradation, the azo bonds (AR–N=N–AR) is cleaved and nitro group and substituted

![Fig. 4. Total ion GC/MS chromatogram of AR 14 ozonation products: $d_0 = 5 \mu m$; $R_d = 250 \mu m$; $Q_L = 24 \text{ L h}^{-1}$; $Q_G = 50 \text{ L h}^{-1}$; $T = 25 \text{ }^\circ \text{C}$; pH = 9; $C_{AR,0} = 200 \text{ mg L}^{-1}$.](image-url)
Naphthalene compounds are produced. Further oxidation gives rise to the opening of an aromatic ring to the formation of organic acids, ketones, aldehydes, alcohols and hydrocarbons. Finally, the mineralization of AR 14 leads to the production of carbon dioxide and water.

The attack of the hydroxyl radicals on the N(11) and N(12) positions forms the state S1. Further oxidation of S1 leads to N(11)–N(12) splitting and S2 and S3 are formed. Simultaneously, because of the high selectivity of ozone in attacking the N-N bonds (Ledakowicz et al., 2001; López-López et al., 2004), ozone

### Table 1

The ozonation intermediates examined by GC/MS.

<table>
<thead>
<tr>
<th>Retention time (min)</th>
<th>Compound identified by MS</th>
<th>Molecular formula</th>
<th>MW</th>
<th>Structural formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.09</td>
<td>1,2-Naphthoquinone</td>
<td>C₁₀H₆O₂</td>
<td>158</td>
<td>D₅ in Fig. 5</td>
</tr>
<tr>
<td>7.62</td>
<td>Benzoic acid, 2-[1-oxopropyl]-, methyl ester</td>
<td>C₁₁H₁₂O₃</td>
<td>192</td>
<td>D₄ in Fig. 5</td>
</tr>
<tr>
<td>8.95</td>
<td>2-Hydroxy-1,4-naphthalenedione</td>
<td>C₁₀H₆O₃</td>
<td>174</td>
<td>D₃ in Fig. 5</td>
</tr>
<tr>
<td>9.45</td>
<td>1,4-Naphthoquinone</td>
<td>C₁₀H₆O₂</td>
<td>158</td>
<td>D₁ in Fig. 5</td>
</tr>
<tr>
<td>9.99</td>
<td>1,2-Benzenedicarboxylic acid, dimethyl ester</td>
<td>C₁₀H₁₆O₄</td>
<td>194</td>
<td>D₁ in Fig. 5</td>
</tr>
<tr>
<td>10.78</td>
<td>1a,7a-Dihydronaphtho [2,3-b] oxirene-2,7-dione</td>
<td>C₁₀H₆O₃</td>
<td>174</td>
<td>D₁ in Fig. 5</td>
</tr>
</tbody>
</table>

**Fig. 5.** The proposed degradation pathways of AR 14 during ozonation.
directly attacks the \(-\text{N}==\text{N}\) double bonds by electrophilic substitution and \(S_{10}\) and \(S_{11}\) are formed. Under the influence of the hydroxyl radicals, state \(S_9\) is transformed into compound \(S_{12}\) which is further oxidized by hydroxyl radicals to form 1,4-naphthoquinone (\(D_5\)). Then, the benzene ring in 1,4-naphthoquinone is oxidized to form \(S_{13}\), \(S_4\) and 1a,7a-dihyronaphtho [2,3-b] oxirene-2,7-dione (\(D_2\)), which can be further decomposed to smaller molecules such as organic acids, ketones, aldehydes, alcohols, hydrocarbons and carbon dioxide. The benzene ring in \(D_5\) is also cleaved to form \(S_{14}\) by further oxidation (Song et al., 2007). \(S_9\) and \(S_{10}\) can also react with methanol to form 1,2-benzenedicarboxylic acid, dimethyl ester (\(D_3\)) and benzoic acid, 2-(1-oxopropyl)-, methyl ester (\(D_4\)).

\(S_5\) is transformed into compounds \(S_3\) and \(S_9\), which can be further oxidized to 2-hydroxy-1,4-naphthalenedione (\(D_6\)) and 1,2-naphthoquinone (\(D_7\)) by the hydroxyl radicals. The benzene ring in \(D_3\) can be cleaved to form \(S_{15}\) (Song et al., 2007). Then the compound \(S_9\) breaks down into smaller molecules, and \(D_6\) can also be further degraded into smaller molecules.

\(S_{10}\) is further oxidized by hydroxyl radicals to form compound \(S_4\) and nitro group. The state \(S_{11}\) then can be transformed into compound 1,2-naphthoquinone (\(D_8\)) by the oxidation of hydroxyl radicals.

The evolution of nitrogen and sulfur in AR 14 ozonation was determined by IC. If all the nitrogen atoms in AR 14 were transformed into the nitrate ions, the nitrate concentration should be 12.35 mg L\(^{-1}\) with an initial AR 14 concentration of 50 mg L\(^{-1}\). However, the low nitrate concentration (2.04 mg L\(^{-1}\)) detected by IC indicated that only small part of the nitrogen atoms in AR 14 were transformed into the nitrate ions. It is worth mentioning that the nitrite ions were undetected by IC due to the fact that nitrite is easy to be oxidized into nitrate by ozone. It was thus concluded that most of the nitrogen atoms were converted into nitrogen in AR 14 ozonation. It is found from the sulfate concentration detected by IC that all the sulfur atoms in AR 14 were transformed into sulfite ions.

### 3.6. Comparison with other gas–liquid contactors

The mass transfer performance of the MTMCR was compared with four kinds of gas–liquid contactors including a cocurrent up-flow packed bed reactor (Farines et al., 2003), a bubble column reactor with porous plate (Zhao et al., 2003, 2004), a column with bubble diffuser (Shin et al., 1999) and a column with an electrostatic sprayer (Shin et al., 1999), and the \(k\alpha\) of these contactors are shown in Table 2. Although the experimental conditions were different, it can still be deduced from Table 2 that the mass transfer coefficient in the MTMCR is much higher than that of other contactors, which means that the MTMCR has a very good gas–liquid mass transfer effect due to its unique structure.

### 4. Conclusions

In this article, the MTMCR was used as a gas–liquid contactor to increase the mass transfer rate of ozone as well as to enhance the ozonation of AR 14 dye. The liquid volumetric mass transfer coefficient in the MTMCR increased with the increase of gas or liquid flow rate. It was deduced that the MTMCR has a better mass transfer performance compared with conventional gas–liquid contactors.

The decrease of the micropore size and the annular channel width of the MTMCR led to the increase of the decolorization efficiency and the ozone utilization efficiency. AR 14 decolorization efficiency increased and ozone utilization efficiency decreased with an increasing ozone-containing gas volumetric flow rate and a decreasing liquid volumetric flow rate, and a maximum decolorization efficiency at the pH of 9 was achieved as a result of the combined action of the hydroxyl radicals and ozone. It was found that the degradation kinetics was a pseudo-first-order reaction with respect to the dye concentration.

A possible degradation pathway of AR 14 involving a hydroxyl radical reaction mechanism was proposed, and six products have been identified as the intermediates of ozonation degradation based on GC/MS analysis. It can be concluded that the splitting of the \(-\text{N}==\text{N}\) bonds in AR 14 is attributed to the attacks by ozone and hydroxyl radicals, and the subsequent degradation of the intermediates is ascribed mainly to the oxidation of hydroxyl radicals. During the ozonation, most of the nitrogen atoms in AR 14 were converted into nitrogen and all the sulfur atoms were transformed into sulfite ions.

### Acknowledgments

This work was supported by National Natural Science Foundation of China (Nos. 21176013 and 20990221), National High-Tech Research Program of China (863 Program) (No. 2009AA033301) and Program for New Century Excellent Talents in University of China (NCET-07-0053).

### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2012.05.083.

### References


