Enhanced removal of refractory pollutant from aniline aerofoil wastewater using combined vacuum ultraviolet and ozone (VUV/O3) process

Xiaoyu Deng, Dachao Zhang, Meng Wu, Philip Antwi, Hao Su and Cheng Lai

ABSTRACT

Aerofloats, such as aniline aerofloat ((C6H5NH)2PSSH), are extensively employed for collection activities in wastewater particularly in cases where minerals are in flotation. Although this aniline aerofloat has efficient collection properties, they are ordinarily biologically persistent chemicals in which case their residual, as well as their byproducts, pose great environmental risks to water and soils. In this study, the removal efficiency of aniline aerofloat (AAF) by a combined vacuum ultraviolet (VUV) and ozone (O3) process (VUV/O3) was evaluated. Furthermore, the impacts of pH, O3, the concentration of AAF and coexisting ions (SiO3^2-, CO3^2-, Cl^- (Na^+), SO4^2-, Ca^{2+}) were systematically studied. The experiments revealed that, with an initial AAF of 15 mg/L, AAF removal >88% was feasible with a reaction time of 60 min, pH of 8 and O3 of 6 g/h. The order of influence of the selected coexisting ions on the degradation of AAF by VUV/O3 was Ca^{2+} > CO3^2- > SiO3^2- > Cl^- (Na^+) > SO4^2-. Compared with VUV and O3 in terms of pollutant degradation rate, VUV/O3 showed a remarkable performance, followed by O3 and VUV. Additionally, the degradation kinetics of AAF by the VUV/O3 process agreed well with first-order elimination kinetics.

Key words | aniline aerofloat, free radical, reaction kinetics, VUV/O3

INTRODUCTION

The increased demand for non-ferrous metals has resulted in an exponential rise in production in recent years. As a result, effluent (wastewater) from such industries has seen a dramatic increase year on year. The total volume of non-ferrous metal industry wastewater has been reported to account for about 30% of the wastewater discharged globally (Bu et al. 2014; Qi et al. 2014; Li et al. 2015a). Among the processes involved in mineral processing, flotation plays a major role. Therefore, to obtain useful mineral components, a large number of flotation reagents are added to the flotation process, which makes mineral processing wastewater complex and so this type of wastewater is unfit for reuse (Song et al. 2015b; Feng et al. 2016; Liu et al. 2017).

In this regard, a practical, economical and effective way to treat such mineral processing wastewater is needed to meet stringent discharge standards and enable the reuse of mineral processing wastewater. Aniline aerofloat ((C6H5NH)2PSSH, AAF) is mainly used for the flotation of non-ferrous metals due to its good selectivity and strong capturing power. AAF has been reported as a typical refractory organic pollutant (Song et al. 2015a; Wang et al. 2015). When the residual AAF in the wastewater enters a natural water body, it generates aniline free radicals and other byproducts, under the action of light, oxygen, and microorganisms, which cause certain biotoxic effects on ecosystems such as rivers and soil (Li et al. 2015b). (Xiang et al. 2018) showed that AAF has a high adsorption capacity in soil, and may accumulate in agricultural soil to pose potential risks to crops. Consequently, efficient treatment for AAF in mineral processing wastewater is an urgent task.
The advanced oxidation processes (AOPs), which can produce highly reactive hydroxyl radicals (·OH), have been considered to be an effective method to degrade organic pollutants compared to other treatment processes (Miklos et al. 2018; Geng et al. 2020). Low-pressure UV lamps can produce vacuum ultraviolet (VUV) (Wen et al. 2019). VUV at a wavelength of 185 nm emits 10% ultraviolet rays, and 90% ultraviolet rays at a wavelength of 254 nm (Zoschke et al. 2014). Strong oxidants (·OH) are produced (Equations (1) and (2)) when VUV irradiates water at 185 nm, meaning the VUV system does not need any additional chemicals. (Imoberdorf & Mohseni 2011; Xie et al. 2018; Jiang et al. 2019; Xie et al. 2019; Geng et al. 2020).

\[
\begin{align*}
H_2O + \text{hv}_{\text{sys}} & \rightarrow \cdot OH + \text{H} \quad \Phi = 0.33 \quad (1) \\
H_2O + \text{hv}_{\text{sys}} & \rightarrow \cdot OH + \text{H}^+ + e_\text{eq} \quad \Phi = 0.045 \quad (2)
\end{align*}
\]

Ozone is highly oxidizing, and can transform macromolecular refractory organic pollutants into small molecular substances (Miklos et al. 2018). However, the organic degradation rate is limited by low O₃ utilization and high energy consumption (Jiang et al. 2019).

The VUV/O₃ process has been developed to remove refractory organic pollutants from wastewater (Fu et al. 2019). When wastewater is irradiated by VUV radiation combined with O₃, it can generate higher concentrations of ·OH, which enhances the degradation effect on organic pollutants (Equations (3)–(5)) (Poyatos et al. 2010; Liu et al. 2011; Jiang et al. 2019). Recent studies have found that VUV combined with O₃ has been used for the degradation of sodium n-butyl xanthate (Fu et al. 2016), diethyl dithiocarbamate collector in flotation wastewaters (Fu et al. 2019), and humic and fulvic acid in incineration leachate (Jiang et al. 2019). However, there have been few reports on the removal of aniline aerofoat by the VUV/O₃ process, and the effects of related parameters and coexisting ions during the flotation process on the degradation of aniline aerofoat have been scarcely studied.

\[
\begin{align*}
\text{O}_3 + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad (3) \\
\text{H}_2\text{O}_2 + 2\text{O}_3 & \rightarrow 2\cdot \text{OH} + 3\text{O}_2 \quad (4) \\
\text{H}_2\text{O}_2 & \rightarrow 2\cdot \text{OH} \quad (5)
\end{align*}
\]

The aim of this study was to evaluate the applicability of the VUV/O₃ system in the elimination of AAF in mineral processing wastewater. Furthermore, some important factors that influence AAF degradation, including solution pH, ozone, initial concentration of AAF and coexisting ions were assessed, and the role of hydroxyl radicals in the degradation of AAF during VUV/O₃ system was discussed as well. This work may be helpful to further promote the application of the VUV/O₃ system in the treatment of aniline aerofoat wastewater.

**MATERIALS AND METHODS**

**Experimental setup and operation**

The experimental setup mainly comprised an ozone generator, reaction device (reactor) and exhaust gas absorption device (Figure 1). The reactor was constructed at laboratory scale with gas-liquid contact dynamics and an effective working volume, height and diameter of about 1,500 mL, 65 mm and 480 mm, respectively. Ozone was produced by an ozone generator (HY-006-20A, Jiahuan Technology Co., Ltd, Guangdong, China) with an output of 20 g/h. The UV lamp (VUV, 254 nm + 185 nm, GPH303T5VH/4P) was purchased from Laishaws Co., Ltd, USA, with the electrical power of 15 W, a length of 303 mm and a diameter of 15 mm. The lamp was placed on the central axis of the reactor, and the lamp tube was covered with a quartz tube. Hydrochloric acid and sodium hydroxide solutions were prepared and used for pH adjustment. The simulated AAF wastewater was fed to the reactor, then the ozone generator was switched on for 3 min. When ozone production had attained a steady state, the reactor and the ultraviolet lamp were switched on. The absorbance of AAF was measured after a specific time interval of the reaction. Industrial-grade AAF was purchased from Guangzhou Yueyouyan Mineral Resources Technology Co., Ltd, Guangdong, China. All other chemicals were of analytical grade and experimental water was deionized water. Each experiment was repeated three times, and the error bar represented the standard deviation.

The literature has reported that dispersants are often needed in flotation, and that SiO₃²⁻ can be used as a dispersant, so lime, sodium carbonate, sulfuric acid or hydrochloric acid are added to adjust the pH of the solution during mineral processing to yield CO₃²⁻, Cl⁻, and SO₄²⁻ (Silvestre et al. 2009; Lin et al. 2019; Nuri et al. 2019). Therefore, this experiment used the appropriate amounts of Na₂SiO₃·9H₂O, Na₂CO₃, NaCl, Na₂SO₄, CaCl₂ as the coexisting anions of the solution. In this study, the preparation of coexisting anions was performed by adding a certain amount of Na₂SiO₃·9H₂O, Na₂CO₃, NaCl, Na₂SO₄.
and CaCl₂ to the AAF wastewater to bring the initial and anion concentrations to 15 mg/L and 5 mmol/L, respectively.

**Analytical methods**

The concentration of AAF that needed to be determined in this experiment was low. Due to the superiority and reliability of ultraviolet spectrophotometry in the determination of low concentrations of substances, an ultraviolet-visible spectrophotometer (SP-756PC, Shanghai Spectrum Instrument Co., Ltd, Shanghai) with a detection wavelength of 230 nm was used in this experiment. The concentration of ozone in the gas stream was measured by an iodometric method: bubbling gas into a potassium iodide solution. The total organic carbon (TOC) concentration of the solution was measured using a TOC analyzer (Vario TOC, Germany). Ca²⁺, Cl⁻ (Na⁺) and SO₄²⁻ were determined by an ion chromatograph (ICS-900, USA). The SiO₃⁻ concentration was determined by the Chemical Reagent-General Method for The Determination of Silicate (GB/T 13171-2008). The determination of CO₃²⁻ was by acid-base indicator titration. The pH was measured with a pH meter (PHS-3C, Shanghai Yidian Scientific Instrument Co., Ltd, Shanghai).

**RESULTS AND DISCUSSION**

**Performance of AAF degradation by VUV, O₃ and VUV/O₃**

The effects of VUV, O₃ and VUV/O₃ on the degradation of AAF were investigated and the results illustrated in Figure 2.

At 25 °C and 15 W light intensity, initial AAF concentration of 15 ± 0.5 mg/L, initial pH of 8.0 ± 0.1, ozone concentration of 6 g/h and an 80 min reaction time, the degradation of AAF by VUV, O₃ and VUV/O₃ increased gradually as the reaction time progressed (Figure 2).

Over the 0–80 min reaction time, the degradation rate of AAF by VUV, O₃ and VUV/O₃ increased exponentially within the first 10 min, 30 min and 25 min for VUV, O₃ and VUV/O₃, respectively. Thereafter, the degradation rate attained a steady state in the remaining reaction time (Figure 2). Under the same reaction conditions, the
degradation efficiency of the three processes on AAF was highest using VUV/O3, followed by O3 and VUV. On average, the degradation rates of the target pollutants by VUV, O3 and VUV/O3 were 23.99%, 60.75% and 88.36% after the first 30 min. These results suggest that the VUV/O3 process greatly improved the degradation of organics (Fu et al. 2016; Hong et al. 2016; Jiang et al. 2019). Thus after 60 min of the reaction time, there was an indication that the VUV/O3 process was a feasible process or method for the treatment of AAF.

Effect of pH on the degradation of AAF by VUV/O3

The conditions were the same as those indicated in the section on ‘Performance of AAF degradation by VUV, O3 and VUV/O3’ (temperature, 25 °C; light intensity, 15 W; initial AAF concentration, 15 ± 0.5 mg/L; ozone concentration, 6 g/h; reaction time, 80 min) except for the pH. Initial pH of 6, 8, 10 and 12 of the solution and their effect on the degradation performance of VUV, O3 and VUV/O3 were evaluated and the results are presented in Figure 3(a).

When the initial pH of the solution was high, the degradation rate of AAF increased exponentially within the first 30–40 min but maintained a steady rate thereafter. When the pH was 8, VUV/O3 performed remarkably well, with a degradation rate of about 15 mg/L (88.36%) of the AAF. The results revealed that AAF could be hydrolyzed by acid or alkali in a strongly acidic or alkaline environment, which will subsequently reduce the degradation effect of VUV/O3 on AAF. Moreover, when the pH = 6–8, with the increase of the initial pH of the solution, more hydroxide ions were generated in this system, which accelerated the decomposition of O3 into ·OH, thereby reducing the amount of O3 directly photolyzed into H2O2 through VUV; H2O2, the precursor of ·OH, was reduced (Equation (6)) (Ratpukdi et al. 2010; Fu et al. 2016; Jiang et al. 2019). The strong oxidizing substances in the solution, such as ·OH, H2O2, O3, etc. increased gradually, which improved the degradation effect of VUV/O3 on AAF (Hu et al. 2019). Then, as the pH of the solution continued to increase, the dissolved amount of O3 decreased gradually and the CO3^2-, HCO3^- in the solution consumed a large amount of ·OH, which reduced the reaction between ·OH and AAF, thus reducing the degradation rate of AAF by VUV/O3.

![Figure 3](http://iwaponline.com/wst/article-pdf/80/12/2250/672982/wst080122250.pdf)
Effect of initial concentration of AAF in solution on the degradation rate

By maintaining all other conditions (temperature, 25 °C; light intensity, 15 W; O3, 6 g/h; pH, 8.0 ± 0.1; and reaction time, 80 min) and varying initial concentration of AAF at 10.00 mg/L, 15.00 mg/L, 20.00 mg/L, the effect of the different AAF concentrations on the effectiveness of the VUV/O3 process on the degradation of AAF was investigated and illustrated in Figure 3(c). As shown in Figure 3(c), the degradation rate of AAF by VUV/O3 correlated with the varied initial AAF concentrations. Notably, the degradation rate increased significantly within the first 40 min but decreased gradually afterward until an equilibrium was reached. It was also observed that VUV/O3 had a good removal effect on AAF when the initial concentration was high.

After 60 min of degradation, the observable removal rates of AAF by VUV/O3 using initial concentrations of 10.00 mg/L, 15.00 mg/L, 20.00 mg/L AAF, were 85.54%, 88.56% and 84.52% respectively, an indication that VUV/O3 process could obtain high degradation (88.36%) effect on wastewater even with an initial concentration of 15.00 mg/L (Figure 3(c)).

Effect of ozone on the degradation of AAF by VUV/O3

Whilst the optimum pH of 8 was found to be in the VUV/O3 process, further investigation was conducted to establish at the optimum dose of ozone. The temperature was maintained at 25 °C, the light intensity at 15 W, the initial concentration of AAF at 15 ± 0.5 mg/L, the initial pH of the solution at 8.0 ± 0.1, and the effect of the VUV/O3 process on the degradation of AAF was investigated under different O3 concentrations: 2, 4, 6, and 8 g/h (Figure 3(b)).

The result suggested that, from 2 to 6 g/h, the degradation rate of AAF by the VUV/O3 process increased with an increase in ozone concentration. When ozone was raised to about 6–8 g/h, the AAF degradation rate decreased gradually along with the increase in O3 concentration. This observation demonstrated that with the increase in O3 dosage, the formation of ·OH via the decomposition of ozone by VUV irradiation was promoted (Ratpukdi et al. 2011; Fu et al. 2019). Therefore contact between the target pollutant, O2 and the strongly oxidizing ·OH, H2O2 and O3 produced in the solution promoted the removal of the target pollutant of AAF. However, with additional O3, the O3 content in the solution rose, which inhibited the solution from stronger oxidative degradation of ·OH, H2O2 and other substances will result in a slight decrease in the degradation rate of VUV/O3 to AAF.

As shown in Figure 3(b), VUV/O3 showed a remarkable degradation effect on AAF, with a rate of degradation that could reach 88.36% when the light intensity, reaction time, ozone concentration and pH were 15 W, 60 min, 6 g/h and 8.0, respectively.

Effect of initial concentration of AAF in solution on the degradation rate

By maintaining all other conditions (temperature, 25 °C; light intensity, 15 W; O3, 6 g/h; pH, 8.0 ± 0.1; and reaction time, 80 min) and varying initial concentration of AAF at 10.00 mg/L, 15.00 mg/L, 20.00 mg/L, the effect of the different AAF concentrations on the effectiveness of the VUV/O3 process on the degradation of AAF was investigated and illustrated in Figure 3(c). As shown in Figure 3(c), the degradation rate of AAF by VUV/O3 correlated with the varied initial AAF concentrations. Notably, the degradation rate increased significantly within the first 40 min but decreased gradually afterward until an equilibrium was reached. It was also observed that VUV/O3 had a good removal effect on AAF when the initial concentration was high.

After 60 min of degradation, the observable removal rates of AAF by VUV/O3 using initial concentrations of 10.00 mg/L, 15.00 mg/L, 20.00 mg/L AAF, were 85.54%, 88.56% and 84.52% respectively, an indication that VUV/O3 process could obtain high degradation (88.36%) effect on wastewater even with an initial concentration of 15.00 mg/L (Figure 3(c)).

Effect of coexisting ions during AAF degradation by VUV/O3

To investigate the effect of co-existing ions on the degradation of AAF (Figure 3(d)), the reaction condition including temperature, light intensity, O3, pH and reaction time were set at 25 °C, 15 W, 6 g/h, 8.0 and 80 min, respectively. Na2SiO3·9H2O, Na2CO3, NaCl, Na2SO4 and CaCl2 at a concentration 5 mmol/L were then added separately.

Inorganic anions, which are widely present in beneficiation wastewater, can affect the VUV/O3 process to varying degrees. As shown in Figure 3(d), coexisting ions inhibited the degradation of AAF by VUV/O3, and the effects were in the order Ca2+ > CO32− > SiO32− > Cl− (Na+) > SO42−. Figure 3(d) also shows that the degradation of AAF wastewater containing Ca2+, CO32−, SiO32−, Cl− (Na+) and SO42− by VUV/O3 reached equilibrium after 50 min. The rate of degradation of AAF in the presence of Ca2+, CO32−, SiO32−, Cl− (Na+) and SO42− was 65.58%, 70.38%, 72.86%, 78.58% and 79.71%, respectively. In comparison to when Ca2+, CO32−, SiO32−, Cl− (Na+) and SO42− were absent, degradation had reduced by 21.81%, 17.01%, 15.53%, 8.81% and 7.68% in the presence of Ca2+, CO32−, SiO32−, Cl− (Na+) and SO42−, respectively.

Consequently, it is estimated that when the pH is alkaline, the addition of Ca2+ will consume a large amount of ·OH, and the calcium hydroxide generated hinders VUV radiation and reduces the generation of ·OH, which results in a reduced AAF removal efficiency by VUV/O3 (Jiang et al. 2019). In acidic or weakly alkaline environments, CO32− hydrolyzes to HCO3−, whereas HCO3− is a ·OH quencher that reacts rapidly with ·OH and produces the secondary reactive species CO32−, which has lower reactivity (Equations (7) and (8); Miklos et al. 2018; Xie et al. 2018;
Wen et al. 2019), thereby reducing AAF removal. In the case of sodium silicate addition, a large quantity of SiO$_2^-$ will inhibit the production of ·OH by photo-degradation and the photocatalytic–ozone process. As a result, the ability of O$_3$ to be dissolved in the solution will be reduced, thus reducing the reaction rate. The addition of Cl$^-$ (Na$^+$) will consume ·OH (Geng et al. 2020); the proportion of hydroxyl radicals by chloride ions can be neglected as the reactions were reversible (Equations (9) and (10); Yang et al. 2014a, 2014b; Wen et al. 2019). Studies have found that chloride ions can strongly absorb photons at 185 nm and generate chlorine atom radicals, and then chlorine atom radicals reacted with Cl$^-$, which produce Cl$_2^-$, which is less reactive (Equations (11) and (12); Furatian & Mohseni 2018; Wen et al. 2019). Therefore, the effect of the chloride ion and ·OH reaction on the degradation effect of AAF may be weakened. In the presence of SO$_4^{2-}$, SO$_2^-$ could react with ·OH in the solution (Equation (13); Geng et al. 2020). SO$_4$ is more oxidative than ·OH (Miklos et al. 2018; Liu et al. 2019). However, the reaction rate constants of SO$_4^{2-}$ and ·OH were significantly lower (Equation (13)), thus its competition for hydroxyl radicals was insignificant (Yang et al. 2018). Therefore, the inhibition by SO$_4^{2-}$ in the reaction will be minimal.

\[
\begin{align*}
\text{CO}_2^+ + \cdot \text{OH} & \rightarrow \text{CO}_3^- + \text{OH}^- & k &= 4 \times 10^8 \text{M}^{-1}\text{s}^{-1} \quad (7) \\
\text{HCO}_3^- + \cdot \text{OH} & \rightarrow \text{CO}_3^- + \text{H}^+ & k &= 8.5 \times 10^6 \text{M}^{-1}\text{s}^{-1} \quad (8) \\
\text{Cl}^- + \cdot \text{OH} & \rightarrow \text{Cl}^- + \text{OH}^- & k &= 4.3 \times 10^9 \text{M}^{-1}\text{s}^{-1} \quad (9) \\
\text{Cl}^- + \text{OH}^- & \rightarrow \text{Cl}^- + \cdot \text{OH}^- & k &= 6.1 \times 10^9 \text{M}^{-1}\text{s}^{-1} \quad (10) \\
\text{Cl}^- + \text{H}_2\text{O} & \rightarrow \text{Cl}_2^-, \Phi & \Phi &= 0.4 \quad (11) \\
\text{Cl}^- + \text{Cl}^- & \rightarrow \text{Cl}_2^- & K_{\text{eq}} &= 1.4 \times 10^5 \text{M}^{-1} \quad (12) \\
\text{SO}_4^{2-} + \cdot \text{OH} & \rightarrow \text{SO}_4^- & k &= 2.0 \times 10^4 \text{M}^{-1}\text{s}^{-1} \quad (13)
\end{align*}
\]

Process kinetics analysis

The kinetics in reactions where initial concentration of AAF in solution was 10.00 mg/L, 15.00 mg/L, 20.00 mg/L employed to facilitate in the degradation of AAF was evaluated under the following conditions: temperature of 25 °C, light intensity of 15 W, ozone concentration of 6 g/h, AAF initial concentration of 15 ± 0.5 mg/L, solution initial pH of 8.0 ± 0.1 and reaction time of 30 min.

The first-order kinetic model was employed to fit the experimental data for the estimation of kinetic parameters (Figure 4 and Table 1). As illustrated and presented in Figure 4 and Table 1, respectively, the estimated coefficients of determination ($R^2$) obtained during the curve fitting for all three concentrations (10.00 mg/L, 15.00 mg/L, 20.00 mg/L) of the solution were above 0.975, an indication that the degradation process of AAF by VUV/O$_3$ conformed to the first-order kinetic equation and had high reliability. The maximum of $R^2$ was for the AAF concentration of 10 mg/L.

Profiles of pH and TOC during AAF degradation

**pH profile in solution during degradation**

The impact of various pH (6.00, 8.00, 10.00, 12.00) on the degradation process of AAF was investigated at 25 °C of temperature, 15 W light intensity, 6 g/h of ozone concentration, initial AAF concentration of 15 ± 0.5 mg/L. Experimental data during VUV/O$_3$ degradation AAF was recorded after 80 min of reaction (Figure 5(a)).

<table>
<thead>
<tr>
<th>Concentration of AAF (mg/L)</th>
<th>Kinetic formula</th>
<th>$k$/min$^{-1}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.00</td>
<td>$\text{Ln } (C_t/C_0) = 0.043 - 0.054 t$</td>
<td>$-0.054$</td>
<td>0.991</td>
</tr>
<tr>
<td>15.00</td>
<td>$\text{Ln } (C_t/C_0) = -0.080 - 0.064 t$</td>
<td>$-0.064$</td>
<td>0.975</td>
</tr>
<tr>
<td>20.00</td>
<td>$\text{Ln } (C_t/C_0) = -0.064 - 0.030 t$</td>
<td>$-0.030$</td>
<td>0.985</td>
</tr>
</tbody>
</table>

Table 1 | Kinetic equations and related parameters of degradation of aniline aerofloat under different initial concentrations
As shown in Figure 5(a), the pH of the solution gradually decreased along with increasing reaction time thus, when the wastewater’s initial pH was 6.00, 8.00, 10.00 and 12.00, the pH of the wastewater had decreased by 1.74, 2.57, 3.10 and 0.15 respectively at the end of the reaction. The decrease in the pH of the solution might be due to the degradation of AAF leading to the formation of organic acids (Geng et al. 2020). Besides, H⁺ ions might be generated by VUV decomposition of H₂O and H₂O₂, and the O₃ decomposition initiated by hydroxide ions could consume hydroxide ions and promote H₂O resolution (Equations (14)–(18)), then the solution released hydrogen ions (Li et al. 2015b).

\[
\cdot \text{OH} \rightarrow \text{H}^+ + \text{O}^- \quad (14)
\]
\[
\cdot \text{OH} + \cdot \text{OH} \rightarrow \text{H}_2\text{O}_2 \quad (15)
\]
\[
\text{H}_2\text{O}_2 \rightarrow \text{H}^+ + \text{HO}_2^- \quad (16)
\]
\[
\text{O}_3 + \cdot \text{OH} \rightarrow \cdot \text{O}_2^- + \text{HO}_2 \quad (17)
\]
\[
\text{O}_3 + \cdot \text{OH} \rightarrow \text{O}_2 + \text{HO}_2^- \leftrightarrow \cdot \text{O}_2 + \text{H}^+ \quad (18)
\]

Variation of total organic carbon in solution during degradation

The change in TOC during AAF degradation by the VUV/O₃ process was investigated and the results are shown in Figure 5(b). Before AAF degradation was initiated, reaction conditions set for the optimum performance of VUV/O₃ process were temperature at 25°C, light intensity at 15 W, the ozone concentration at 6 g/h, initial AAF concentration at 15 ± 0.5 mg/L, initial solution pH at 8.0 ± 0.1 and reaction time at 30 min.

As shown in Figure 5(b), AAF degradation by the VUV/O₃ process reached equilibrium after 50 min with degradation rates of AAF and TOC of 87.39% and 50.92%, respectively. The results revealed that AAF cannot be completely oxidized to inorganic substances including CO₂ and H₂O, but other micro-molecular intermediates could be produced that still affected the TOC of the solution (Zhao et al. 2015; Orge et al. 2014).

Mechanism associated with AAF degradation

The reaction mechanism involved during AAF degradation by the VUV/O₃ process was investigated using tert-butanol
(TBA) as a hydroxyl radical inhibitor (Yang et al. 2014a, 2014b; Bai et al. 2016). Conditions set for the reaction were temperature at 25 °C, light intensity at 15 W, ozone concentrations at 6 g/h, initial AAF concentration at 15 ± 0.5 mg/L and initial solution pH at 8.0 ± 0.1. The degradation effect of VUV/O3 on AAF was observed in 80 min after adding 0 mg/L, 20 mg/L and 50 mg/L TBA to the wastewater.

The degradation rates of AAF by VUV/O3 observed after 80 min is illustrated in Figure 5(c). When 0 mg/L, 20 mg/L, 50 mg/L and 100 mg/L of TBA was added, the degradation rates were 88.36%, 75.12%, 66.54% and 52.81%, respectively. The results suggested that the addition of TBA could inhibit the degradation of VUV/O3 on AAF. According to research, the free radical reaction can contribute 67.7% to the degradation of AAF (Zhao et al. 2015). It can be considered that hydroxyl radicals play a major role in the degradation of AAF.

CONCLUSION

In this study, the enhanced removal of a refractory pollutant from aniline aerofloat wastewater using a combined vacuum ultraviolet and ozone (VUV/O3) process was investigated, and the following conclusions were drawn.

(1) AAF could undergo acidolysis or alkaline hydrolysis in strong acidic or alkaline environments and this could reduce the degradation capacity of AAF. (2) The optimum degradation rate of 88.36% was observed with a light intensity of 15 W, reaction time of 60 min, O3 concentration of 6 g/h, pH of 8.0. (3) Five coexisting ions, CO3\(^2-\), Ca\(^2+\), SiO\(_3\)\(^2-\), SO\(_4\)\(^2-\) and Cl\(^-\) (Na\(^+\)), inhibited the degradation of AAF by the VUV/O3 process in the order Ca\(^2+\) > CO\(_3\)\(^2-\) > SiO\(_3\)\(^2-\) > Cl\(^-\) (Na\(^+\)) > SO\(_4\)\(^2-\). (4) With AAF doses of 10 mg/L, 15 mg/L, and 20 mg/L, degradation rates achieved with the VUV/O3 process after 60 min were 85.54%, 88.36%, and 84.52%, respectively, an indication that removal of AAF by the VUV/O3 process was feasible within a relatively wide range of concentrations. (5) After 50 min of reaction time, degradation of AAF by VUV/O3 reached a steady state with the TOC degradation rate reaching 50.92%. (6) When 30 min were allotted for the VUV/O3 degradation process, the experimental results fit well with the pseudo-first-order kinetics (R\(^2\) > 0.975), an indication that the rate constant k in the VUV/O3 oxidation of AAF concentration of 15 mg/L reached 0.064 min\(^{-1}\).

ACKNOWLEDGEMENTS

This study was supported financially by the Science and Technology Research Project of Jiangxi Province Education Department, China (Grant Number GJJ180434) and the Scientific Research Start-up Fund of Jiangxi University of Science and Technology, China (Grant Number JXXBS18033). The authors are grateful to these institutions for the success of this research.

REFERENCES


First received 15 October 2019; accepted in revised form 17 January 2020. Available online 5 February 2020