Degradation of gas–liquid gliding arc discharge on Acid Orange II

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Abstract

The effects of pH value, initial concentration of dye solution and temperature on the degradation efficiency of Acid Orange II (AO7) using gas–liquid gliding arc discharge were investigated. The influences of pH value and temperature on degradation efficiency were not apparent. Increasing initial solution concentration caused the decrease of degradation rate and the increase of absolute degradation quantity. Considering energy efficiency and absolute degradation quantity, the gas–liquid gliding arc discharge is fit for treating high concentration organic wastewater. A possible mineralization pathway was proposed through the analysis of intermediate products detected by gas chromatograph coupled with mass spectrophotometer (GC–MS) and ion chromatograph (IC). Hydroxyl radicals reacted with the azo linkage-bearing carbon of a hydroxy-substituted ring, leading to the cleavage of $-C-N-$ and degradation of AO7. The solution biodegradability was significantly improved (BOD_5/COD from 0.02 to 0.43). The toxicity of intermediate products was lower than that of the initial Acid Orange II.
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Keywords: Gliding arc; Acid Orange II; Degradation efficiency; Biodegradability

1. Introduction

A variety of new synthetic organic dyes are widely used by textile industries, however, the removal of dye-containing wastewater becomes a major environmental problem, because most chemicals are biorefractory organic compounds and present non-negligible toxicity, and resist conventional biological methods. Recently, advanced oxidation processes (AOPs), such as ultraviolet (UV) photolysis, Fenton process, direct ozonation, ultrasonification and non-thermal plasma, have gotten rapid developments, and some of them have been utilized for the purpose of degrading organic pollutants in wastewater [1–4].

Gliding arc discharge (GAD), a newly low-temperature and non-equilibrium plasma [5], has been used to the treatment of organic contaminants in gases [6–9] and aqueous solutions [4,10,11]. In the application of GAD for water purification, gas gliding arc discharge reactor [4,11] and gas–liquid gliding arc discharge reactor [10,12,13] are the two main kinds of experi-

mental apparatus, and the latter has a higher energy efficiency compared to the former [10,12,13]. At present, the detailed mechanism of GAD degrading organic pollutants in wastewater are still not fully understood, but physical and chemical processes are considered to act simultaneously on organic compounds and have synergetic effect during the treatment process. Physical processes are the effects of ultraviolet light, high-energy electrons and shock-waves [1,2,10]. Chemical processes are the reactions initiated by various active species $OH^\bullet$, $HO_2^\bullet$, H_2O_2 and O_3, and most of these species are strong oxidizing agents. The major active species involved in the degradation of organic pollutants are hydroxyl radicals. Hydroxyl radicals can nearly oxidize all organic pollutants due to their high oxidation potential [2,13–17].

The GAD plasma technique is a promising alternative method for degrading recalcitrant compounds biologically in wastewater, because it has extensive adaptability and no secondary pollution.

Du et al. [10] applied gas–liquid GAD to the treatment of phenol solution, and the relations between degradation efficiency and electrode material, nature of the carrier gases and solution concentration have been investigated. Moussa and Brisset [11] mineralized spent tributylphosphate (TBP) from nuclear industry by using gas GAD. Burlica et al. [12] investigated the effects

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of the type of gas and two different gliding arc reactors on the bleaching of reactive blue 137. However, the effects of some parameters about the characteristics of wastewater, such as initial pH value, the solution temperature, *etc.*, were rarely studied. The assessments of biodegradability and toxicity for degraded solution have not been carried out.

In this paper, Acid Orange II (AO7), a typical non-biodegradable azo dye used in the textile industry, is selected as an object pollutant. The effects of initial pH, the solution concentration and the temperature on the degradation of AO7 were examined using a laboratory-scale gas–liquid GAD reactor. Furthermore, a simplified reaction pathway was proposed based on the analysis of intermediate products and mineralization products. The assessments of the biodegradability and toxicity of degraded solution were also carried out in current work.

2. Materials and methods

2.1. Experimental setup and experimental methods

The gas–liquid gliding arc discharge experimental setup has been described in detail in the previous work [10], including 220 V/10 kV transformer, solution storage tank, water pump, flowmeter, two stainless steel electrodes, a nozzle and a water-cooling system.

An arc formed at the minimum gap between two stainless steel electrodes connected to a 220 V/10 kV transformer. The arc was dragged by the gas flow along the electrodes until it finally broke into a plume, and then a new arc occurred and developed in the same way. With above cycles, a larger volume of non-thermal plasma region was created. At the same time, the solution to be treated was sprayed into the plasma and was contacted with the plasma only for a short time, and then influxed to receiving vessel. Degraded liquid passed through plasma region again by water pump and achieved recycled target.

The supply voltage, carrier gas flow rate and minimum electrode gap distance was 10 kV, 0.4 m^3/h and 3.5 mm, respectively, and was kept constant in all experiments. AO7 was purchased from the Third Dye Plant in Tianjing without further purification, and dissolved in distilled water. The total volume of 100 ml of AO7 solution with 500 mg/l concentration was circulated, and solution flow rate was 20 ml/min. Samples were taken after each 1, 2, 3 and 4 treatment cycles, and the duration of one cycle was 5 min.

2.2. Analytical methodology

Dye concentration was determined spectrophotometrically in the visible region at 484 nm corresponding to maximum absorbance wavelength of Acid Orange II by using a TU1800 spectrophotometer. Chemical oxygen demand (COD) is a measure of the total quantity of oxygen required to oxidize all organic material into carbon dioxide and water. COD analysis was performed by a 5B-3 COD meter. Biochemical oxygen demand (BOD) is a measure of the amount of oxygen that bacteria will consume while decomposing organic

matter under aerobic conditions. BOD$_5$ was measured according to the GB7488-87 standard method. The pH value was measured by a digital pHS-2F acidic meter and adjusted by using NaOH and H$_2$SO$_4$. Inorganic anions were analyzed by 792 Basic IC equipped with a suppressor of background conductivity.

The aqueous solution after 20 min degradation was extracted by acetic ether, and then the phase of acetic ether was distilled and condensed to 2 ml at $40 \pm 1\,^\circ$C under reduced pressure. The identification of intermediate products was performed on a high-resolution gas chromatograph (HRGC)/low-resolution mass spectrometer (LRMS) (Finnigan Voyger Thermal Trace 2000). Chromatographic separation was carried out on a 30-m DB-5quartz capillary column. The flow rate of carrier gas, i.e., helium, was set as 1.2 ml/min. The temperature program for GC oven with the initial temperature $100\,^\circ$C, was held for 2 min; and then held for 3 min at 100–$200\,^\circ$C with the rate of $10\,^\circ$C/min; finally held for 20 min at 200–$280\,^\circ$C with the rate of $3\,^\circ$C/min. Each sample volume was the same: 1 μl. The mass spectrum condition was: electron impact ionization 70 eV; electron multiplier voltage 420 V; ion source temperature $220\,^\circ$C; interface temperature $250\,^\circ$C; selected ion monitoring mode (SIM).

2.3. Seed germination toxicity test

Prior to germination, the wheat seeds were surface-sterilized in 0.1% Javel water for 20 min, and dipped in distilled water for 1 h, and finally rinsed with distilled water, airing. Seed germination was tested in petriplate where a piece of filter paper was placed on it and moistened with 5.0 ml in different time treatment solution and initial solution conditions. The control was maintained by moistening the filter paper with 5-ml distilled water. Thirty seeds of each variety were placed in each culture dish, and covered by lid with incubated in aerated incubator in dark at $25 \pm 1\,^\circ$C for 48 h. Germination percentage was calculated by counting the number of germinated seeds [18]. Each treatment was replicated three times. Distilled water, initial solution and treatment solution were replaced by fresh ones every 12 h, respectively.

3. Result and discussion

3.1. Effect of pH

The initial pH of AO7 was adjusted to 3, 7, and 11, respectively. Fig. 1 displayed that a relatively higher AO7 degradation rate could be achieved on both the acidic and alkaline conditions after 5-min treatment, but degradation efficiency of AO7 was much the same on all pH conditions after 20-min treatment.

Above observations could be explained as following. H$_2$O$_2$ and O$_3$ are also the important reactive species produced by gas–liquid GAD with O$_2$ as carrier gas [10,16]. The acidic condition favours H$_2$O$_2$ to decompose OH$^\bullet$ [19], and the alkaline condition favours O$_3$ to decompose OH$^\bullet$ [20]. OH$^\bullet$, a strong oxidant inferior to fluorine, is the major active species produced in gas–liquid GAD [14,19], and it accelerated AO7 to be
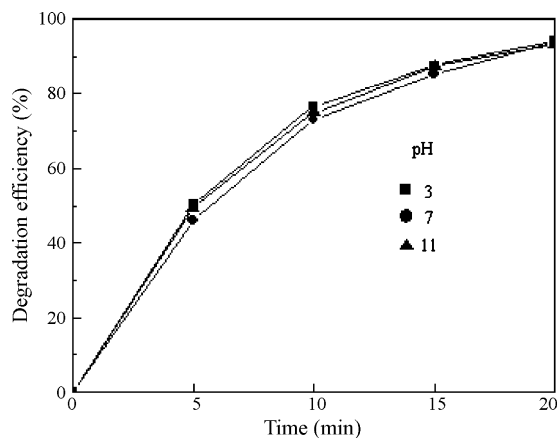
Fig. 1. Variation of degradation efficiency of AO7 vs. time at initial pH value. $U = 10$ kV, $C_0 = 500$ mg/l, $Q_{oxygen} = 0.4$ m^3/h, and $Q_{AO7} = 20$ ml/min.

degraded. However, for the solutions with initial pH 7 and 11, degraded solution pH values decreased quickly to 3.08 and 3.26, respectively, after 5-min treatment (Fig. 2). Degraded solution pH values were acidic, so the effect of pH became small with treatment time increasing and could be neglected for 20-min treatment solution.

3.2. Effect of gas source

Different carrier gases affected the formation of the reactive species and degradation of the organic pollutants, so O_2, air and N_2 in our experiment were chosen as the carrier gases to be investigated (Fig. 3). Fig. 4 showed the effects of gas sources on the degradation efficiency of AO7 were ranked as follows: $O_2 >$ air $> N_2$.

The reason for the highest removal with carrier gas O_2 was that ozone was produced during the glidarc discharge process [21,22], and ozone reacted with the AO7 or converted to OH$^\bullet$ oxidizing the organic pollutants. However, with carrier gas N_2, less reactive species formed, so the removal of AO7 was less than that of O_2 or air. The results were consistent with Hao et al. [22] results.
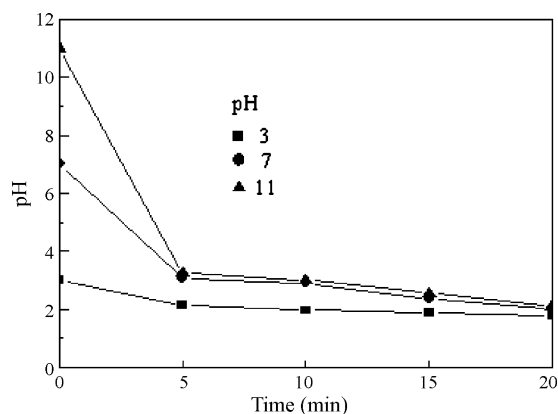

Fig. 2. Variation of AO7 solution pH with the plasma treatment time. $U = 10$ kV, $C_0 = 500$ mg/l, $Q_{oxygen} = 0.4$ m^3/h, and $Q_{AO7} = 20$ ml/min.
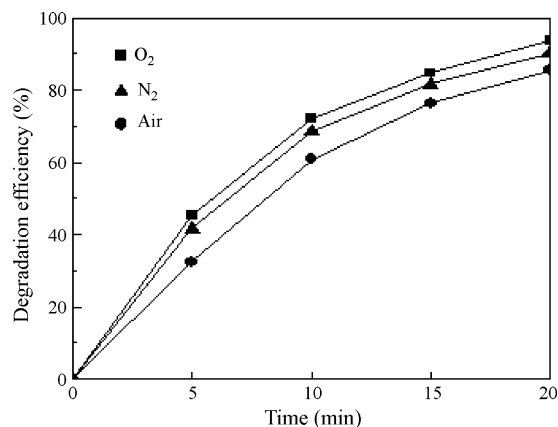

Fig. 3. Influence of gas source on degradation efficiency of AO7. $U = 10$ kV, $C_0 = 500$ mg/l, $Q_{oxygen} = Q_{air} = Q_{nitrogen} = 0.4$ m^3/h, $Q_{AO7} = 20$ ml/min, and pH$_0$ 6.20.
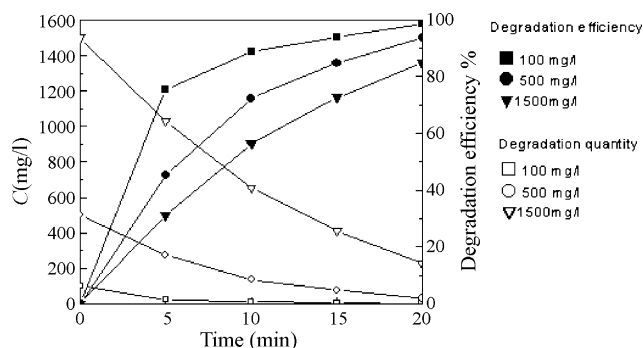

Fig. 4. Effect of initial concentration on the decomposition rate and absolute degradation quantity of AO7. $U = 10$ kV, $Q_{oxygen} = 0.4$ m^3/h, $Q_{AO7} = 20$ ml/min, and pH$_0$ 6.20.

3.3. The effect of concentration

The initial concentration was 100, 500, and 1500 mg/l, respectively, and the influence on degradation of AO7 was shown in Fig. 5. The degradation rate decreased (from 98 to 94% and to 84%), but the absolute degradation quantity increased (100 mg/l declined to 1.78 mg/l, 500 mg/l declined to 31.75 mg/l,
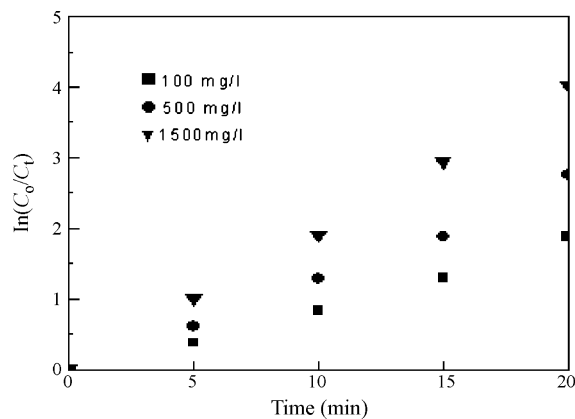

Fig. 5. Plot of regression analysis for the first-order reaction for three different initial concentrations. $U = 10$ kV, $Q_{oxygen} = 0.4$ m^3/h, $Q_{AO7} = 20$ ml/min, and pH$_0$ 6.20.

Table 1
Reactions of Acid Orange II degradation at three different concentrations

Concentration (mg/l)	First-order kinetic equation	k	R^2
100	$\ln(C_0/C_t) = 0.1987t$	0.1987	0.999
500	$\ln(C_0/C_t) = 0.1322t$	0.1322	0.995
1500	$\ln(C_0/C_t) = 0.08952t$	0.08952	0.994

and 1500 mg/l declined to 229.65 mg/l) with the increasing initial concentration.

The degradation reactions of AO7 followed the first-order law, and the kinetic pathway could be expressed as follows:

$$\ln\left(\frac{C_0}{C_t}\right) = k_{AO}t$$

where C_0, C_t, k_{AO} and t were the initial concentration, the concentration of AO7 at a given reaction time, the rate constant and reaction time, respectively. Plots of regression analysis for the first-order reactions were displayed in Fig. 5. The equations of three initial concentrations were depicted in Table 1, and the relevant coefficients R^2 indicated the linearity in regression analysis.

Energy efficiencies of the above three concentrations were calculated as 147, 702, and 1905 mg/kWh, respectively. Considering the absolute degradation quantity and the energy efficiency, the gas–liquid GAD is fit for degrading high concentration organic wastewater. Energy efficiency of gas–liquid GAD reactor was higher than that of gas GAD reactor described by Burlica et al. [12] and Abdelmalek et al. [4].

3.4. The effect of temperature

The influence of temperature on degradation efficiency has two sides: on the one hand, increasing temperature accelerates reactive radicals to collide and leads to their extinguishments, so degradation rate decreases; on the other hand, the increase of temperature could enhance reaction rate constants, and increases degradation efficiency. The temperature of the solution was maintained, respectively, at 283, 303, and 323 K. Experimental results were shown in Fig. 6, with which we found that the
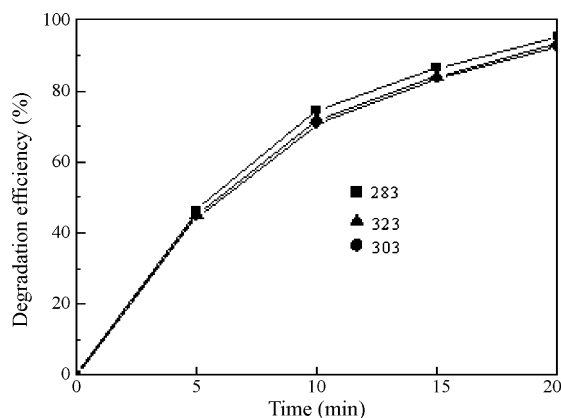

Fig. 6. Influence of temperature on degradation efficiency of AO7. $U = 10$ kV, $C_0 = 500$ mg/l, $Q_{oxygen} = 0.4$ m^3/h, $Q_{AO7} = 20$ ml/min, and pH$_0$ 6.20.
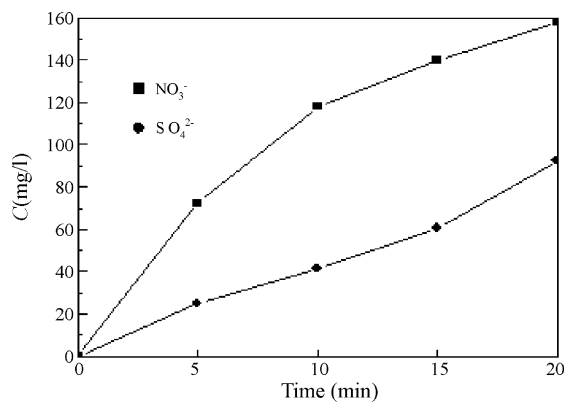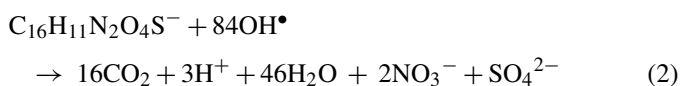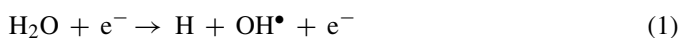

Fig. 7. Formation of NO$_3^-$ and SO$_4^{2-}$ by plasma chemical degradation of AO7 concentration. $U = 10$ kV, $C_0 = 500$ mg/l, $Q_{oxygen} = 0.4$ m^3/h, $Q_{AO7} = 20$ ml/min, and pH$_0$ 6.20.

degradation efficiency decreased with the increase of temperature.

This result indicated the activation energy of the reactions occurring during gas–liquid GAD process was very low, and the enhancement of reaction rate constants was not remarkable. In this case, the concentrations and the live time of radicals were two main factors influencing the degradation efficiency [3]. The negative effect of temperature on reactive species was higher than the positive effect of temperature on reaction rate constants, so increasing temperature led to a decreasing degradation rate. However, this difference was not so obvious.

3.5. Mineralization products

$$H_2O + e^- \rightarrow H + OH^\bullet + e^- \tag{1}$$

$$C_{16}H_{11}N_2O_4S^- + 84OH^\bullet$$
$$\rightarrow 16CO_2 + 3H^+ + 46H_2O + 2NO_3^- + SO_4^{2-} \tag{2}$$

Known from Eqs. (1) and (2), if AO7 solution with 500 mg/l concentration is mineralized completely, it will theoretically produce 177.14 mg/l NO$_3^-$ and 137.14 mg/l SO$_4^{2-}$.

The concentrations of NO$_3^-$ and SO$_4^{2-}$ increased with treatment time and achieved 157.60 and 92.4 mg/l after 20-min treatment, and accounted for 95 and 72% of the theoretic value, respectively. The results were shown in Fig. 7. The practical amount of NO$_3^-$ was equal to theoretic quantity approximately, i.e., organic nitrogen was almost mineralized to inorganic nitrogen completely. Nevertheless, the actual concentration of SO$_4^{2-}$ was less than theoretic value, i.e., organic sulphur was mineralized to inorganic sulphur partially and existed in organic state partly, which could be demonstrated by the detection of benzene sulfonic acid with GC–MS.

Besides, the concentration of CO$_2$ during gas–liquid GAD was also monitored. Fig. 8 illustrated the concentration of CO$_2$ increased with treatment time, and reached 543.8 ppm at 20 min.
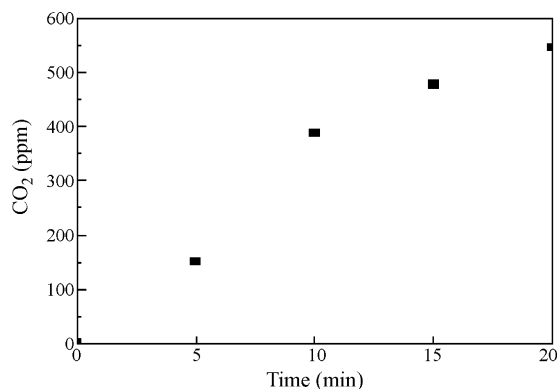
Fig. 8. CO_2 concentration in the exhaust gas with treatment time. $U = 10$ kV, $C_0 = 500$ mg/l, $Q_{oxygen} = 0.4$ m^3/h, $Q_{AO7} = 20$ ml/min, and pH$_0$ 6.20.

Fig. 10. The COD, BOD$_5$ and BOD$_5$/COD variations solution with treatment time. $U = 10$ kV, $C_0 = 500$ mg/l, $Q_{oxygen} = 0.4$ m^3/h, $Q_{AO7} = 20$ ml/min, and pH$_0$ 6.20.

3.6. Intermediate products

In a typical gas–liquid GAD degradation experiment, the following intermediates were identified: phenol, naphthalene, β-naphthol, benzendicarboxylic acid, 1,3-isobenzofurandione, 2-hydroxymethylbenzoic acid, 3-hydroxylhypnone, oxalic acid, acetic acid and malonic acid.

Two reaction mechanisms have been proposed by scholars for mineralizing azo-dye molecules by oxidative action of hydroxyl radicals formed in advanced oxidation processes. First, nitrogen-containing organic compounds having lower molecular weight are created with the cleavage of azo bond (−N=N−) by hydroxyl radicals [23–25] and then further degraded. Second, most organic nitrogen converts to molecular nitrogen with the process of hydroxyl radicals attacking the azo linkage-bearing carbon of a hydroxy-substituted ring (−C−N−), and then molecular nitrogen volatilizes or further was oxidized to NH_4^+, NO_2^- and NO_3^- [26–29], and other organic compounds are further degraded.

Nitrogen-containing organic compounds were not found in the intermediate products detected by GC–MS. Moreover, the practical amount of NO_3^- was equal to theoretic quantity approximately, i.e., organic nitrogen was almost mineralized
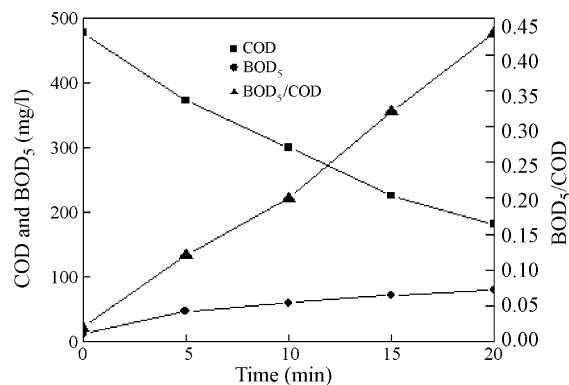
to inorganic nitrogen completely. So we consider the reaction pathway of most of AO7 oxidation to follow the second mechanism mentioned above. As schematically shown in Fig. 9, hydroxyl radicals reacted with the azo linkage-bearing carbon of a hydroxy-substituted ring, with which process-substituted phenyldiazene and naphthoxy radicals were produced. Both of them were unstable extremely and could react further with hydroxyl radicals resulting in the degradation of aromatic ring.

3.7. Enhancement of the biodegradability

The BOD$_5$/COD ratio is commonly used to assess the biodegradability of wastewater in the literature. The dependences of COD, BOD$_5$ and BOD$_5$/COD with the degradation time were illustrated in Fig. 10. The initial AO7 solution was not biodegradable because of its quite low BOD$_5$/COD ratio (0.02). The BOD$_5$/COD increased from 0.02 to 0.32 after 15 min of oxidation and this value became 0.43 after 20-min treatment. Above observation showed that the biodegradability of solution was significantly enhanced with the treatment time.

The increase of BOD$_5$/COD, induced by the increase of BOD$_5$ and the decrease of COD, indicated the conversion of the complex non-biodegradable dye molecule to more biodegrad-
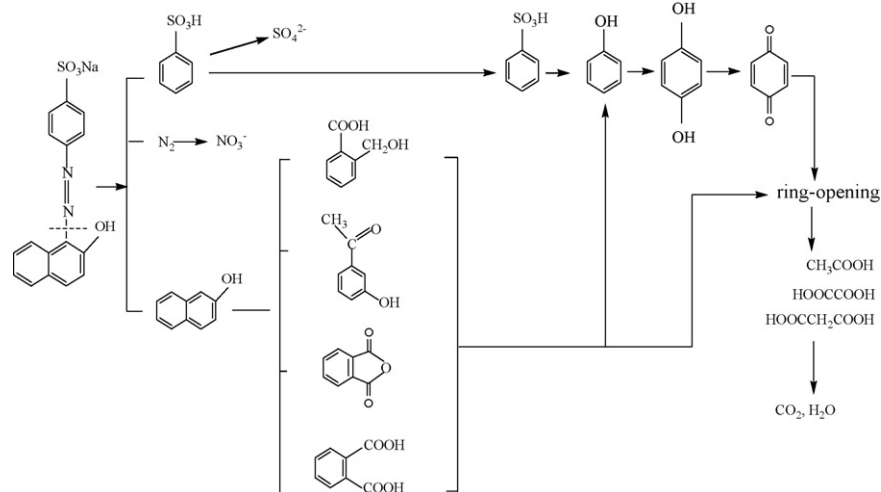

Fig. 9. The AO7 degradation pathway scheme by gas–liquid gliding arc discharge. $U = 10$ kV, $C_0 = 500$ mg/l, $Q_{oxygen} = 0.4$ m^3/h, $Q_{AO7} = 20$ ml/min, and pH$_0$ 6.20.

Table 2
Effect of treatment solution on index of seed germination

Solution	Degradation efficiency (%)	pH	Seed germination (%)	Seed germination inhibition (%)
Initial solution	0	6.20	82.2 ± 0.045	17.8
Degraded solution after 5-min treatment	45.36	3.67	83.3 ± 0.022	16.7
Degraded solution after 10-min treatment	72.28	2.93	86.7 ± 0.033	13.3
Degraded solution after 15-min treatment	84.71	2.36	91.1 ± 0.057	8.9
Degraded solution after 20-min treatment	93.65	2.02	87.8 ± 0.061	12.2
Control	–	7.00	93.3 ± 0.033	6.7

able compounds, i.e., the formation of intermediate products with hydroxy and carboxy functional groups, organic acid and denitrogenation of the degradation process [28]. Compared with the maximum BOD_5/COD ratios in the range of 0.27–0.56 reported in the literature for different substituted aromatics [30–32] using other advanced oxidation process, the value of BOD_5/COD after 20-min oxidation treatment (0.43) was indicative of wastewater easily biodegradable.

3.8. Toxicity analysis

Besides biodegradability, the toxicity of wastewater is also an important issue to the effectiveness of AOPs. It has been demonstrated by several researches such as Fenton's treatment, ozonation, ultrasonic irradiation and perozonation, etc. In this experiment, the seed germination tests were performed in petriplate for the evaluation of toxicity of initial solution and degraded solution with different treatment time (5, 10, 15, and 20 min). The results were shown in Table 2.

The seed germination increased and the germination inhibition decreased with increasing the degradation efficiency of AO7, i.e., the less quantity of AO7 in solution, the higher seed germination would be. This detection indicated the by-products produced during oxidation process had lower toxicity compared to that of parent compound.

Nevertheless, the seed germination decreased when degradation efficiency of AO7 achieved 96.35%. As shown in Table 2, the pH value decreased from 6.20 to 2.02 within 20 min, which implied the formation of organic acids. The results of GC–MS also proved the existence of organic acids such as acetic acid, oxalic acid. When pH value was 2 or so, organic acids existed in molecular state. The acute toxicity to wheat seed germination in molecular state was higher than that in ionic state, so the seed germination decreased.

4. Conclusions

The effects of pH and temperature on degradation efficiency were not evident. Increasing initial solution concentration caused decrease of the degradation efficiency and increase of absolute degradation quantity of AO7, the energy efficiencies with three different initial concentrations were calculated. Considering the energy efficiency and absolute degradation quantity, the gas–liquid GAD suited to degrade high concentration organic wastewater. The degradation reaction of AO7 obeyed the first-order law.

Organic nitrogen was almost converted to NO_3^- completely, while organic sulphur was mineralized partially and existed in the organic state partly. The possible mineralization pathway was put forward by the analysis of the intermediates. Hydroxyl radicals reacted with the azo linkage-bearing carbon of a hydroxy-substituted ring, causing the breaking of $-C-N-$ bond and the degradation of azo-dye.

The biodegradability of AO7 was significantly improved, and the BOD_5/COD radio increased from 0.02 to 0.43 after 20-min treatment. The toxicity test, performed by using wheat seed germination rate, showed the toxicity of intermediate products was lower than that of original compound.

The results obtained from the experimental studies proved that GAD was a potential technique for degradation and biodegradability enhancement of azo dyes. It could be also taken as a pretreatment method to convert initially biorecalcitrant compounds to more readily biodegradable intermediates, and then the mineralization of intermediate organic products could be accomplished through biological methods.

References

[1] H.J. Wang, J. Li, X. Quan, Decoloration of azo dye by a multi-needle-to-plate high-voltage pulsed corona discharge system in water, J. Electrostat. 64 (2006) 416–421.
[2] A.T. Sugiartoa, S. Itoa, T. i Ohshimaa, Oxidative decoloration of dyes by pulsed discharge plasma in water, J. Electrostat. 58 (2003) 135–145.
[3] J.Z. Gao, X.Y. Wang, Z.G. Hu, Plasma degradation of dyes in water with contact glow discharge electrolysis, Water Res. 37 (2003) 267–272.
[4] F. Abdelmaleka, S. Gharbia, B. Benstaalia, et al., Plasmachemical degradation of azo dyes by humid air plasma: Yellow Supranol 4 GL, Scarlet Red Nylosan F3 GL and industrial waste, Water Res. 38 (2004) 2338–2346.
[5] H. Lesueur, A. Czernichowski, Device for generating low-temperature plasmas by formation of sliding electric discharges, Patent FR2639172 (1990).

[6] V. Dalaine, J.M. Cormier, P. Lefaucheux, A gliding discharge applied to H_2S destruction, J. Appl. Phys. 83 (1998) 2435–2442.

[7] K. Krawczyk, M. Mlotek, Oxidation and decomposition of N_2O by gliding discharge combined with a bed of catalyst, High Temp. Mater. Process. 5 (2001) 349–353.

[8] K. Krawczyk, M. Mlotek, Combined plasma-catalytic processing of nitrous oxide, Appl. Catal. B: Environ. 30 (2001) 233–245.

[9] A. Czernichowski, GlidArc assisted preparation of the synthesis gas from natural and waste hydrocarbons gases, Oil Gas Sci. Technol. 56 (2001) 181–198.

[10] J.H. Yan, C.M. Du, X.D. Li, Plasma chemical degradation of phenol in solution by gas–liquid gliding arc discharge, Plasma Sour. Sci. Technol. 14 (2005) 637–644.

[11] D. Moussa, J.L. Brisset, Disposal of spent tributylphosphate by gliding arc plasma, J. Hazard. Mater. B 102 (2003) 189–200.

[12] R. Burlica, M.J. Kirkpatricka, W.C. Finneya, Organic dye removal from aqueous solution by glidarc discharges, J. Electrostat. 62 (2004) 309–321.

[13] J.H. Yan, Ch.M. Du, X.D. Li, B.G. Cheron, M.J. Ni, Degradation of phenol in aqueous solutions by gas–liquid gliding arc discharges, Plasma Chem. Plasma Process. 26 (2006) 31–41.

[14] B. Benatali, P. Boubert, B.G. Cheron, Density and rotational temperature measurements of the OH and NO radicals produced by a gliding arc in humid air, Plasma Chem. Plasma Process. 22 (2002) 553–571.

[15] P. Lukes, B.R. Locke, Plasmachemical oxidation processes in a hybrid gas–liquid electrical discharge reactor, J. Phys. D: Appl. Phys. 38 (2005) 4074–4081.

[16] R. Burlicaa, M.J. Kirkpatrickb, Formation of reactive species in gliding arc discharges with liquid water, J. Electrostat. 64 (2006) 35–43.

[17] C.M. Du, J.H. Yan, X.D. Li, K.F. Cen, Treatment of 4-chlorophenol solution by gas–liquid gliding arc discharge, Proc. CSEE 26 (2006) 89–93.

[18] S. Srivastav, I.S. Thakur, Evaluation of bioremediation and detoxification potentiality of *Aspergillus niger* for removal of hexavalent chromium in soil microcosm, Soil Biol. Biochem. 38 (2006) 1904–1911.

[19] D.R. Grymonpre, K. Sharma, The role of Fenton's reaction in aqueous phase pulsed streamer corona reactors, Chem. Eng. J. 82 (2001) 189–207.

[20] D.Z. Sun, Advanced Oxidation Techniques of Environmental Engineering, Chemical industry publishing company, Beijing, 2002.

[21] J. Li, M. Sato, T. Ohshima, Degradation of phenol in water using a gas–liquid phase pulsed discharge plasma reactor, Thin Solid Films 515 (2007) 4283–4288.

[22] X.L. Hao, M.H. Zhou, Y. Zhang, L.C. Lei, Enhanced degradation of organic pollutant 4-chlorophenol in water by non-thermal plasma process with TiO_2, Plasma Chem. Plasma Process. 26 (2006) 455–468.

[23] E. Guivarch, S. Trevin, C. Lahitte, Degradation of azo dyes in water by electro-Fenton process, Environ. Chem. Lett. 1 (2003) 38–44.

[24] F. Abdelmalek, M.R. Ghezzar, M. Belhadj, A. Addou, Bleaching and degradation of textile dyes by nonthermal plasma process at atmospheric pressure, Ind. Eng. Chem. Res. 45 (2006) 3–29.

[25] M. Joseph, H. Destaillats, H.M. Hung, The sonochemical degradation of azobenzene and related azo dyes: rates enhancements via Fenton's reactions, J. Phys. Chem. A 104 (2000) 301–307.

[26] K. Wang, Y.X. Chen, F.X. Ye, Photo degradation of dye pollutants over Tio_2 particles under UV–vis light irradiation, Acta Energ. Solaris Sin. 26 (2005) 39–43.

[27] J. Donlagic, J. Levec, Comparison of catalyzed and noncatalyzed oxidatiob of azo dye and effect on biodegradability, Environ. Sci. Technol. 32 (1998) 1294–1302.

[28] J.T. Spadaro, L. Isabele, V. Renganathan, Hydroxyl radical mediated degradation of azo dyes: evidence for benzene generation, Environ. Sci. Technol. 28 (1994) 1389–1393.

[29] A. Sema, V. Aviyente, Experimental and modeling approach to decolorization of azo dyes by ultrasound: degradation of the hydrazone tautomer, J. Phys. Chem. A 109 (2005) 3506–3516.

[30] F. Gökcen, T.A. Özbelge, Enhancement of biodegradability by continuous ozonation in Acid Red-151 solutions and kinetic modeling, Chem. Eng. J. 114 (2005) 99–104.

[31] G. Yu, W.P. Zhu, Z.H. Yang, Pretreatment and biodegrability enhancement of DSD acid manufacturing wastewater, Chemosphere 37 (1998) 487–494.

[32] J.L. Morais, P.P. Zamora, Use of advanced oxidation processes to improve the biodegradability of mature landfill leachates, J. Hazard. Mater. B123 (2005) 181–186.