Non-thermal plasma treatment of *Radix aconiti* wastewater generated by traditional Chinese medicine processing

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ABSTRACT

The wastewater effluent from *Radix aconiti* processing, an important step in the production processes of traditional Chinese medicine (TCM), is a type of toxic wastewater and difficult to treat. Plasma oxidation methods have emerged as feasible techniques for effective decomposition of toxic organic pollutants. This study examined the performance of a plasma reactor operated in a dielectric barrier discharge (DBD) to degrade the effluent from *R. aconiti* processing. The effects of treatment time, discharge voltage, initial pH value and the feeding gas for the reactor on the degradation of this TCM wastewater were investigated. A bacterium bioluminescence assay was adopted in this study to test the toxicity of the TCM wastewater after non-thermal plasma treatment. The degradation ratio of the main toxic component was 87.77% after 60 min treatment with oxygen used as feed gas and it was 99.59% when the initial pH value was 8.0. High discharge voltage and alkaline solution environment were beneficial for improving the degradation ratio. The treatment process was found to be capable of reducing the toxicity of the wastewater to a low level or even render it non-toxic. These experimental results suggested that the DBD plasma method may be a competitive technology for primary decomposition of biologically undegradable toxic organic pollutants in TCM wastewater.

Introduction

Water safety is a very important issue throughout the world, and the problem of water pollution is becoming more and more serious, nowadays. Traditional Chinese medicine (TCM) has been used and developed for several thousand years in China. As a splendid part of the culture of the Chinese nation, it occupies a very important status in the medicine domain due to its unique effectiveness. In recent years, the TCM industry has been developing rapidly, which results in a corresponding increase in TCM wastewater production. TCM wastewater is a type of high strength organic wastewater, which contains a great variety of pollutants and complicated components, for example much raw TCM wastewater is mainly composed of glucide (amylose), protein, lignin, organic acids, resins, alkaloids, amino acids, hydroxybenzene and suspended solids (Chen et al., 2009a). TCM wastewater usually has a low BOD_5/COD ratio (approximately 20%). It was estimated that approximately half of the TCM wastewater was discharged directly without specific treatment (Shi et al., 2005). For treated wastewater, the general treatments usually involve anaerobic processes because of their macromolecular

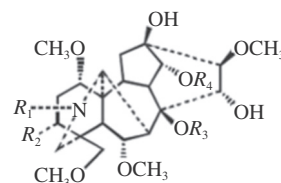* *Corresponding author*. E-mail: kfliu@fudan.edu.cn (Kefu Liu).

composition and ease of foaming in aerobic biodegradation (Chen et al., 2008, 2009a,b; Liu et al., 2007). However, some kinds of TCM such as *Radix aconiti* have very strong toxicity to the biodegradation organisms; hence, biological treatment is not very suitable. Without good treatment these pollutants will pose a great danger to organisms when they are discharged into the environment.

R. *aconiti* is a well-known toxic plant of the genus *Aconitum* in the *Ranunculaceae* family, and grows widely in Northern Asia and North America. *Aconitum* species have been used as an important drug in TCM for a long time. The tubers and roots of *R. aconiti* are commonly used to treat various illnesses and poor health conditions, such as syncope, rheumatic fever, painful joints, gastroenteritis, diarrhea, edema, bronchial asthma, various tumors, and in some endocrine disorders such as irregular menstruation (Singhuber et al., 2009). The roots of *R. aconiti* are shown in Fig. 1. However, *Aconitum* alkaloids including Aconitine (ACO), Hypaconitine (HYP), Mesaconitine (MES), Benzoylhypacoitine (BHY), Benzoyl-aconine (BAC) and Benzoylmesaconine (BME) in *R. aconiti* (especially in their roots) are known as cardiotoxins and neurotoxins, which act on the voltage-sensitive sodium channels of excitable membranes, including the myocardium, nerves and muscles, and the estimated lethal dose in humans is 2 mg of pure aconitine, 5 mL of aconite tincture and 1 g of the wild plant (Chan, 2009). The chemical structures of *Aconitum* alkaloids are shown in Fig. 2 (Niitsu et al., 2013). As a consequence in TCM, *R. aconiti* is used only after it is processed to greatly reduce the *Aconitum* alkaloid content (Singhuber et al., 2009; Chan, 2011). However, a large amount of toxic water containing a large amount of *Aconitum* alkaloid is produced during *R. aconiti* processing. Today, this kind of wastewater still lacks appropriate treatment.

Advanced oxidation processes (AOPs) have great potential in water treatment. These methods are based on the generation of strong oxygen-based oxidizers: hydroxyl radicals (OH.), ozone (O_3), ozone radical ions (O_3^-), atomic oxygen (O), hydrogen peroxide H_2O_2) and hydroperoxyl radicals ($HO_2.$). In particular, the formation of hydroxyl radicals, which are among the strongest oxidizers and react non-selectively with various types of pollutants, is desired (Esplugas et al., 2007;

Fig. 1 – Roots of *Radix aconiti*.

Alkaloids		R_1	R_2	R_3	R_4
Aconitines	Aconitine	C_2H_5	OH	$COCH_3$	COC_6H_5
	Mesaconitine	CH_3	OH	$COCH_3$	COC_6H_5
	Hypaconitine	CH_3	H	$COCH_3$	COC_6H_5
Benzoylaconine	Benzoylaconine	C_2H_5	OH	H	COC_6H_5
	Benzoylmesaconine	CH_3	OH	H	COC_6H_5
	Benzoylhypacoitine	CH_3	H	H	COC_6H_5

Fig. 2 – Chemical structures of *Aconitum* alkaloids.

Méndez-Arriaga et al., 2008; Trovó et al., 2008). Non-thermal plasma generated in electrical discharges in liquid or at the gas–liquid interface also leads to the formation of oxidizers: radicals (H., O., OH.) and molecules (H_2O_2, O_3, *etc.*) (Lukes et al., 2005; Locke and Thagard, 2012). Considering the factors above, as an AOP method, non-thermal plasma may be a viable alternative for water treatment. Nowadays, many studies have been carried out on the use of non-thermal plasma water treatment in environmental protection. Non-thermal plasma has been investigated for the oxidation of various organic compounds in water: organic dyes (Benetoli et al., 2012; Tichonovas et al., 2013), potential endocrine disrupting compounds (EDCs) (Gerrity et al., 2010; Krause et al., 2009) and pharmaceutical compounds (Magureanu et al., 2010; Dobrin et al., 2013) *etc.* However, the treatment of TCM wastewater with non-thermal plasma methods, especially toxic TCM wastewater, has not yet been investigated.

In this study, the potential treatment of a strongly toxic TCM wastewater, which was produced from *R. aconiti* processing, using non-thermal plasma generated by pulse dielectric barrier discharge was investigated. The degradation of the toxic components of the TCM wastewater including ACO, HYP, MES, BHY, BAC and BME was evaluated and the details of the degradation were discussed. Bacterial bioluminescence assays were used to evaluate the acute toxicity of the wastewater both before and after the treatment.

1. Materials and methods

1.1. *R. aconiti effluent*

The *R. aconiti* used in this study was provided by Beijing Tong Ren Tang Group Co., Ltd., China. The preparation of the effluent was based on the TCM method of processing *R. aconiti*. First, 200 g *R. aconiti* was prepared and then broken into small pieces. The pieces were then soaked in 2.5 L tap-water for about 12 hr. The solution was filtered and the filtrate was saved. The *R. aconiti* pieces left after the first soaking and filtering were selected and soaked in 2.5 L tap-water for about 12 hr, again.
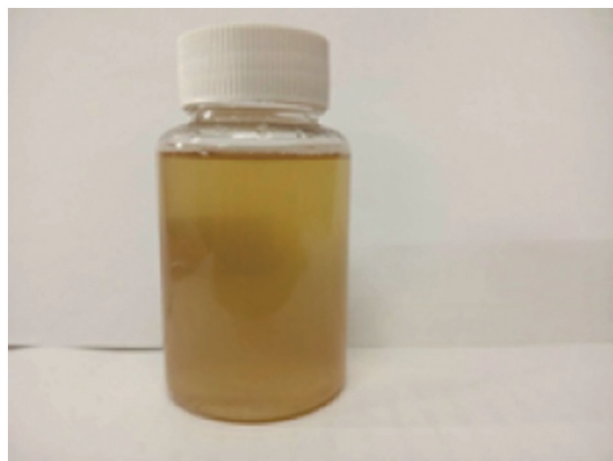
Fig. 3 – The *Radix aconiti* effluent.

Fig. 4 – The basic schematic of the pulsed-power generator.

The samples were soaked in this way 4 times, providing 10 L R. *aconiti* effluent. A picture of R. *aconiti* effluent is shown in Fig. 3. H_2SO_4 solution and NaOH solution were used for the adjustment of the initial pH value. The characteristics of the original R. *aconiti* wastewater sample are shown as following: pH 5.60 ±0.1, conductivity 1110 ± 100 μS/cm, COD 3920 mg/L, ACO 1.17 mg/L, MES 3.24 mg/L, HYP 13.71 mg/L, BAC 0.56 mg/L, BME 5.23 mg/L, BHY 1.30 mg/L, other alkaloids, saccharides, and protein.

1.2. Pulsed-power generator

The schematic of the pulsed-power generator is shown in Fig. 4. The pulsed-power generator operates as follows: TL is a transmission line with an equivalent capacitance of 2 nF. TL was charged by DC high voltage source through current-limiting inductance L1. When the voltage of TL reached a certain value, the hydrogen thyratron was triggered on and the energy was quickly released to the load, thus forming a pulse. Since the voltage on the diode D3 was reverse-biased at this time, it was in the off status. When the discharge current fell to zero, T turned off automatically. The peak voltage was 30 kV, the peak current was 200 A, the max repetition rate was 500 Hz and the rise time was ~100 ns.

1.3. Plasma reactor and electrical circuit

The discharge reactor and the pulsed dielectric barrier discharge (DBD) schematic diagram employed in this work are shown in Fig. 5. The whole processing system included a rectangular acrylic container (100 × 100 × 400 mm); DBD electrodes; separating plates; a water pump, an air source and a sprayer. The DBD electrodes consisted of two parts. Copper (diameter: 2 mm, length: 13 cm) was used for the DBD metal electrodes, with a quartz glass tube (length: 13 cm; outside diameter: 4 mm; inside diameter: 2 mm) around the copper bar, and about 1 cm of copper bar protruded outside the tube so it could connect to the power source well. 5 positive electrodes and 6 negative electrodes were staggered and fixed in the same plane. The gap between two adjacent quartz glass 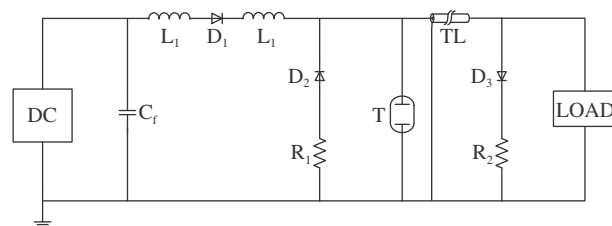tubes was 4 mm. A separating plate made of acrylic was mounted under the DBD electrodes and used for lengthening the residence time of wastewater and water re-distribution. There were five rows of tiny holes whose diameter were 2 mm in the plate. In the separating plates the distance between adjacent holes was 5 mm. The wastewater was delivered by the pump and sprayed from the sprayer at the top of container; then the wastewater sprayed into the discharge area and fell onto and through the separating plates layer by layer. Because of the cyclic flow of the wastewater and the low temperature characteristic of the nanosecond pulsed DBD, the solution temperature was maintained below 35°C (initial water temperature 27.2°C; after treatment 32.5°C). Considering the size of container and the efficiency, five rows of electrodes and four separating plates were adopted and the distance between the electrode row and the separating plate was 10 mm. The typical discharge waveform of voltage and current is also shown in Fig. 5.

1.4. Analysis

In this study, the discharge voltage and current were measured with a digital oscilloscope (Tektronix TDS1012B-SC) equipped with a voltage probe and a current probe.

The concentration of the *Aconitum* alkaloids was determined using a high performance liquid chromatography/ HPLC (Waters 2695-2996, Waters, USA,) equipped with chromatographic column phenomenex C18 (4.6 mm × 250 mm, 5 μm, Phenomenex, USA). The flow rate was 1.0 mL/min and the temperature was kept at 35°C. The mobile phase A was acetonitrile: tetrahydrofuran (25:15) and the mobile phase B was 0.1 mol/L ammonium acetate (0.5 mL glacial acetic acid was contained in every 1 L of the mobile phase B). The UV detection wavelength was set at 235 nm and the elution flow rate was 1.0 mL/min. The degradation efficiency of each sample was calculated from the following Eq. (1):

$$\eta = \left(\frac{C_0 - C_t}{C_0}\right) \times 100\% \tag{1}$$

where, η (%)is the degradation efficiency of the *Aconitum* alkaloids; C_0 (mg/L) is the initial concentration of the *Aconitum* alkaloids before the plasma treatment and C_t (mg/L)is the residual concentration of the *Aconitum* alkaloids after discharge treatment.

Reference materials containing the *Aconitum* alkaloids were purchased from the National Institute for the Control of Pharmaceutical and Biological Products, China. An example spectrum showing the resolution of the *Aconitum* alkaloids involved in the experiment is shown in Fig. 6.
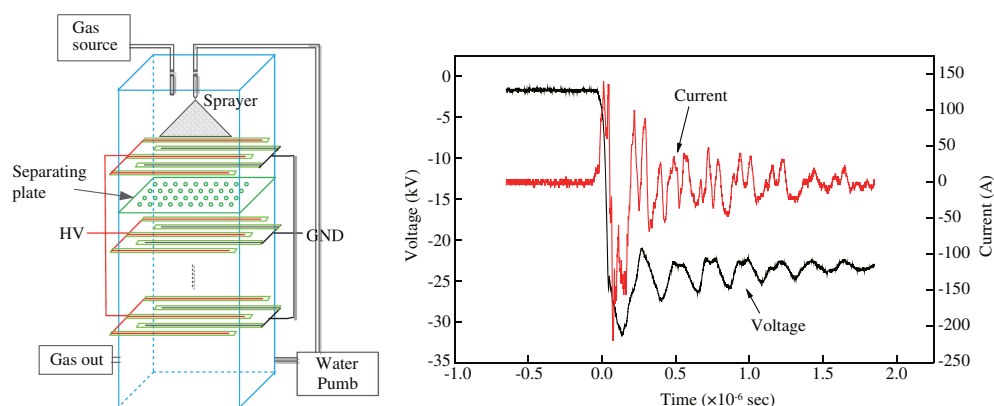
Fig. 5 – Diagram of the reactor and discharge waveform of voltage and current HV: high voltage; GND: ground.

1.5. Toxicity tests

The acute toxicity tests of *R. aconiti* wastewater samples after each treatment applied were conducted by *Photobacterium phosphoreum T₃* spp. (*P. phosphoreum T₃* spp.) bioassays, a type of bacterial bioluminescence assay. Bacterial bioluminescence assays based on measurement of the reduction of light output of luminescent bacteria (Fernández-Alba et al., 2001; Kelly et al., 2004) are typical methods of acute toxicity testing and are widely used (Farré and Barceló, 2003; Huang and Wang, 2007; Zhu et al., 2009, 2011; Liu et al., 2013). Fifty percent effective concentration (EC_{50}/LC_{50}) values are used to express the toxic effect. The toxicity of treated water samples was tested with the luminescent bacteria *P. phosphoreum T₃* spp. (supplied by Institute of Soil Science, Chinese Academy of Sciences, Nanjing, China), according to GB/T 15441-1995 (water quality-determination of the acute toxicity-luminescent bacteria test). The inhibition of bacteria bioluminescence was measured using a Toxicity Analyzer (Model DXY-2, Institute of Soil Science, Chinese Academy of Sciences, Nanjing, China). The toxicity of the wastewater was determined from the inhibition of bacterial bioluminescence by comparing the response given by bacteria in a saline control solution to those exposed to *R. aconiti* wastewater after non-thermal plasma treatments. In consideration that H_2O_2 was produced after the plasma treatment and the bacteria was sensitive to H_2O_2 (Zhang et al., 2012), Catalase from bovine liver (CAT, 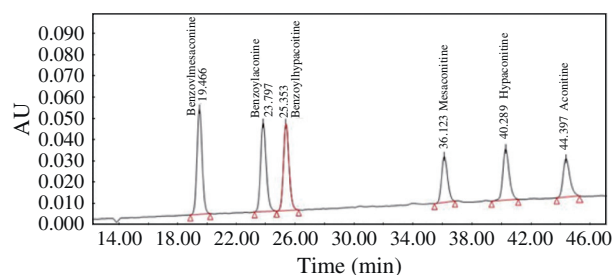Sigma C-9322, 2000–5000 u/mg protein) was added to control H_2O_2 The sensitivity of the freeze-dried bacteria was tested with 18.7 mg/L Cr(VI), and the inhibition ratio must be kept between 20%–80% after 15 min parallel tests. The concentrations of the test samples were set as 80%, 50%, 33.33%, 25.00%, 16.67%, 12.50%, 8.33% and 6.25%. The luminescence inhibition ratio LIR (%), the EC_{50} value and the GL value (according to Wasserhaushaltsgesetz) were calculated using the MicrotoxOmni Windows Software. The osmolality of all samples was adjusted to the osmolality of 3% NaCl using NaCl. The pH of the samples was adjusted to 7. The exposure time was 15 min and the temperature was maintained at 25 ± 1°C.

2. Results and discussion

2.1. Degradation of *R. aconiti* wastewater by non-thermal plasma

The degradation efficiency of the *R. aconiti* wastewater during the treatment of non-thermal plasma was expressed

Fig. 6 – Example spectrum showing the resolution of the *Aconitum* alkaloids involved in the experiment.
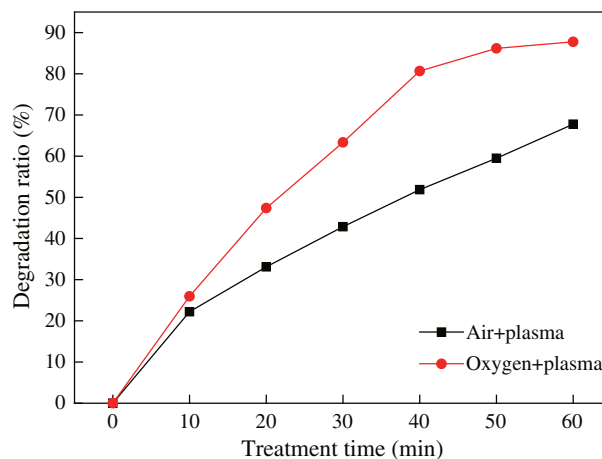

Fig. 7 – Degradation efficiency of the main *Aconitum* alkaloids (discharge voltage 29 kV; discharge frequency 300 Hz; initial pH = 5.6; gas flow 5 L/min; wastewater 500 mL).
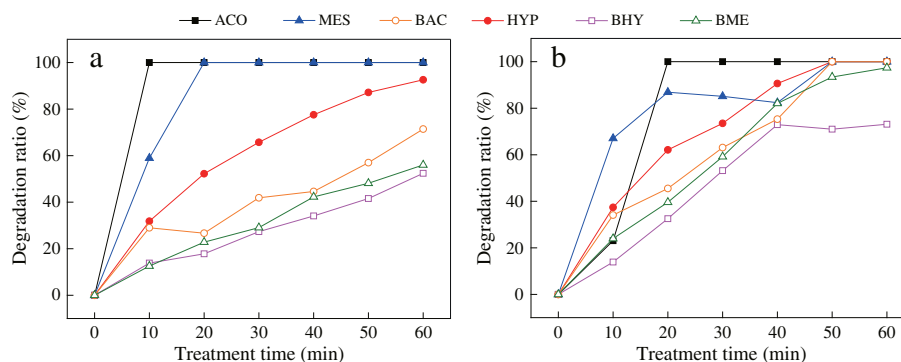
Fig. 8 – Degradation efficiency of each *Aconitum* alkaloid: (a) treated with air; (b) treated with oxygen. ACO: Aconitine, HYP: Hypaconitine, MES: Mesaconitine, BHY: Benzoylhypacoitine, BAC: Benzoylaconine, BME: Benzoylmesaconine.

as the degradation ratio. The degradation efficiency of the main *Aconitum* alkaloids (sum of ACO, HYP, MES, BHY, BAC and BME) during non-thermal plasma treatment is shown in Fig. 7. When using oxygen as a feed gas, the degradation efficiency was higher than when air was used as a feed gas. The average discharge power when using oxygen was 386.7 and 390.6 W when using air. The degradation ratio of the main *Aconitum* alkaloids was 87.77% after treatment for 60 min when oxygen was used as feed gas for the reactor, while it was 67.75% using air. The largest gap between the degradation ratios of oxygen plasma and air plasma appeared at 40 min, at 28.82%. The gap began at approximately 15% after 20 min treatment and it rose to over 20% at 30 min. Therefore, using oxygen as a feed gas during non-thermal plasma treatment significantly enhanced the efficiency of *Aconitum* alkaloid degradation.
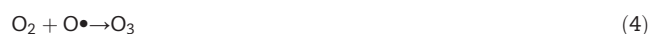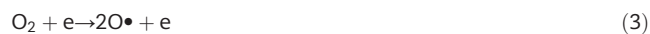
The degradation efficiency curves for the *Aconitum* alkaloids were different, as shown in Fig. 8. The degradation of ACO and MES was easy and their degradation ratios were much higher than other *Aconitum* alkaloids, both in oxygen and air after treatment for 20 min. In addition, compared with Benzoylaconines (BAC, BHY and BME), HYP was degraded faster as is clearly shown in Fig. 8a, since all of them exhibited high degradation efficiency when treated in oxygen as shown in Fig. 8b. The degradation ratios of Benzoylaconines were low in air discharge, and the degradation efficiency of the main *Aconitum* alkaloids was lower than for discharge in oxygen. After treatment for 60 min, the degradation ratios of ACO, HYP, MES, BHY, BAC and BME were 100%, 92.61%, 100%, 52.40%, 71.41% and 56% in air, respectively. The degradation ratios of ACO, HYP, MES, BHY, BAC and BME after treatment for 60 min were 100%, 100%, 100%, 73.12%, 100% and 97.39% in oxygen, respectively.

Hydroxyl radical was an important oxidant both in oxygen and air when *Aconitum* alkaloids were treated by non-thermal plasma. The generation of OH· in the presence of water during non-thermal plasma treatment mainly follows Reaction (2) (Sato et al., 2010):

$$H_2O + e \rightarrow OH\bullet + H\bullet + e. \tag{2}$$

When oxygen was introduced into the reactor, oxygen reacted with plasma and other radicals, then many highly reactive radicals like H., OH., O. and O_3 were generated by Reactions (3), (4) and (5) (Marotta et al., 2011):

$$O_2 + e \rightarrow 2O\bullet + e \tag{3}$$

$$O_2 + O\bullet \rightarrow O_3 \tag{4}$$

$$O\bullet + H_2O \rightarrow 2OH\bullet. \tag{5}$$

These indicated that the oxidizing ability was stronger than when only air was used, with more active species in the non-thermal plasma treatment when oxygen was introduced into the reactor. In addition, the double bond of O_2 is more easily broken than the triple bond of N_2, and it was reported that introducing nitrogen into the discharge system could decrease the degradation ratio for treatment by pulsed high-voltage discharge (Bian et al., 2013). There is only 21% of oxygen in air, while nitrogen makes up 78%. Therefore, the degradation ratio in air plasma was lower than in oxygen plasma. In the case of oxygen, more active species would then be produced (Gumuchian et al., 2014) and the oxidizing ability was stronger. According to Reactions (3) and (4), the increasing production of ozone when oxygen was introduced could also promote the degradation efficiency of pollutants.

The bond energy of O–H in CH_3OH was 464 kJ/mol, and the bond energy of O-$COCH_3$ in $H_3COCOCH_3$ was 406 kJ/mol. Benzoylaconines were more stable relative to aconitines (ACO, HYP and MES). The difference of their molecule structure was that H was the R_3 group in the structure of Benzoylaconines while it was acetyl in the structure of Aconitines as shown in Fig. 2, indicating that Aconitines were more easily degraded. Another evidence of the stability of Benzoylaconines was that Aconitines could be hydrolyzed to form Benzoylaconines at high temperature (160–170°C) (Singhuber et al., 2009). These were the probable reasons why the degradation efficiency of Aconitines was higher than the degradation efficiency of Benzoylaconines.

2.2. Effect of the discharge voltage

Discharge voltage had an important influence on the input energy and electric field strength in the plasma region. These factors could influence the degradation efficiency of *Aconitum*
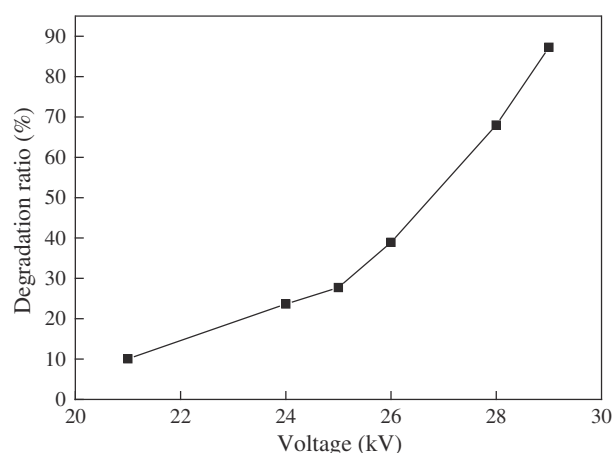
Fig. 9 – Effect of the discharge voltage (treatment time 60 min; initial pH = 5.7; oxygen 5 L/min).

Fig. 10 – Effect of initial pH value (oxygen 5 L/min).

alkaloids. In order to study the effect of the discharge voltage on the degradation efficiency of *Aconitum* alkaloids, the degradation of *Aconitum* alkaloids was studied with discharge voltages of 21, 24, 25, 26, 28 and 29 kV, respectively. The variation tendency of the degradation efficiency is shown in Fig. 9. The degradation efficiency grew when discharge voltage increased. However, the degradation ratio was only 10.06% when the discharge voltage was 21 kV, while it was 87.26% when the discharge voltage was 29 kV. The promotion of degradation was significant with increasing discharge voltage. The effect of discharge voltage was divided into 2 stages for this reactor according to the degradation efficiency of the *Aconitum* alkaloids: the low voltage stage (21 to 25 kV) and the high voltage stage (25 to 29 kV), as shown in Fig. 9. In the low voltage stage displacement current was dominant, the discharge current of plasma was low, the energy of the electrons was small, the generation efficiency of the reactive radicals in the reactor was low and the degradation efficiency of the *Aconitum* alkaloids was below 30%. But when the high voltage stage was reached, the discharge voltage value was higher than the breakdown voltage and the discharge current of plasma was high, so that the energy of the electrons was large, too. Thus the generation efficiency of reactive radicals in the reactor was high. As a result, the degradation efficiency in this stage was higher.

2.3. Effect of initial pH value

In this experiment, *R. aconiti* wastewater with initial pH values of 3.0, 5.57 and 8.0 was treated using non-thermal plasma, respectively. A 10 mL sample was taken every 10 min from the solution to determine the *Aconitum* alkaloid concentrations. The effect of initial pH value on the degradation ratio of *Aconitum* alkaloids is shown in Fig. 10. The maximum degradation ratio of 99.59% was obtained when the initial pH value was 8.0 after 60 min treatment. When the initial pH values were 3.0 and 5.57, the degradation ratios after 60 min treatment were 74.08% and 87.77%, respectively. Therefore, the degradation ratios of *Aconitum* alkaloids varied with
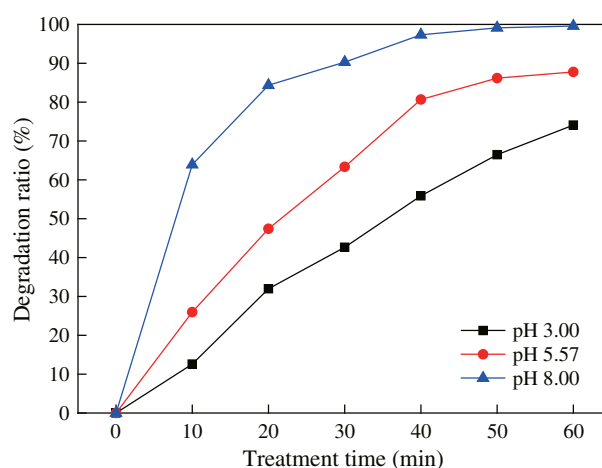
different initial pH values for equal degradation times. The degradation ratios showed a decreasing trend as the solution initial pH decreased from 8.0 to 3.0. This trend was opposite to the results of other studies of difficult-to-degrade pollutant decomposition, which showed that the degradation ratios increased from high pH to low pH (Zhang et al., 2012). It was also different from the results of Huang et al., whose results showed that the degradation ratios exhibited a decreasing trend in acidic, alkaline, and neutral solutions (Huang et al., 2010).

Two possible reasons for these phenomena are proposed. First, as discussed in Section 2.1, Aconitines could be hydrolyzed to form Benzoylaconines at high temperature. This hydrolysis was also promoted when the pH increased, and it was observed by Yue et al. (2008) that the concentrations of Aconitines were markedly decreased and the concentration of Benzoylaconines became much higher as pH increased. This indicated that this hydrolysis could be classified as alkaline hydrolysis (Singhuber et al., 2009; Ohta et al., 1997; Yue et al., 2008). Thus the stability of Aconitines was weak in alkaline solution and they were more easily degraded. The second possible reason was related to ozone. Ozone was generated by plasma when oxygen was present in the reactor. In addition to the direct reaction of *Aconitum* alkaloids and ozone, when the reaction took place in alkaline solution the OH⁻ species could enhance the decomposition of O_3 and produce hydroxyl radical. The oxidizing ability of the hydroxyl radical is much higher than that of ozone. As a result, more *Aconitum* alkaloids were degraded because of the increase in hydroxyl radical. These two pathways both contribute to the degradation of *Aconitum* alkaloids. Thus the degradation ratios of *Aconitum* alkaloids rise in alkaline solution. Though some of the hydroxyl radicals probably would combine with OH⁻ to form water and decrease the concentration of hydroxyl radical at high levels of hydroxyl radical, the influence is very small.

2.4. Energy efficiency

The energy efficiency was expressed using the energy yield of the degradation, which was defined as the amount of

Aconitum alkaloids decomposed per unit of energy consumed in the process and calculated following Eqs. (6) and (7).

$$Y = \frac{(C_0 - C_t) \cdot V}{Pt} \qquad (6)$$

$$P = f \int_0^{t1} V_t I_t dt \qquad (7)$$

where, Y (g/kWh) is the energy yield of the degradation, P (kW) is the average power input in the discharge, t (hr) is the treatment time, V (L) is the solution volume and C_0 (g/L) and C_t (g/L) are the initial concentration and the concentration of time t, respectively; f (Hz) is the discharge frequency, $t1$ (sec) is the effective time in one discharge process (the time when $V_t \neq 0$ in one voltage pulse. When $V_t = 0$ the integral to the voltage is 0, so it has no contribution to power. In one voltage pulse, $V_t \neq 0$ from $t = 0$ to $t = t1$; $V_t = 0$ from $t = t1$ until another voltage pulse begins), V_t (kV) and I_t(A) are the discharge voltage and the discharge current in time t, respectively. The oscillograms of the discharge voltage and the discharge current are shown in Fig. 5.

The energy efficiency is shown in Fig. 11. The energy efficiency decreased when the treatment time was increased no matter whether air plasma or oxygen plasma was used. The decrease in the energy efficiency was probably due to competition between the degradation of the reactant and the decomposition of the intermediate products (Magureanu et al., 2010). However, the energy efficiency was higher in oxygen plasma than air plasma. The highest energy efficiency using oxygen was 50.79 mg/kWh when treated for 10 min, while it was 42.8 mg/kWh using air for equal treatment time. After treatment for 60 min the energy efficiency using oxygen was 28.61 mg/kWh and the energy efficiency using air was 21.75 mg/kWh.

The structure of the target compound had an influence on the energy efficiency of non-thermal plasma treatments. Magureanu et al. (2008) obtained high energy yields (5 g/kWh) for the degradation of methylene blue, while Krause et al. (2009) reported low energy yields (17×10^{-3} g/kWh) for the degradation of clofibric acid, with both groups using corona discharges. Besides, not all of the energy was used in degrading *Aconitum* alkaloids. *Aconitum* alkaloids were not the only organic compounds in the *R.*

aconiti effluent. So part of the energy was used in degrading other organic compounds (such as other alkaloids, saccharides and protein) in the *R. aconiti* effluent. Some of the energy was converted to thermal energy due to the resistance of the electrode and quartz tube walls.

2.5. Variation of pH and conductivity during the treatment

The variation of pH and conductivity during the treatment is shown in Fig. 12. In the first 10 min the solution pH values increased for treatment in both air and oxygen, while the conductivities dropped. After 10 min the solution pH values dropped for treatment in air and oxygen, and the conductivities increased. The pH values of solutions treated in oxygen were lower than for those treated in air, but the difference in the conductivities of solutions between air and oxygen treatments was small. The variation of pH values differed from that of Tichonovas et al. (2013) who also used tap water; because of the variation in the first 10 min, the current results differed from those in most of the studies (Benetoli et al., 2012; Zhang et al., 2012; Dojčinović et al., 2011). However, He et al. (2009) obtained similar results when treating Rhodamine B using a photocatalytic method. The increase of pH values in first the 10 min took place because the solution of *R. aconiti* was acidic. When the parent *Aconitum* alkaloids and other organic compounds that were acidic were decomposed, the pH values rose. Then, some organic acids and even nitric acid (products from the decomposition of nitro-organic compounds) were produced after further degradation. Therefore, pH values dropped after 10 min treatment.

The NO_3^- concentration of solutions after 60 min treatment in oxygen and air (discharge frequency 200 Hz) was 82.44 and 25.74 mg/L, respectively. The pH values of tap water before and after the plasma treatment changed little in oxygen plasma, while they decreased by about 0.5 pH units in air plasma. So the generation of organic acids and nitric acid (products from the decomposition of nitro-organic compounds) was the reason that pH values changed in oxygen plasma; the generation of organic acids and nitric acid (products from nitrogen discharge and the decomposition of
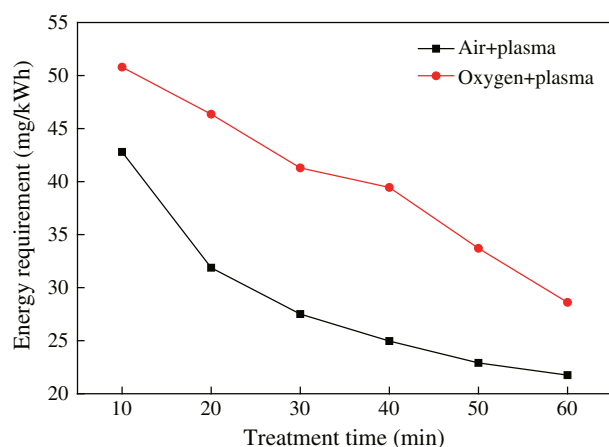
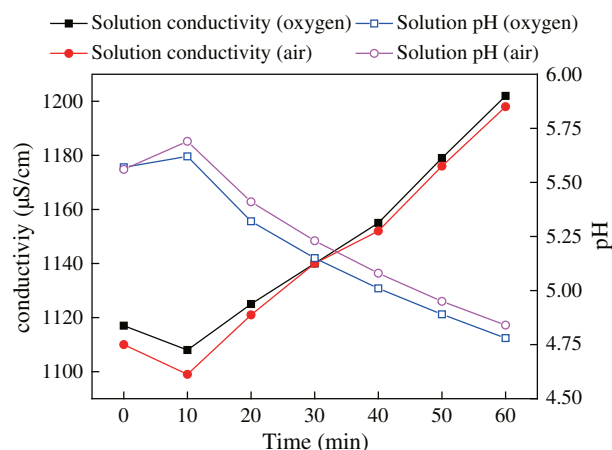**Fig. 11 – Energy efficiency for different treatment times.**

Fig. 12 – The variation of pH and conductivity during the treatment.

nitro-organic compounds) was the reason that pH values changed in air plasma. The variation of conductivity followed the changes in the concentrations of ions. The degradation by-products during the treatment led to variation in the ion concentrations.

2.6. Toxicity bioassay

The toxicity of the *R. aconiti* effluent before and after non-thermal plasma treatment was evaluated by using luminescent bacterium assays and expressed as LIR and GL values. Before the acute toxicity test, 500 mL *R. aconiti* effluent was treated with air or oxygen for 1.5 hr at the conditions of initial pH value 8.0 and discharge voltage 29 kV. After treatment, the treated water was saved for two samples: one with CAT added and the other not. The acute toxicity test results are shown in Fig. 13. The EC50 of the *R. aconiti* effluent before treatment was 49.4% (95% confidence range: 39.65 to 61.55) and the GL value was 6. Without adding CAT, the EC50 of the sample treated with air was 137.4% (EC50 value was greater than 100%; 95% confidence range: 36.79 to 513.3) and the GL value was 3; the EC50 of sample treated with oxygen was 57.17% (95% confidence range: 47.35 to 69.02) and the GL value was 4. It showed great toxicity both before and after plasma treatment. The toxicity removal after plasma treatment was unsatisfactory, especially the toxicity of the sample treated with oxygen, which was very near that of the untreated *R. aconiti* effluent. However, the toxicity became very low when CAT was added to the samples treated with air or oxygen. Their LIR values were almost near 0 and below 0; in particular, the one treated with oxygen was below 0, much lower than that of the *R. aconiti* effluent; their GL values were 2 and 1, respectively.

Without the effect of H_2O_2, the results of acute toxicity testing showed a large removal of toxicity. It indicated that the degradation products of the targeted toxic substances such as ACO, HYP, MES, BHY, BAC and BME in the *R. aconiti* effluent were validated to be non-toxic to *P. phosphoreum T3* spp. Therefore, it was safe for bioprocessing after being treated by non-thermal plasma. On the other hand, in our previous work (Jiang et al., 2014), it was proved that discharge with oxygen promoted the yield of H_2O_2 better than discharge with air. That was the main reason for the high toxicity of the sample treated with oxygen but without CAT.

3. Conclusions

Non-thermal plasma treatment was an effective treatment for the *R. aconiti* wastewater generated by TCM. Using oxygen, a high discharge voltage and alkaline solution improved the degradation efficiency of the wastewater. The degradation of Aconitines was easier than that of Benzoylaconines. The energy efficiency of *Aconitum* alkaloids using oxygen or air as a feed gas was different, at 28.61 and 21.75 mg/kWh on average for 60 min treatment, respectively. The energy efficiency still needs to be increased, although the complexity of the wastewater composition should be taken into consideration. The variation of pH and conductivity were possibly due to the production of by-products during the treatment. The degradation of *Aconitum* alkaloids without the effects of impurities and degradation by-products still needs to be investigated in future work. It was confirmed by the toxicity bioassay that after non-thermal plasma treatment, the *R. aconiti* wastewater becomes non-toxic and can be further treated using biological treatments.
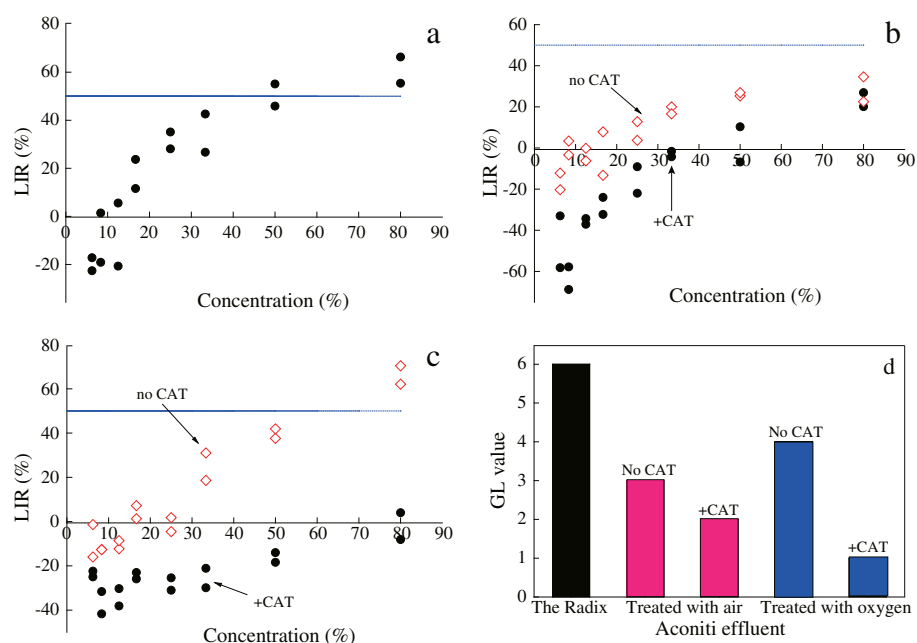

Fig. 13 – The acute toxicity test results for the wastewater samples before and after treatment. (a) The acute toxicity test results for the *Radix aconiti* effluent; (b) the acute toxicity test results for the *Radix aconiti* effluent after treatment with air, (c) the acute toxicity test results of the *Radix aconiti* effluent after treatment with oxygen, (d) the dilution factor value of each sample.

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