Plasma induced degradation of Indigo Carmine by bipolar pulsed dielectric barrier discharge(DBD) in the water-air mixture

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Abstract: Degradation of the Indigo Carmine (IC) by the bipolar pulsed DBD in water-air mixture was studied. Effects of various parameters such as gas flow rate, solution conductivity, pulse repetitive rate and ect., on color removal efficiency of dying wastewater were investigated. Concentrations of gas phase O_3 and aqueous phase H_2O_2 under various conditions were measured. Experimental results showed that air bubbling facilitates the breakdown of water and promotes generation of chemically active species. Color removal efficiency of IC solution can be greatly improved by the air aeration under various solution conductivities. Decolorization efficiency increases with the increase of the gas flow rate, and decreases with the increase of the initial solution conductivity. A higher pulse repetitive rate and a larger pulse capacitor C_p are favorable for the decolorization process. Ozone and hydrogen peroxide formed decreases with the increase of initial solution conductivity. In addition, preliminary analysis of the decolorization mechanisms is given.

Keywords: water treatment; water-air mixture; DBD; Indigo Carmine

Introduction

Non-thermal pollution technique is one of the advanced oxidation technologies (AOPs) and it has been extensively studied for gas cleaning(Oda, 2002; Chang, 2003; Wu, 2003). Electrical discharges for water purification have only recently received interests. Discharge in water must be different from that in air due to the different physical characteristics of water and air. Breakdown voltage of water is reported to be on the order of ~ MV(Sunka, 2001).

Electrical discharges in water have been demonstrated to generate plasma that initiates a variety of physical and chemical effects such as high electric field, intense UV radiation, over pressure shock waves, aqueous electrons, and in particular, chemically active species (OH·, H·, O·, H_2O_2, etc.)(Clements, 1987; Sun, 1999; Sunka, 2001) that can act on the biological cells and chemical compounds dissolved in water. Pulse electrical discharges in water have been studied to remove several organic species such as phenol (Sun, 1999; Sharma, 1993), acetophenone(Wen, 1999) and dyes (Gao, 2003; Sugiarto, 2003) from wastewater streams.

Several methods have been developed to improve the plasma generated and enhance the removal efficiency of the plasma technology, which include (1) modification of the electrode configurations(use point to plane electrode configuration to obtain a high partial electrical strength); (2) changing of the physical characteristics of solutions(bubbling gas into the water to decrease the breakdown voltage); (3) changing of the power supply from DC to pulsed power (to minimize power wasted on ionic migration). But many underlying drawbacks such as the quick erosion of the point electrode, the limited volume of treated water and the requirement of a shunt resistor when using a barrier type electrode(Hoeben, 2000) ect., still limit their industrial usage. Most of the researches are carried out on the laboratory study scales.

In our previous studies, bipolar pulsed discharges in the

air/oxygen have been proved to efficiently enhance the O_3 production (Liu, 2002). Direct discharge of the bipolar pulsed power in water (or water-air mixture) has not seen much report. In order to get a higher instant electric field and strong ionization and production of more active species, combinations of the bipolar pulsed power and DBD electrode configuration reactor were accomplished in our studies. Compared with the unipolar pulse power(Zhang, 2002), this system showed a higher performance on the dying water decolorization.

This paper aims to study degradation of Indigo Carmine induced by the dielectric barrier discharge plasma initiated by the bipolar pulsed power in water-air mixture, and try to clarify the color removal mechanisms during the discharge.

1 Experimental

1.1 Experimental setup

The schematic diagram of the experimental setup is shown in Fig.1. The reactor is a highly transparent polished plexiglas cylinder ($\Phi_{in} \times L = 80$ mm $\times$ 1000 mm), with grounded reticulate stainless steel electrode tightly attached to its inner side. A stainless steel high voltage electrode, having dimensions of 60 mm outside diameter and 800 mm in length, is concentrically placed in the Plexiglas reactor. An insulator glass fully covers the whole surface of the stainless steel electrode to protect it from erosion, and to enhance the inner electric field between the two electrodes. Air aerator which can give bubbles of micron size is fixed at the bottom of the reactor and the distance between the aerator and the bottom end of the high voltage electrode is 3 cm.

Water flows into the electrode space through the water inlet. Air is aerated into the reactor through the aerator and dispersed into the water, forming a well-mixed micro-bubble-liquid mixture. Treated water and gas are discharged through the water outlet and gas outlet, respectively.

A 60 mm and 50 mm diameter iron electrode was used respectively to regulate the gap distance. The corresponding gap distance was 5 mm and 10 mm.
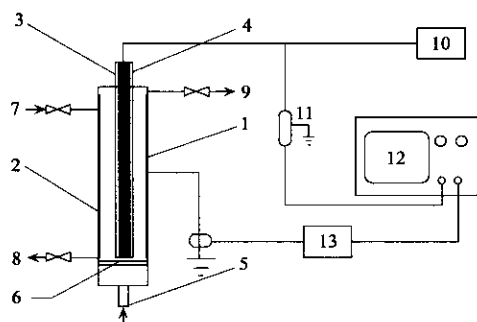
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Fig.1   Diagram of the experimental system
1. reactor body; 2. grounded reticulate electrode; 3. glass insulator; 4. high voltage electrode; 5. gas inlet; 6. aerator; 7. water inlet; 8. water outlet; 9. gas outlet; 10. bipolar pulsed power; 11. high voltage probe; 12. HP 54820A oscillograph; 13. current probe and amplifier

A bipolar pulsed power supply was used to provide pulsed energization of the high voltage discharge electrode with peak-to-peak voltage(Vpp) in the range of 0—40 kV, pulse width of 500—1000 ns, pulse rise time of 40—100 ns, and pulse repetition frequency of 1—200 Hz. All the experiments were typically conducted at an applied voltage of 15 kV for a 5 mm gap distance and 29 kV for a 10 mm gap distance, respectively.

The applied voltage and discharge current were measured by HV-P60 pulse high voltage probe (IWATSU Electric Co. Ltd.), TM6303 pulse current probe(Tektronix Co. Ltd.), and a digital oscillograph(HP 54820A).

1.2   Materials and methods

Analytical grade potassium chloride and Indigo Carmine (IC) were used. Potassium chloride and Indigo Carmine solutions were prepared using deionized water. Concentration of the standard IC solution is 118.04 mg/L, with an absorbance of 2.533 and initial solution conductivity of 280 μs/cm. Deionized water were used to dilute the standard IC solution to different absorbance in the experiments and KCl was added to give different conductivities.

ORION 828 pH meter and HANNA EC215 conductivity meter were used for the analysis of the solution pH and conductivity. Measurement of absorbance of IC solution was performed on a Unico 2102C UV-Vis spectrometer at 608.2 nm, with deionized water used as blank. Color removal efficiency of IC solution for each sample is expressed as:

$$\eta = \frac{A_0 - A_t}{A_t} \times 100\% \ ,$$

where η is the color removal efficiency; A_0 is the initial absorbance of IC solution; A_t is the absorbance of IC solution after t treatment time.

Initial experiments were conducted in potassium chloride solutions with different initial conductivities to determine concentrations of the aqueous phase H_2O_2 and gas phase ozone. IC solution was also used to examine the dying wastewater treatment performance of the reactor.

Ozone concentrations in the effluent gases were determined by the standard potassium iodide titration method, and aqueous phase H_2O_2 concentration was measured by the method of Joshi(Joshi, 1995).

Typically, 10 ml samples were taken from the reactor vessel at 1 min intervals during each run. Temperature, pH,

conductivity and absorbance of the solution were measured before and immediately after each experiment. Three trials were made for each experimental condition and resulted in errors of less than 5%.

2   Results and discussion

2.1   Electrical discharge characteristics

Intense electrical discharge occurred in the water-air mixture at an applied voltage of 15 kV. Light was emitted out from the up-rising bubbles accompanied with sizzles. Waveforms of the applied voltage and the discharge current are shown in Fig.2.
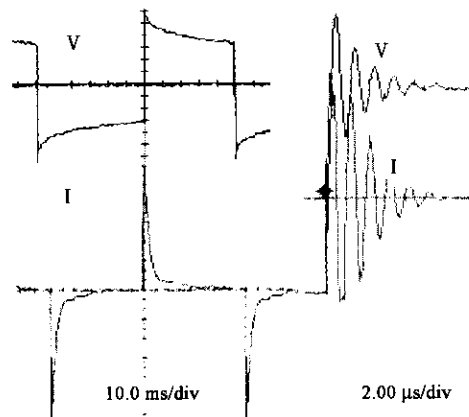

Fig.2   Typical waveforms of voltage and discharge current
Vpp = 15 kV; f = 50 Hz; φ = 0.75 m³/h; C_p = 10 nF; IC solution; V: voltage; I: discharge current

2.2   Measurement of the effluent gas phase O_3 and aqueous H_2O_2 concentration

Ozone and hydroxyl peroxide was formed during the electrical discharge process in water-air mixture. Ozone is a powerful oxidant and can react with varieties of organic substances dissolved in water. As shown in Fig.3, O_3 and H_2O_2 concentrations decreased with the increase of initial solution conductivity. And for a given voltage, a smaller gap distance is favorable for O_3 and H_2O_2 generation.

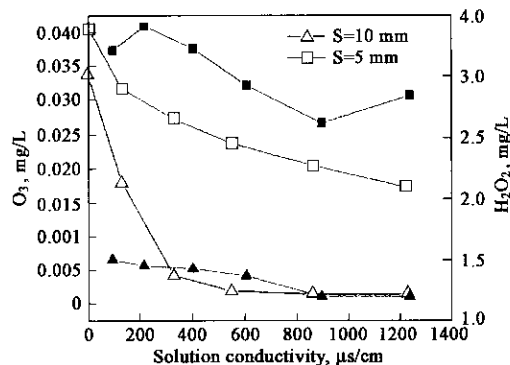Fig.3   Effect of solution conductivity on O_3 and H_2O_2 concentration
Vpp = 15 kV; f = 50 Hz; φ = 0.75 m³/h; C_p = 10 nF; KCl solution; O_3: open; H_2O_2: solid

Under the same experimental conditions, concentrations of ozone and hydroxyl peroxide produced in IC solutions are much lower than those of the pure KCl solutions having the same initial conductivity, which indicated that, on one hand,

the presence of the impurities in water substantially reduced the O_3 and H_2O_2 concentrations, and on the other hand, removal of the solution colorness indicated that pollutant substances got oxidized during this process. V. L Goryachev found similar results when he studied the H_2O_2 formation in the distilled water and tap water using point-plane electrode (Goryachev, 1998).

2.3   Effect of the air bubble

Relationships between color removal efficiency and the treatment time are shown in Fig.4(Vpp = 15 kV). As can be seen, when there is no gas bubbling, no decolorization effect of IC solution was obtained. No obvious discharge occurred under this experimental condition. Electrolysis became the dominant electrode reaction process. Whereas under the condition with only gas bubbling but without the electrical discharge plasma, a slight decolorization of no more than 8% was achieved even after 30 minutes treatment time.

For the given voltage(15 kV), as the introduction of the gas bubbles into the reactor, color removal efficiency is significantly increased. For example, when Vpp = 15 kV, $\varphi_{air} = 0$, color removal efficiency is 0 after 10 min treatment time. Increase the gas flow rate to $\varphi = 0.25$ m³/h, color removal efficiency quickly increases to 39.06% after 6 min treatment time. Decolorization efficiency is 2.35 times of that of the $\varphi = 0.25$ m³/h for $\varphi = 0.5$ m³/h. And when the gas flow rate is increased further ($\varphi = 0.75$ m³/h), the time needed to gain the same color removal efficiency is reduced by almost 50%, reaching 3.5 min.
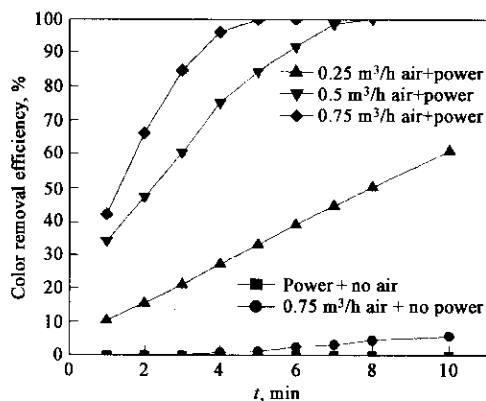

Fig.4   Effect of the gas flow rate on color removal efficiency
Vpp = 15 kV; $f = 50$ Hz; $\sigma = 480$ μs/m; $S = 5$ mm; $\varphi = 0.75$ m³/h; $C_p =$ 10 nF; Abs0 = 1.039

In addition, discharge current(Fig. 5) increases with the increase of the air flow rate, indicating that electrical discharges in the water-air mixture become more intense. The quantities of the active species produced also increase significantly, leading to the quicker increase of the color removal efficiency.

The above-mentioned results proved that the presence of air bubbles in water leads to the decrease of the breakdown voltage of the solution. As known, pure water is a good dielectric insulator with a high permittivity, discharge in water requires a high electric strength on the order of $\sim$ MV/cm(Sunka, 2001). When water is polluted or there are dissolved gases, breakdown voltage would decrease greatly and electrical discharges often initiate in the bubbles or the
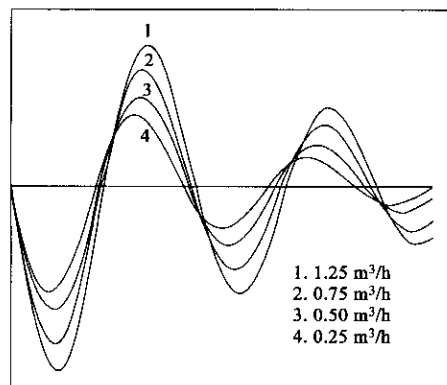

Fig.5   Current waveforms under different air flow rates
Vpp = 15 kV; $f = 50$ Hz; $C_p = 10$ nF; $S = 5$ mm; $\varphi = 0.75$ m³/h; IC solution; $\sigma = 480$ μs/m; Abs0 = 1.039

particles suspended in water. In addition, breakdown can also initiate by artificially created bubbles in water (Goryachev, 1997). Breakdown voltage of the water-air composite depends on the gaseous breakdown voltage(Arii, 1991). At a higher air flow rate, there would be more bubbles present in water and the discharges thus become more intense. Non-thermal plasma spatially distributes in the whole volume between the electrodes. Active species contained in the plasma react with IC in the bubble-water boundary and induced a series of chemical reactions such as dehydrogenation, addition, bond cleavage, and so on. Large molecule IC was degraded to smaller organics such as organic acid, aldehyde and so on, and then got completely mineralization.

2.4   Effect of the initial solution conductivity

Fig. 6 shows the color removal efficiency of the IC solution at different initial solution conductivities. After 4 min treatment time, Abs of the 230 μs/cm IC solution decreases from 1.039% to 0.01%, 99.01% of the color is removed. Color removal efficiencies decrease to 96.08%, 82.77% and 68.62% for 480 μs/cm, 860 μs/cm and 1160 μs/cm conductivity solutions, respectively. At even higher initial conductivity(1700 μs/cm), only 46.12% of the initial colorness can be removed in the same treatment time.
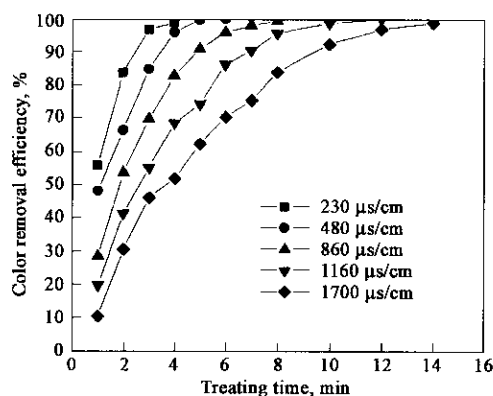

Fig.6   Effect of initial solution conductivity on color removal efficiency
Vpp = 15 kV; $f = 50$ Hz; $C_p = 10$ nF; $S = 5$ mm; $\varphi = 0.75$ m³/h; IC solution; $\sigma = 480$ μs/m; Abs0 = 1.039

Consider a bubble of permittivity ε_2 immersed in a homogeneous and uncharged medium of permittivity ε_1 and

subjected to a uniform electric field E_0, the electrical field intensity inside the bubble can be expressed by $E = 3E_0\varepsilon_1/(2\varepsilon_1 + \varepsilon_2)$. For a given ε_2, E is determined by both E_0 and ε_1. As the conductivity of the solution increases, ε_1 decreases, leading to a decrease of E and thus the number of the discharge bubbles decreases.

In addition, in KCl solution, KCl dissociates into ions of K^+ and Cl^-. As the conductivity increases, concentration of ions increases. The quantities of ions present in the solution can strongly alter the propagation of the streamer by quickly compensating the space charge electric field on the streamer head of the plasma channel and that lead to the decrease in the generation of chemically active species. This can be seen from O_3 and H_2O_2 concentration curves respectively(Fig.3).

2.5   Effect of the pulse repetitive rate

Color removal efficiency of IC solution increases with the pulse repetitive rate, as is shown in Fig.7. At higher pulse repetitive rate, much more energy is injected into water per unit time and a higher energy density per unit volume of water-air mixture obtained. Under the same experimental conditions(Vpp, initial solution characteristics and gas flow rate), the number of micro-discharges during every unit of time increases, broken down bubbles and the quantities of chemically active species would greatly increase, which finally leads to the increase in the collision and even reacting probabilities of the generated species with the pollutants. The absolute quantities of reacting active species increase and higher color removal efficiency is obtained.

2.6   Effect of capacitance of the pulse capacitor(C_p)

Fig.8 shows the effect of the capacitance of the pulse capacitor on color removal efficiency. Color removal efficiency is 64.76% for $C_p = 6$ nF after 3 min treatment time, when capacitance of C_p increases to 8 nF, color removal efficiency would greatly increase to 80.13%. At an even higher $C_p = 10$ nF, almost all the initial color ness (93.18%) is removed.
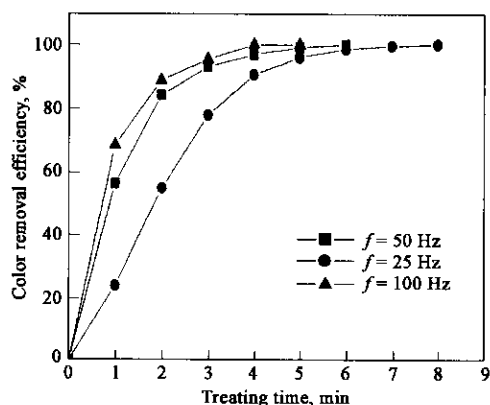

Fig.7   Influence of pulse repetitive rate on decolorization
Vpp = 18 kV; f = 50 Hz; C_p = 10 nF; S = 5 mm; φ = 0.75 m³/h; IC solution; σ = 230 μs/m; Abs0 = 1.543

For the electrical circuit used in the investigation, C_p discharges through the rotary spark switch to the reactor. During this process, the reactor gets energy and produces discharge plasma. Since energy is proportionally distributed
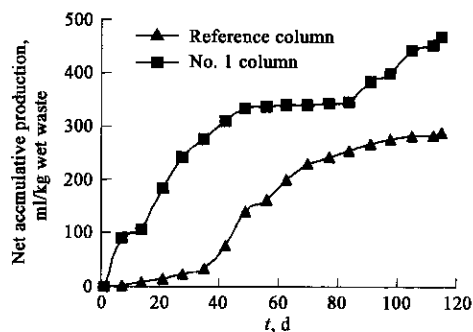

Fig.8   Effect of C_p on color removal efficiency
Vpp = 18 kV; f = 50 Hz; C_p = 10 nF; S = 5 mm; φ = 0.75 m³/h; IC solution; σ = 230 μs/m; Abs0 = 1.543

between C_p and the static capacitance of reactor, C_r, the larger C_p is, the more energy would be injected to the reactor. Quantities of active species generated during each discharge would be greatly increased and higher color removal efficiency would be achieved.

However, matching of a high-voltage pulse generator to a corona plasma reactor (here we mean the relationship between C_p and C_r) is much more important for that optimizing the energy transfer to the reactor increases the initial radical production, and improving the energy conversion efficiency reduces both investment and operational costs. Relevant work was reported in our previous work (Zhang, 2003).

3   Preliminary analysis of the IC decolorization

Indigo Carmine(Indigo-5, 5'-disulphonic acid, Fig.9) is one of the Indigoid dyes. The basic color-producing structure is a cross-conjugated system or H-chromophore, consisting of a single C = C double bond substituted by two NH donor groups and two C = O acceptor groups.
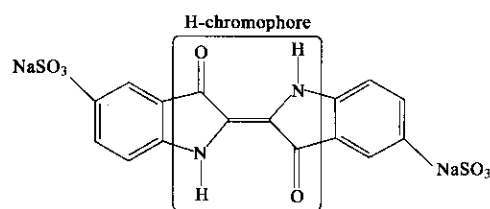

Fig.9   Molecular formular of IC

The central C = C double bond in the IC molecular has been found very reactive. Presence of the sulfonate electro-attractor groups in the IC molecular weakens the electronic density of the aromatic rings, which favors the electrophilically attack of the nitrogen atoms in the dye molecule. Any reaction that leads to the destruction of the chromophore in the IC molecular can result in decolorization.

Several processes may account for the color removal process in this reactor, including (1) high electric field; (2) electrolysis; (3) gas bubbling; (4) active species (OH·, H_2O_2, O_3 etc.) contained in the non-thermal plasma.

In our experiments, for the condition that with only applied voltage but with no air bubbling, no discharge occurs, electrostatic field and electrolysis became the

dominant electrode reaction process. This demonstrates that processes induced by the electrostatic field (1) and electrolysis (2) are negligible.

For the case with both gas bubbling(0.75 m^3/h) and the discharge plasma, 99.9% of the initial colorness is reduced only within 5 min treatment time, whereas under the conditions that with only gas bubbling, even after 30 min treatment time, color removal efficiency is still no more than 8%, which reveals that decolorization process due to the gas bubbling (3) can also be neglected for a 6 min treatment time.

As the gas flow rate increase, discharge current and color removal efficiency of the reactor simultaneously increase significantly, proving that chemical reactions induced by the discharge plasma in air bubbles are the main mechanism of color removal. P. Sunka has proved the formation of OH· during the electrical discharge process in water using spectral analysis method(Sunka, 2001). Sun *et al*. detected H_2O_2 during the discharge in deionized water(Sun, 1997). But it is still hard to directly measure " *in situ* " the quantities of OH· produced. Further work concerning this subject is under investigation by our research group and will be reported in the near future.

For a given experimental condition, electrical discharges in the KCl solutions produced more O_3 and H_2O_2 than those in the (IC + KCl) solution with the same initial conductivities. Thus we can deduce that ozone and hydroxyl peroxide or their precursors play important roles in the color removal process.

Hydroxyl radicals and other active species in the discharge plasma attack the central C = C double bond or the aromatic ring by addition or the abstraction of sulfonic substituent, leading to the destruction of the C = C bonds and cleavage of aromatic ring. Blue Indigo Carmine then became colorless. Preliminary analysis of the degradation by HPLC showed there is nitrobenzene produced.

However hydroxyl radicals can not only be formed during the discharge process, but by the UV-catalyzed decomposition of hydrogen peroxide and ozone. And reversely, at high concentrations, hydroxyl radicals in the aqueous phase can combine into hydrogen peroxide through the reaction OH· + OH· → H_2O_2. Due to the special and complex relationship among OH·, H_2O_2, O_3 in aqueous solutions, it is still hard to tell the exact degree that each of them weighs during the color removal process. Relevant work needs to be done in the near future.

4 Conclusions

It has been shown in the present study that dielectric barrier discharge initiated by bipolar pulsed power in water-air mixture is an effective way of generation of highly active species. Effects of parameters such as the gas bubbling, pulse repetitive rate, gas flow rate, and C_p, pulse repetitive rate on the performance of the bipolar pulsed DBD water treatment reactor have been investigated. The roles that

physical and chemical processes accompanying the electrical discharge play on the color removal are determined. Preliminary analysis of the decolorization mechanisms is given.

This study not only provides a promising alternative for the degradation of the non-biodegradable pollutants in water, but promotes clarification of the mechanisms of the chemically active species generation, which in turn will help to perfect the operation and device the next generation water treatment reactor.

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