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Visualization of coupled mass transfer and reaction in a gas–liquid dielectric barrier discharge reactor

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HIGHLIGHTS

- Visualized gas–liquid mass transfer and reaction in a plasma reactor by reactive-PLIF.
- Evaluated the effects of discharge voltage and atmosphere on water decoloration.
- Revealed the convective transportation of reactive species in the liquid induced by plasma.
- Determined the role of reactive species, e.g., O_3, H_2O_2, $^{\cdot}OH$, etc. in gas–liquid plasma.

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ABSTRACT

A novel approach, i.e., the reactive planar laser induced fluorescence (reactive-PLIF) technique, is employed to visualize the coupled mass transfer and reaction in a gas–liquid dielectric barrier discharge (DBD) reactor, by quantitatively recording the dynamic change of concentration field of fluorescence dye (e.g., Rhodamine B) in the liquid layer during its decoloration process. Firstly, the decoloration dynamics are revealed under the conditions of different discharge voltages in oxygen atmosphere. Increasing the discharge voltage can give rise to the increase of the density of DBD plasma filaments impacting on the surface of the liquid layer. Thus, more reactive species (O_3, H_2O_2, $^{\cdot}OH$ and other radicals detected by optical emission spectroscopy) are generated, together with the intensification of the convective transport in the liquid layer confirmed by Particle Image Velocimetry (PIV) measurement. Consequently, it can be demonstrated that the simultaneous intensification of the coupled mass transfer and reaction is the reason for the significant enhancement of the decoloration efficiency when increasing the discharge voltage. Secondly, the decoloration dynamics in the discharge atmosphere of inert gas (i.e., argon) are revealed in comparison with the oxygen discharge at the same discharge voltage. It is found that O_3 plays a more important role in the reactive species for Rhodamine B degradation. This study provides straightforward analysis on the mechanism of the interaction between discharge plasma and polluted water, which will be beneficial to develop highly efficient cold plasma techniques for advanced oxidation processes (AOPs).

1. Introduction

Over the last few decades, more and more attention has been paid to the protection of the water environment. Wastewater from dye houses represents one of the most problematic groups of polluted water. It is strongly colored with the complicated color-causing compounds that can have severe impacts on the aquatic environment. This has attracted the critical attention of public and local authorities. Various conventional methods including biological, physical, chemical, and combination treatments have been used to treat the dyed wastewater, but none of these methods are satisfied to handle the highly toxic and refractory organic dyes with complex molecular structure. Meanwhile, the conventional methods all end up with a secondary waste product which needs to be further dealt with [1–4]. Fortunately, limitations of these conventional decoloration techniques can be overcome by the so-called advanced oxidation processes (AOPs) thanks to the *in situ* generation of strong oxidizing agents ($^{\cdot}OH$, O_3, H_2O_2, $^{\cdot}O$, etc.) for the destruction of refractory and hazardous pollutants until mineralization. For example, AOPs include ozonation, photochemical and photocatalytic degradation and high energy radiation, etc. [5–7].

Recently, we started to pay considerable attention to the decoloration of the organic dyes with the development of a rich variety

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of plasma discharge reactors [8–12]. Cold plasma technology integrates the subjects of AOPs with both chemical effects of formation of various reactive chemical species such as O_3, H_2O_2 and radicals ($^{\cdot}OH$, $^{\cdot}H$, $^{\cdot}O$, etc.) and physical effects of intense electric field, UV radiation and shock waves in water [13–15]. In order to accelerate the mass transfer between reactive species and the pollutants in the liquid, the water is often in the form of falling film or water droplets in the reactors to achieve the high efficiency for the water treatment [16,17]. However, it still remains a challenge to make the processes effective and practical due to a lack of full understanding on the considerable complexity of fundamental plasma physics and plasma chemistry [18] involved in the interaction between discharge plasma and polluted water. Since the plasma water treatment process includes the mass transfer of reactive species in the plasma and the simultaneous reaction with pollutants in the liquid phase, researchers have made an attempt recently to understand the removal mechanism of pollutants [19] and the transport mechanism of reactive species [20] between plasma and liquid phase. However, the complex coupling effects of the mass transfer and chemical reactions remain an open question far from being clearly understood.

A novel approach, i.e., a non-intrusive reactive planar laser induced fluorescence (reactive-PLIF) technique, has been developed in our group to experimentally investigate the coupled mixing (or mass transfer) and chemical reaction performance characterized by the concentration information in liquid–liquid phase [21,22] and gas–liquid phase [23]. Furthermore, the reactive-PLIF technique utilizing the fluorescence dye Rhodamine B was employed for the first time to demonstrate the basic characteristics of the coupled mass transfer and reaction performance between plasma and liquid phase in two DBD atmospherical plasma reactors for water treatment in our previous work [24]. In the present work, we aim to quantitatively illustrate the factors (e.g., discharge voltage and discharge atmosphere) affecting the decoloration processes by visualizing the coupled processes of mass transfer and reaction between plasma and liquid phase using this novel reactive-PLIF technique in a gas–liquid DBD reactor. The concentrations of hydrogen peroxide and ozone produced under different discharge conditions are determined and the radical species are detected by the optical emission spectroscopy (OES). Besides, Particle Image Velocimetry (PIV) technique is employed to help understand the effect of flow field on the coupled mass transfer and reaction performance revealed by PLIF experiments. As a result, we try to provide straightforward explanation for the mechanism on the direct interaction between the discharge plasma and the dyed water with focus on the fundamental plasma physics and chemistry.

2. Experimental

2.1. Visualization techniques

2.1.1. Reactive-PLIF

PLIF is a non-intrusive diagnostic technique that can visualize and quantitatively measure liquid mixing or mass transfer processes characterized by the tracer concentration or temperature field. The principle of PLIF for measuring concentration field is based on the monotonous relationship between the fluorescent tracer concentration and the fluorescence intensity. The reactive-PLIF technique is developed from the PLIF principle but aims to investigate the physical mixing or mass transfer processes with simultaneous chemical reactions, which can be implemented by using an oxidation reaction to quench the fluorescence signal. In this work, the inexpensive dye, i.e. Rhodamine B ($C_{28}H_{31}ClN_2O_3$), is selected as the fluorescent tracer, which is also chosen as a model pollutant dye for water treatment. The oxidation reaction induced by the *in situ* DBD plasma changes the molecular structure of Rhodamine B in the liquid layer, which leads to the fluorescence quenching and decoloration. A CCD camera is employed to capture the change of fluorescence intensity so that the concentration field is quantitatively recorded. Consequently, the coupled processes of mass transfer and reaction between plasma and liquid phase during the decoloration process are visualized quantitatively in time and space.

2.1.2. Particle Image Velocimetry (PIV)

PIV is a novel technique of flow visualization used to measure a two-dimensional velocity field. During the measurement, the fluid is seeded with tracer particles and illuminated by a planar light (usually a laser). Images of the seeding particles which are assumed to faithfully follow the flow dynamics are captured by a camera at known frequency. The velocities can be obtained by determining the displacements of particles between two consecutive images using the statistic method of correlation techniques [25].

In this work, the fluorescent polystyrene particles (Duke Scientific Corp., CA, USA) with 2 μm diameter, 1.05 g cm^{-3} density, 542 nm excitation wavelength and 612 nm emission wavelength were chosen as the tracer particles and dispersed in the fluids with about 0.01% volumetric particle concentration. A 1.5 W diode pumped solid state continuum laser (PIV Co., Ltd., Beijing, China) with a combination of cylindrical and spherical lens was used as the illumination source to generate a thin laser sheet with a thickness of 0.36 mm at characteristic wavelength of 532 nm. A computer controlled 12-bit high speed CCD camera (IMPERX, IPX-VGA210-L) with a high-pass filter in front of it was placed perpendicular to the laser to obtain images of the lighted flow filed with a frequency of 20 fps at spatial resolution of 7.4 μm/pixel.

2.2. Experimental procedure

The whole experimental apparatus consists of two gas supply cylinders (O_2: 99.999%; Ar: 99.99%) controlled by digital mass flow-meters, a DBD plasma reactor, an OES system including an optical probe and a spectrometer and the PLIF measurement equipment including the laser and the computer controlled CCD camera as shown in Fig. 1. The DBD plasma reactor is made up of high-voltage electrode (discharging electrode), ground electrode and reactor vessel (70 mm in diameter, 95 mm in height) sealed by a PTFE cap (25 mm in height). The high-voltage electrode is a stainless steel tube (9 mm in diameter, 100 mm in length) connected with a bronze sheet (30 mm in diameter, 2 mm in thickness) and a conjoint quartz dielectric plate (50 mm in diameter, 2 mm in thickness). The ground electrode submerged in water with a distance of 18 mm under gas–liquid interface is a stainless steel mesh with a diameter of 30 mm. The DBD plasma is initiated in a discharge distance of 6 mm between the upper quartz dielectric plate and the surface of Rhodamine B liquid layer by a sinusoidal AC high voltage power (Nanjing Coronalab, CTP-2000P) at atmospheric pressure. Experimental gas (oxygen or argon) is compressed into the reactor vessel, which contains the Rhodamine B solution (1 mg/l initial concentration, 150 ml volume), through a gas inlet tube at flow rate of 500 ml/min. It should be noted that the experimental gas is flowed through the reactor vessel for 10 min in order to eliminate the air in the reactor before the application of a high voltage to the discharging electrode. During the decoloration process, the planar laser sheet is used to illuminate the vertical midplane of the Rhodamine B liquid layer while the CCD camera is placed perpendicular to the laser to record the coupled mass transfer and reaction performance on the lighted plane at a frequency of 2 fps. To obtain the concentration field of Rhodamine B, the *in situ*