Pulsed Discharge Plasma over a Water Surface Induces Decoloration of Dyes

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Abstract. It was well known that plasma can be defined as a partially ionized gas composed of ions, electrons and neutral species. Recently, plasma-water interaction has attracted growing interest as it may provide experimental chemists with a quite unique reaction medium. In this work, decoloration of dyes in water as a reaction media and the effects of various parameters with pulsed high-voltage discharge plasma are studied. Such as plasma applied under hydrothermal conditions generates high-energy electrons, ions, and radicals, which in turn may generate new reaction fields, leading to effective organic compounds oxidation for both homogeneous and heterogeneous reactions. Here, we utilize pulse discharge plasma over water surface to study the decoloration of Orange G, Orange II, Congo Red, and Naphthol Blue Black. They were directly fed as starting materials without additives. The experiments were conducted under argon atmospheric at 313 K using a batch type reactor. The products were directly analyzed by UV-Vis (ultra violet-visible) spectrophotometer V-550. The decoloration rate increased with increasing peak pulse voltage and pulse numbers, presumably due to the increased electric field energy. Based on these results, the present system may be promising.

1. Introduction

Dyes or synthetic dyes make our world beautiful, but they bring pollution. Although, the greatest environmental polluter is the chemical industry, of which only a relatively small part pertains to the organic colorants industry, their degradation in wastewater have always been of great interest to the field of environmental protection. Therefore, the removal of these dyes from effluents becomes the major environmental problem of the multiproduct industry [1-5]. Generally, dyes containing wastewaters can be treated in two ways [6]: (i) by chemical or physical methods of dye removal, which refers to the process called decoloration and (ii) by a biodegradation process.

Several advanced oxidation technologies have been utilized for the purpose of degrading organic pollutants in wastewater, such as UV photolysis, photocatalysis, sonochemistry, supercritical water oxidation, electrical discharge plasma technology and electron-beam irradiation [7-13]. In this work, the pulsed discharge plasma over a water surface is considered to be an applicable method for removal of organic pollutants from wastewater [14-15]. In general, several kinds of inorganic salts or other chemicals were added on the decolorization of dyes using advanced oxidation processes [1,16-18]. Here, the synthetic wastewater was directly fed as a starting material without chemical reagents. It is simple and versatile technique that has gained much attention because of its capability and feasibility

in the decomposition of large quantities of wastewater from industries. The utilization of pulsed discharge plasma has demonstrated to be effective at degrading aromatic compounds in aqueous solutions as it not only produces a hydroxyl radical but also atomic species with high oxidation potential [19-21], which in turn become important reactants. These active species include hydrogen peroxide, hydrogen, and oxygen, along with other oxidative species such as hydroperoxyl radicals and reductive species such as hydrogen radicals, superoxide radical anions, and aqueous electrons. The OH radical is particularly known to play an important role in the oxidative purification of water and the degrading of organic compounds [22]. Sugiarto et al. [1] and Sun et al. [23] observed also that the streamer produced by pulsed discharge could induce decomposition of H_2O_2 and produce OH radical, which led to the increase of the degradation efficiency of organic compounds.

Such as pulsed discharge plasma applied to degrade the organic compounds, the degradation of dyes during an electrical discharge in water also agree that OH radicals are the major species responsible for decolorization and the extent to which a dye will be degraded depends on the reactivity between OH radicals and the dye functional groups and substitutes [1-3,16,18,23-29]. When the discharge plasma was conducted on the water surface, the active species products will diffuse in the gas phase and dissolve in the water through the surface layer to react with the organic materials in water. Sugiarto et al. [1,2] and Wang et al.[4] explained that OH radicals played a key role in pulsed discharge systems for decoloration processes of Rhodamine B, Methyl orange, and Chicago sky blue, reacts readily with the carbonate ions generated through the breakdown of the organic compounds, but does not react with organic compounds, or their intermediates during the oxidation processes under the basic solution condition. Sunka et al. [29] investigated decolorization of C.I. Reactive Blue 137 (50 mgL^{-1}) by using corona discharge reactor. They reported that decolorization of reactive dye solution is very low, while the addition of Fe ions in the system improved color removal and in 5 minutes of treatment the complete color removal was obtained. Recently, Sun et al. [30] also reported that the active species generated by discharge in the gas phase include ozone (O_3), OH radical, peroxide (O_2^-) and atomic oxygen (O) can dissolve into the water solution and form hydrogen peroxide in the solution. They found that the concentration of hydrogen peroxide in the solution increased when the O_3 concentration in the gas phase increased. Consequently, these active species generated at the gas-liquid interface helped the rapid decoloration of the organic dye. However, as an explained above, the additives was still used in their decoloration process.

In the present study, experiments have been performed for degrading dyes as organic pollutants using pulsed discharge plasma under argon atmospheric pressure. Orange G, Orange II, Congo Red, and Naphthol Blue Black were selected as the model organic contaminants, which were dissolved in distilled water to form a synthetic wastewater. Under argon atmosphere, pulse discharge plasma might serve as an intense source of ultraviolet radiation [31-35]. Argon is one of the most studied and utilized chemical elements, and dense argon is a promising reaction media alternative. Like carbon dioxide, argon possesses easily obtainable critical points and it is also non-polluting (T_c = 150.9 K, P_c = 4.9 MPa) [36-38]. As reported by Bogaerts et al. [32], when a potential difference is applied between two electrodes under argon atmospheric, the argon gas will break down into electrons and positive ions. This ionization will create new electrons and ions, therefore, the self-sustaining plasma of glow discharge occurred. Mishra et al. [35] found that the relative yield of hydrogen gas from methane increases in the presence of argon. It is suggested that argon could act as a promoter and also had certain influences on the density and energy distribution of electrons, and thus assist the production of various active species during the formation of plasmas. In addition, argon has also catalytic effects on the production of ozone [33].

2. Experimental

The dyes Orange G ($C_{16}H_{10}N_2Na_2O_7S_2$; 80%), Orange II ($C_{16}H_{11}N_2NaO_4S$; 92%), Congo Red $C_{13}H_{22}N_6Na_2O_6S_2$; 85%), and Naphthol Blue Black ($C_{22}H_{14}N_6Na_2O_9S_2$; 85%) commercial products purchased from Sigma Chemical Co. USA, and used without further purification. The synthetic wastewater was prepared by dissolving of each dye with distilled water at 1000 mg/L as an initial

concentration. As a reaction media, water conductivity plays an important role in the generation of arch discharge plasma and on the production of chemically active species [23,39,40].

The reactor contained two inspection windows to monitor the performance of plasma production and was made of stainless steel (SUS-316, AKICO, Japan). The detailed experimental setup and procedure have been described extensively elsewhere [14]. Therefore, the experimental procedure is briefly described here. To begin the experiment, feed containing 1000 mg/L of dye (12 mL) was loaded to the reactor manually. The reactor was repeatedly (three times) purged of air using argon gas with a pressure of about 0.2 MPa; it was then heated up to 313 K.
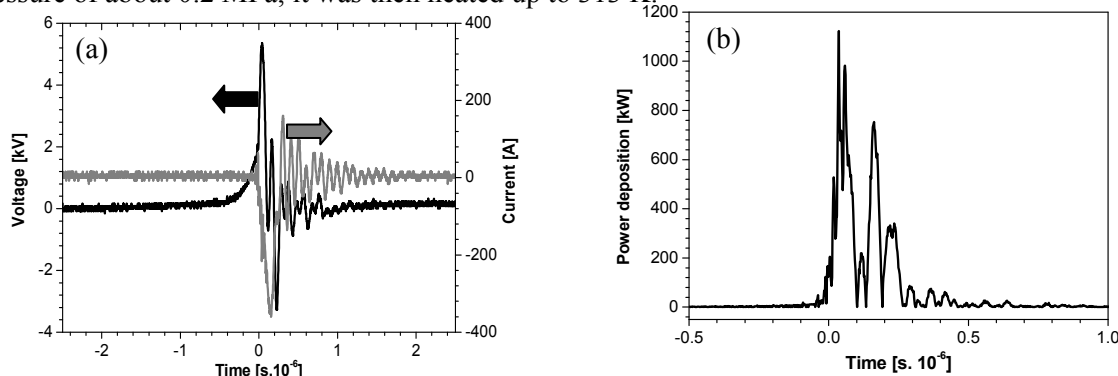

Figure 1. (a). Typical waveform by MPC under argon atmosphere at 0.2 MPa, 313 K with 5 kV peak pulse voltage applied. Black is voltage; grey is current. (b). Electric power deposition at 5 kV peak pulse voltage applied under argon atmosphere at 0.2 MPa, 313 K.

Figure 1(a) shows the waveform profile of pulsed voltage and current under argon atmosphere. To evaluate the energy deposition process of the pulsed discharge plasma, the voltage across the electrode and the discharge current were measured. After the discharge initiation, an electric discharge pulse appears immediately. The energy deposited during one discharge pulse is estimated from the measured voltage and current. Figure 1(b) showed the energy deposition waveform defined by the curve $P = VI$, where P is power (W), V is voltage (V), and I is current (A). After the reaction time had elapsed, the electric current was cut off and the reactor was opened. The products were directly identified by UV-Vis spectrophotometer V-550. The maximum absorbance wavelength (λ max) of Orange G, Orange II, Congo Red, and Naphthol Blue Black are 476, 486, 499, and 620 nm, respectively. The conductivity and pH of the sample liquid was measured using a conductivity meter (ECTestr 11, EUTECH Instruments, Singapore) and pH meter (Compact pH Meter AS-211, Horiba. Ltd, Japan). At 1000 mg/L, the conductivity of Orange G, Orange II, Congo Red, and Naphthol Blue Black were 280, 240, 310, and 290 μS/cm, respectively. On average, the initial pH of them was 9.15, 7.60, 8.18, and 9.40, respectively.

3. Results and Discussion

Generally, the colour of water which polluted with organic colourants could be reduced by the cleavage of the -C = C- bonds, the -N = N- bonds and heterocyclic and aromatic rings occurs. These bonds are intentionally designed to resist biodegradation, i.e. the wastewater originated from reactive dye processes is characterized by poor biodegradability, passing unaffected through conventional treatment systems and discharging into the environment. The absorption of light by the associated molecules shifts from the visible region to the ultraviolet region or infrared region of the electromagnetic spectrum [6]. To estimate the decoloration of dyes after treatment by pulse discharge plasma under argon atmospheric, the liquid products were analyzed by UV-Vis spectrophotometer; this is a useful tool for studying decoloration of dyes, contains, e.g. ethylene group, amine group and its derivatives, since many intermediate products as well as of the resulting products are known to be strongly colored. Figure 2 showed some results for dyes conversion when the pulse discharge plasma was applied. At the same numbers of discharge plasma, the conversion of dyes increased significantly with increasing the peak pulse voltages applied. These figures depicted also that the dyes degradation

efficiency increases with increasing peak pulse voltage applied and discharge numbers of plasma. Pulse discharge plasma can be conveniently grouped into localized and extended effects depending on the region. When pulse discharge plasma occurs, the following individual effects occurred simultaneously: over pressure shock wave, strong electrical field, production of various free radicals, and intense ultraviolet radiation [23]. In this case, the arc discharge directly contacted over the water surface where the streamer channel propagates along the surface of the water. They will cleavage active side on the dye structure especially amine group which promoted by the various reactive chemical species such as radicals (OH, H, O, HO_2) and molecular species (H_2O_2, H_2, O_2). With increasing voltage, the electric field strength between the electrode increases resulting in more energetic electrons which dissociate more efficiently water, gas and dye molecules. Therefore, at higher voltage, the discharge produces more active species which enhance the oxidization of dyes yielding lower molecular weight products. It was found also that the electrons wherein the zone have more energy and bombard the water molecules and dye molecules with higher speeds. Wang et al. [4] suggested that the decoloration rate of azo dye increased with increasing peak pulse voltage, presumably due to the increased electric field energy. Based on these results, the dyes degradation increases with increasing peak pulse voltage which leads to the formation of its derived compounds.
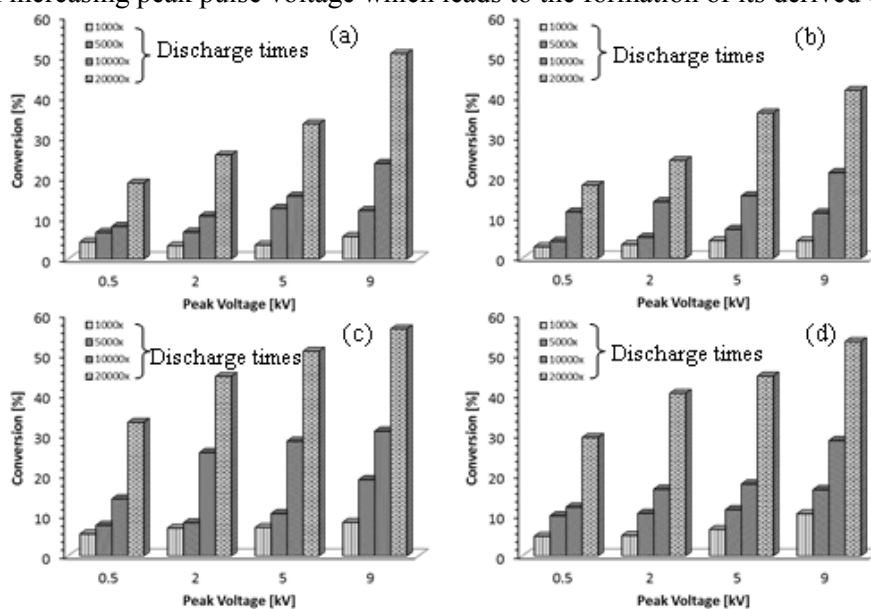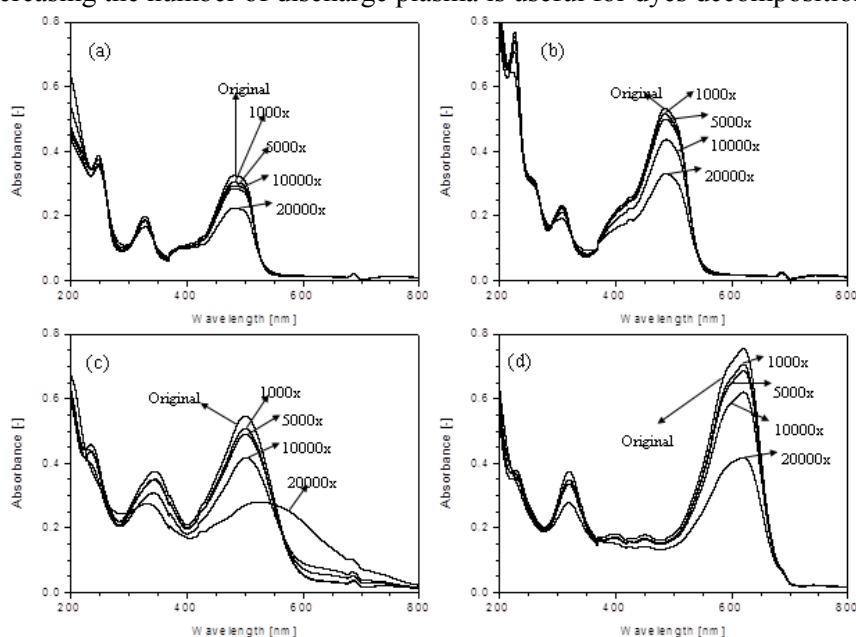

Figure 2. Conversion of dyes after treatment by various peak pulse voltage under argon atmosphere at 313 K (a. Orange G; b. Orange II; c. Congo Red; d. Naphthol Blue Black).

In this work, decoloration of several kinds of dyes has been tested using the pulsed discharge plasma over water surface. The results obtained after treatment with different pulse discharge times are shown in figure 3. In this case, the electric fields which generated by pulse discharge plasma over water surface initiate both chemical and physical processes. The intense electrical discharge disassociates water molecules to yield active radicals, due to collisions of high energy electrons with molecules. These radicals will combine with almost dye compounds and/or dye derived compounds in a very efficient manner. The chemical reactions induced by pulse discharge plasma over water surface are dependent on several factors. For example, the aqueous solution composition can affect the reactions through the presence of electrolytes and radical quenchers. Conductivity affects the electrical discharge over water surface, leading to lower rates of formation of active species, but higher rates of formation of UV light [41].

As shown in the figure 3, the pulse discharge numbers had significant effect on the decoloration rate of dyes. To examine this effect, the experiments were conducted in widely range (1000-20000x discharge numbers). At each reaction conditions, the decoloration rate significantly increased with discharge numbers. For example, the decoloration rate Naphthol Blue Black was around 10% at 1000x discharge

times and increased gradually to 53% at 20000x discharge times when the peak pulse voltage applied was 9 kV. In this case, the energy input to the electric field is directly proportional to the numbers of discharge plasma. It could increase the quantity and energy of the high-energy electron. More frequent and energetic electron bombardment with the water molecule can create more active species that would attack dye to its derived compounds. Due to the transfer of the dye compounds from the liquid phase to the gas phase where they can react with the active species of the discharge, especially radicals. Therefore, increasing the number of discharge plasma is useful for dyes decomposition.

Figure 3. Absorbance of dyes after treatment by various pulse discharge numbers at 313 K with 5 kV peak voltage (a. Orange G; b. Orange II; c. Congo Red; d. Naphthol Blue Black).

Table 1 showed liquid conductivity of feed solutions after treatment by pulse discharge plasma with 5 kV peak voltage. It can be shown that solution conductivity increases greatly after pulse discharge plasma treatment. As reported by Wen et al. [42], many active species, such as •OH, •O, •H, •HO$_2$, and O$_2^-$, etc., were produced during pulse discharge plasma process in distilled water as reaction media. These active species can react with dye compounds to result in some conductive products which increase the conductivity of solution. The increasing the conductivity of the solution will lead to decrease streamer formation and lower quantities of reactive radicals [23]. As shown in the table 1 that the pH values of solution products decreased significantly due to the pulsed discharge plasma treatment. The pH of the solution is one of important parameters because it can vary the surface charge of the electrode and also shifts the potential of some redox reaction [1-3,43]. As an explained before, the conductivity solution products largely increased with the discharge times of plasma. The observed phenomenon of the dramatic decrease of pH and increase of conductivity corresponds to the several literatures where the active species generated through electrical discharge during treatment process [1-3,23,43,44]. Sugiarto et al. [1] conducted degradation of organic dyes by the pulsed discharge plasma. They reported that the dye molecules decompose into organic acids, aldehydes, resulting in a decrease in pH values and an increase in water conductivity. Mok et al. [3] also reported that the degradation products from Orange II using a gas phase dielectric barrier discharge reactor in water like organic acids could decrease the pH value and increase the solution conductivity.

To evaluate the performance of the pulse discharge plasma systems, the energy yield was estimated [45-48]. Table 1 showed the energy yield values of dye molecules degradation after treatment by pulse discharge plasma. They were changing as a pulse discharge times even under the same reaction condition. The energy yield decreased significantly with increasing the pulse discharge times. These observations are in good agreement with the literature [45-48]. Kim et al. [46] reported that the best

results are found in the small specific input energy region where the removal rate is low. They also pointed out that the nature of the energy yield was determined from the relationship between the removed amount of molecules and the specific input energy.

Table 1. Calculated value of energy yield and change of pH and conductivity of the feed solutions after treatment by various pulse discharge numbers with 5 kV peak voltage.

Feed	Discharge times [-]	pH	Conductivity (μS/cm)	Energy yield, G (mg/mJ)	Degradation [wt %]
Orange G	1000	6.74	340	2.81	3.44
	5000	6.04	480	0.51	12.51
	10000	4.07	530	0.25	15.55
	20000	3.42	840	0.10	33.42
Orange II	1000	6.32	280	2.78	4.36
	5000	6.00	310	0.54	7.13
	10000	4.74	540	0.25	15.47
	20000	3.05	750	0.09	36.00
Congo Red	1000	6.52	290	2.70	7.02
	5000	6.12	390	0.52	10.50
	10000	4.10	510	0.21	28.51
	20000	2.02	790	0.07	50.86
Naphthol Blue Black	1000	6.90	290	2.71	6.53
	5000	6.08	320	0.51	11.46
	10000	5.78	690	0.24	17.84
	20000	3.42	900	0.08	44.68

4. Conclusions

The experiment of dyes degradation by pulsed high-voltage discharge plasma over water surface at 313 K, 0.2 MPa argon atmospheres in a batch-type reactor has been performed. Under these conditions, dyes were degraded into its derived compounds with the appearance of light color. UV-Vis spectrophotometer analyzed that the intermediate compounds from the degradation of dyes consist primarily of aromatic compounds which contain nitrogen functional groups. At each reaction conditions, the decoloration rate of Orange G, Orange II, Congo Red, and Naphthol Blue Black significantly increased with peak pulse voltage applied and discharge numbers. The maximum degradation of them was 50.05%, 41.64%, 44.98%, and 53.25%, respectively. With increasing the pulse discharge times, the pH and the conductivity of dye solutions changed clearly. Based on these results, it is proposed that this method is applicable as a medium for dyes degradation despite the stability of the compound and its inability to be easily cleaved under these conditions.

5. Acknowledgement

6. References

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