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Optimizing the electrical excitation of an atmospheric pressure plasma advanced oxidation process

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HIGHLIGHTS

- We investigate the pulse modulated generation of plasma on dye degradation efficiency.
- We examined the impact of both the duty cycle and period of the pulse modulation envelope.
- Decreasing duty cycle to 25% yields a 2.1 times increase in dye degradation efficiency.
- Decreasing duty cycle to 25% yields a 20 times reduction in nitrate contamination of the sample.
- The improvements are attributed to enhanced O_3 production and reduced NO production in a pulsed plasma.

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ABSTRACT

The impact of pulse-modulated generation of atmospheric pressure plasma on the efficiency of organic dye degradation has been investigated. Aqueous samples of methyl orange were exposed to low temperature air plasma and the degradation efficiency was determined by absorbance spectroscopy. The plasma was driven at a constant frequency of 35 kHz with a duty cycle of 25%, 50%, 75% and 100%. Relative concentrations of dissolved nitrogen oxides, pH, conductivity and the time evolution of gas phase ozone were measured to identify key parameters responsible for the changes observed in degradation efficiency. The results indicate that pulse modulation significantly improved dye degradation efficiency, with a plasma pulsed at 25% duty showing a two-fold enhancement. Additionally, pulse modulation led to a reduction in the amount of nitrate contamination added to the solution by the plasma. The results clearly demonstrate that optimization of the electrical excitation of the plasma can enhance both degradation efficiency and the final water quality.

1. Introduction

Advanced oxidation processes (AOPs) have received considerable interest for wastewater treatment [1]. Of the many AOPs currently under investigation, atmospheric pressure plasma shows great promise as it combines chemical, mechanical and electrical processes with a proven capability for degrading the most intransigent substances; examples include plasma-induced degradation of phenol [2,3], methylene blue [4,5], and trace contaminants in tertiary-treated water [6]. Plasma generates an abundance of oxidizing species including OH^*, O^*, H_2O_2 and O_3 and potentially shockwaves, high temperatures, and large fluxes of UV photons - all of which contribute to the degradation of persistent chemicals [7].

Decolorization of organic dyes is a promising area for which plasma-based AOPs have been considered. It is estimated that 12% of the total 7×10^5 t of organic dye used annually is discharged into the environment worldwide [8], due mostly to inefficiencies in the dyeing process. Many dyes cannot be degraded using conventional means due to their stable molecular structure [4]. Dyes discharged into the environment disrupt the ecosystem and are toxic to both fauna and flora [8,9].

In plasma-mediated dye decolorization studies, the primary benchmark when comparing reactor designs for industrial feasibility is electrical efficiency [9]. Recently, Malik conducted a review of 27 common types of plasma reactor used to decolorize various dyes [10]. In the study, efficiency was defined as the amount of energy required to reduce the initial dye concentration by 50%; efficiency yields for the 27 plasma reactors differed by up to five orders of magnitude, highlighting that reactor design and electrical excitation have an enormous impact on the efficiency of the

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process. Critically, the review by Malik examined data gathered from a wide variety of studies that employed a variety of reactor configurations, plasma generation techniques and dye composition/concentrations. Due to these variations it is difficult to pinpoint the most efficient reactor configuration and excitation technique; however, it is clear that both factors play a major role in determining the efficiency of the system.

In terms of optimizing the plasma generating waveform to maximize degradation efficiency Grabowski et al. demonstrated that the efficiency of ozone production in a pin over liquid film reactor can be doubled by changing pulse frequency [2,3]. Sano et al. found that the discharge polarity in a similar pin over water reactor had a significant effect on phenol degradation [11]. Studies by Simek et al. have shown that ozone production efficiency can be increased by decreasing duty cycle for plasmas generated in pure oxygen and synthetic air [12,13]. Indeed, many other works in the field of plasma science have demonstrated the ability to tailor the excitation dynamics of a plasma discharge [14]. Essentially, the recent literature on plasma based AOP's indicates that two key factors dictate the efficiency of the process: (1) the design of the reactor, which should be optimized to promote the mass transfer of reactive species and (2) the electrical parameters of the plasma source, which should be optimized to generate an abundance of oxidizing species with minimal energy input.

In this contribution, the degradation of methyl orange (MO) in the aqueous phase was optimized using a pulse-modulated surface barrier discharge (SBD) reactor. Pulse modulation of plasma is known to enhance electrical efficiency and minimize undesirable aspects associated with plasma generation; including gas heating and electrode wear [7]. To demonstrate the advantage of pulse modulation, this study systematically investigated pulse waveform parameters including pulse period, pulse repetition rate and input power in order to establish the optimum operating parameters. An SBD reactor generates a layer of plasma on a dielectric surface that is positioned millimeters above the sample surface; as such, it operates on a fundamentally different principle to many of the plasma reactor designs reported in the literature. The SBD configuration does not require the sample solution to act as an electrode hence it is immune to changes in the electrical properties of the sample. Changes in the electrical properties are inevitable during plasma exposure; in direct-contact reactors, these changes influence the plasma dynamics and the degradation efficiency varies accordingly. In the context of this study, it is essential to separate the effects observed through intentional changes to the electrical excitation to those occurring through the drift of the electrical properties of the sample.

A drawback of the SBD configuration is the inefficient transport of reactive species from the plasma to the liquid phase; a process which is less efficient than in direct-contact reactors. Since species with high oxidation potentials also have the shortest lifetimes, the spacing between the SBD and sample limits the flux reaching the sample surface and efficiency drops. However, in the context of industrially-viable water treatment, the SBD reactor has significant benefits. Placing electrodes in contact with the sample can lead to further contamination and accelerated electrode wear, a factor deemed to be one of the major obstacles preventing widespread use of plasma AOP's. Direct contact plasma systems commonly involve high pulsed currents, conditions which impact electrode longevity. The remote SBD reactor employed in this study exhibits minimal heating and provides little opportunity for further contamination of the sample solution. The choice of a surface discharge reactor was therefore made for two practical purposes: to allow the consistent study of the effects of the plasma generating waveform on efficiency and because surface discharge reactors are versatile, scalable and practical on an industrial scale.

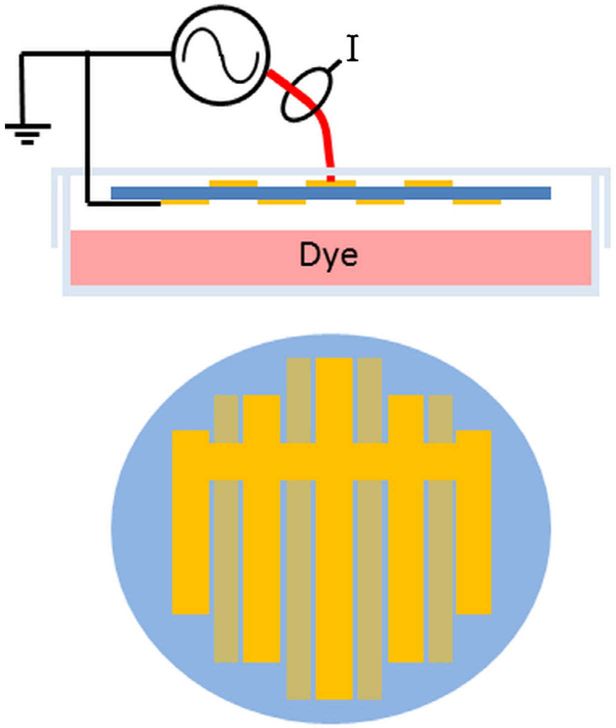

Fig. 1. Diagram of experimental reactor showing superimposed representation of the glass dielectric barrier with copper electrodes attached to either side.

2. Experimental setup

2.1. Apparatus

The plasma reactor used in this study is depicted in Fig. 1. The SBD electrode employed copper strips adhered to both sides of a 75 mm diameter, 1 mm thick quartz disc, thus forming a dielectric barrier discharge (DBD) configuration. The electrodes placed on one side of the disc were attached to the power source and the electrodes on the opposite side (sample facing) were grounded. The exposed sample in the reactor had a surface area of 56.7 cm^2 with a separation of 9.4 mm between the grounded electrode and sample surface. The space above the sample liquid had a total volume of 53 mL.

The plasma generating source produced a sinusoidal signal at a frequency of 35 kHz and enabled the independent variation of the period and duty cycle of the pulse-modulation envelope. Mean plasma power was determined using the mean of the product between the applied voltage and current over 200 cycles. Fig. 2(a) shows current and voltage waveforms with the SBD operating at a mean power of 5 W. Typical of a DBD operating in a molecular gas, the current waveform exhibits multiple short current peaks, indicating the presence of micro-discharges [15]. Short-exposure imaging of the discharge formation, also shown in Fig. 2(a), confirmed that the plasma consisted of multiple micro-discharges forming at imperfections on the electrode. The area of plasma generation was calculated based on photographs of the system operating at 5 W and was found to be approximately 5.8 ± 0.5 cm^2.

2.2. Reagents

In all experiments, deionised (DI) water from a Purite DC7 deioniser was used. Microscopy grade Fluka methyl orange ($C_{14}H_{14}N_3NaO_3S$, Sigma Aldrich 68250-25G) was dissolved in DI water without further modification.

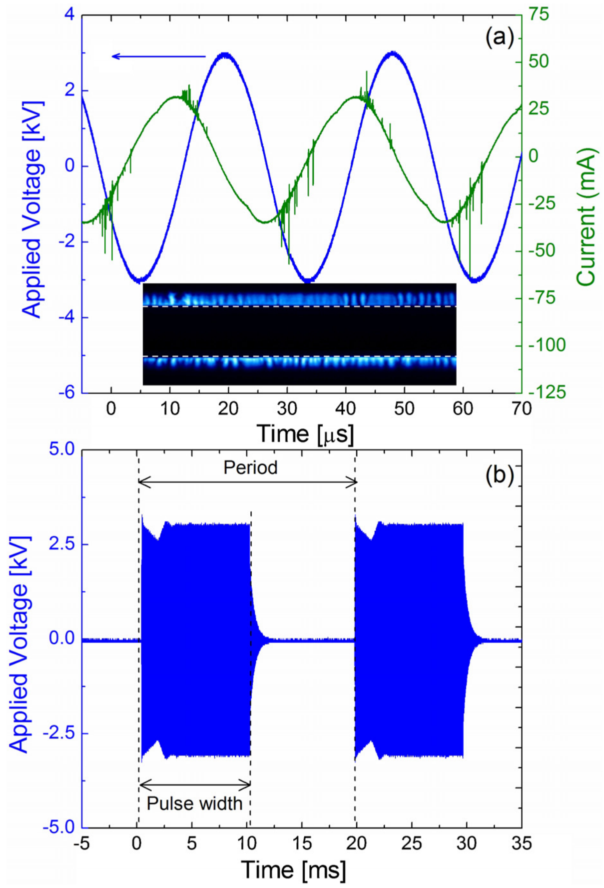

Fig. 2. Typical discharge current and voltage waveforms of the surface discharge: (a) current and voltage waveforms on microsecond timescale, inset showing 20 ns exposure iCCD image, (b) voltage waveform on millisecond timescale showing pulse modulation envelope (50% duty cycle, 20 ms period).

2.3. Analysis methods

Decolorization of the dye sample was measured by absorbance spectroscopy using an Ocean Optics USB4000-UV–vis spectrometer and quartz cuvette. An Ocean Optics DH-2000 UV–vis–NIR light source was employed to measure absorbance from 200 to 800 nm. Absorbance measurements were conducted in triplicate using 12 mL samples. MO at a concentration of 20 mg/L was tested for decolorization at various power and duty cycle settings. Samples were placed in a vial immediately after plasma treatment and sealed. 2 mL aliquots were sampled into a quartz cuvette for absorbance testing and the remainder of the sample was stored in a cool, dark place. Absorbance measurements were taken 5 min after the end of each test, with a second measurement being made 24 h after treatment.

All plasma treatments were conducted with a total energy of 1.8 kJ (constant energy density of 150 kJ/L). This was accomplished by adjusting the duration of treatment for the various power cases. For example, tests conducted with a plasma power of 2.5 W were 12 min in duration, 5 W tests were 6 min in duration and 10 W tests were 3 min in duration. The plasma power in continuous tests was adjusted by varying the amplitude of the high voltage sinusoid. To investigate the impact of pulse modulation on degradation efficiency two key parameters were considered: the duty cycle and period of the pulse modulation envelope. The influence of duty cycle, which is expressed as a percentage of plasma 'on' time to the signal's period was considered. In this investigation, duty cycles of 25%, 50% and 75% were examined. Fig. 2(b) shows a 50% duty cycle case with a period ~20 ms. In all pulse modulated cases, the plasma 'on' power was 5 W. The average power of pulse modulated tests was therefore proportional to the duty cycle and their test time was adjusted accordingly; for example, the 50% duty cycle case had an average power of 2.5 W and was therefore run for 12 min. The rationale for investigating multiple 'on' times comes from the anticipated differences in formation time of reactive species, which evolve on a millisecond timescale [16,17]. Pulse modulated cases with periods of 2 ms, 20 ms and 2 min were considered; with the exception of the 25% duty cycle case with a period of 2 ms, as it was found that plasma could not be generated with an 'on' time of less than 1 ms. Table 1 summarizes the experimental conditions considered.

Table 1
Table showing experimental conditions.

Condition	Mean power (W)	Duty cycle (%)	Period (s)	Test duration (min)
1	10	100	–	3
2	7.5	100	–	4.5
3	5	100	–	6
4	3.75	75	0.002, 0.02, 120	8
5	2.5	50	0.002, 0.02, 120	12
6	1.25	25	0.02, 120	24

Decolorization was determined by:

$$D = \frac{A_0 - A}{A_0} \times 100\% \tag{1}$$

where D is decolorization, A is the measured absorbance at MO's maximum peak of 664 nm and A_0 is the measured reference absorbance with no decolorization. Since all tests were conducted with the same total energy, volume and dye concentration, efficiency (in g/kW h) is proportional to decolorization:

$$\text{efficiency} = D \times \frac{C \times V}{E} = 0.48D \tag{2}$$

where D is decolorization (expressed as a ratio, $0 \leq D \leq 1$) and C, V and E are the dye concentration, sample volume and total consumed energy, respectively.

Ozone concentration was determined by UV absorbance at 253.37 nm. In all cases a path length of 3 cm was used and the absorption cross-section for ozone was assumed to be 1147×10^{-20} cm^2 at 253.65 nm as proposed by Hearn [18]. Other reactive species present in the gas phase were analyzed in-situ using a JASCO FT/IR 4200 system with the plasma generating electrodes inserted within a 10 cm path length gas cell. To obtain an FTIR measurement, the electrode arrangement was sealed within the gas cell and energized for 2 min prior to recording data.

The concentration of nitrite and nitrate in solution was determined by treating pure DI water in the reactor under the same plasma conditions as those used for the dye degradation. A Dionex 120 Ion Chromatograph employing a IonPac AS9-HC Carbonate Eluent Anion-Exchange column was used to determine both nitrate and nitrite concentration. In each case, 25 μL of the treated solution was sampled and peak retention time was used to confirm the identity and the peak height used to calculate concentration.

To determine the relative concentration of ionic compounds generated in solution, the pH and conductivity were measured using a Hanna pH meter and a Hanna conductivity meter, respectively. It is a well-established pattern for the conductivity of a plasma treated water sample to rise with treatment time and for the pH to lower [11–13]. It has been reported that the semi products of MO include acids and ionic compounds; these semi products are likely partially responsible for the post treatment change in conductivity and pH [4,13]. To establish the relative concentrations of ionic compounds generated solely by the SBD

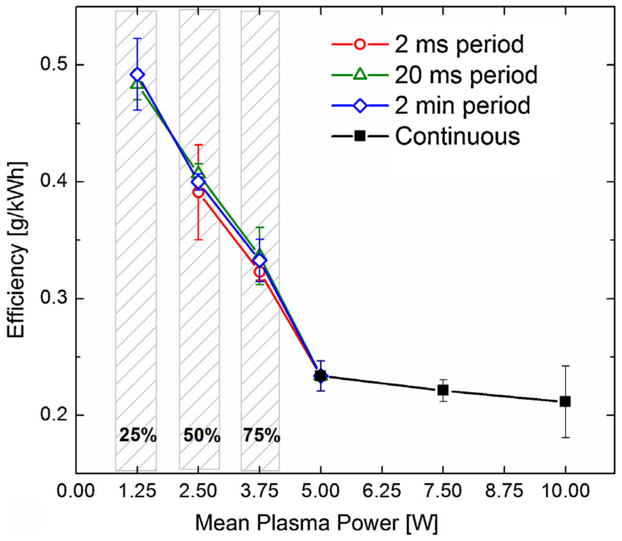

Fig. 3. Energy efficiency with respect to mean plasma power for various duty cycles and periods. Powers below 5 W relate to pulse modulated cases, where the percentage shown indicates duty cycle used.

reactor, 12 mL samples of DI water were treated and their pH and conductivity were measured immediately after each test.

3. Results and discussion

3.1. Dye decolorization

The decolorization of organic dye using plasma is a complex process involving the generation of active species by the plasma discharge, the transport of those species to the liquid layer, breakdown of dye molecules into intermediate products and the competition between those products for active species. The tests conducted in this investigation employed no forced stirring; hence, mixing in the reactor was limited to diffusion only. Fig. 3 highlights the degradation efficiency of MO under the different plasma generation conditions detailed in Table 1. Critically, it is observed that reducing the duty cycle whilst maintaining a constant input energy can double the overall degradation efficiency, up to an improvement of 2.11 times with a 25% duty cycle. These results can be partly explained by considering the densities of gas phase reactive species during the plasma on and off times. During the plasma on time the density of many reactive species in the reactor increase rapidly while in the plasma off time, many of the production pathways of such species are eliminated while the loss pathways remain, resulting in a decay of species. Given the long half-life of some reactive species present in the reactor, such as O_3 and H_2O_2, it is reasonable to assume that the decolorization effect of such species is still present after the plasma is extinguished. As the 25% duty cycle test involves the sample being held in the treatment reactor four times longer than in the continuous case, it is likely that longer lived plasma species remaining during the plasma off time contribute to the overall degradation effect. Interestingly, samples treated with continuous plasma at 5 W for 6 min and left to sit undisturbed in the treatment reactor for a further 18 min, such that the time in the reactor is equivalent to that of a 25% duty cycle test, showed no obvious improvement in degradation efficiency. This result indicates that the enhanced efficiency observed when pulse modulation is employed is not solely due to samples being held in the reactor for a longer time.

The results for the various pulse-modulated cases show that the period of the pulse modulation envelope does not have a noticeable effect on the degradation efficiency. This is an unexpected result. It was hypothesized that short plasma on-times could potentially offer access to alternative discharge chemistries as it is known that the generation of reactive plasma species can take several ms to reach equilibrium [16]. Under the experimental conditions considered in this investigation it is clear that no benefit is gained by using short plasma-on times, indicating that the discharge chemistry has reached equilibrium << 1 ms, which is beyond the shortest plasma-on time considered.

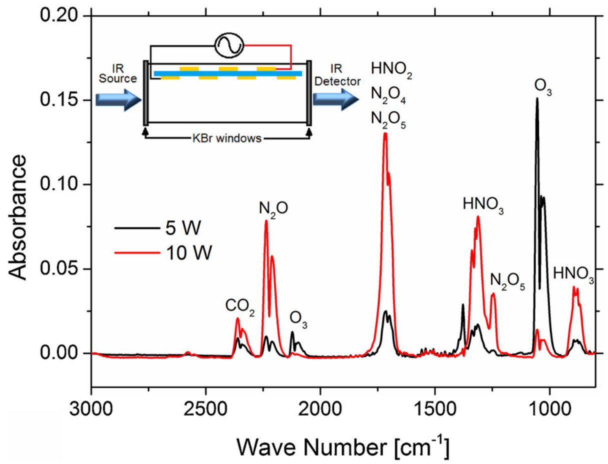

Fig. 4. In situ absorbance measurements of the gas phase species at plasma powers of 5 W and 10 W. Inset shows the experimental set up.

An increase in input power, under continuous operation (100% duty cycle), showed a slight decrease in degradation efficiency. These results can be attributed, in part, to the dynamics of ozone generation, discussed in the following section. Finally, absorbance measurements conducted 24 h after plasma treatment indicated a further 10% decolorization; indicating that long-lived aqueous phase species play a minor role in decolorization.

3.2. Reaction kinetics in the plasma, gas and liquid phase

As this study considered the use of a non-contact SBD reactor the primary degradation pathway is likely to be through oxidation by long-lived plasma species, especially ozone [19]. As air is used as the working gas, the production of ozone is affected by plasma power and ozone-quenching gases such as nitrogen oxides [20]. Degradation efficiency is also affected by the residence time of ozone inside the reactor and the ozone absorption rate of the sample solution. Using a zero-dimensional air plasma model and considering the diffusion of neutral species to the gas phase, Sakiyama et al. showed that highly reactive species such as O and OH are rapidly quenched within ∼100 ns. Additionally, O and OH are predominantly produced through dissociation by energetic electrons in the plasma phase, there are few energetic electrons beyond the visible discharge hence little additional O or OH is produced in the gas phase. In essence, it can be concluded that the reactive short lived plasma generated species do not play a direct role in the dye degradation process [17].

Fig. 4 shows in-situ FTIR measurements obtained with the discharge operating in a sealed gas cell at 5 W and 10 W. The figure indicates that gas phase species vary significantly with the dissipated plasma power. At a power of 5 W the gas phase chemistry is dominated by ozone. As the plasma power is increased to 10 W, the discharge chemistry becomes dominated by nitrogen based species, including: N_2O, N_2O_4, N_2O_5, HNO_2 and HNO_3. Critically, in atmospheric pressure air plasma, the creation of NO is known to occur through the reaction of vibrationally-excited nitrogen

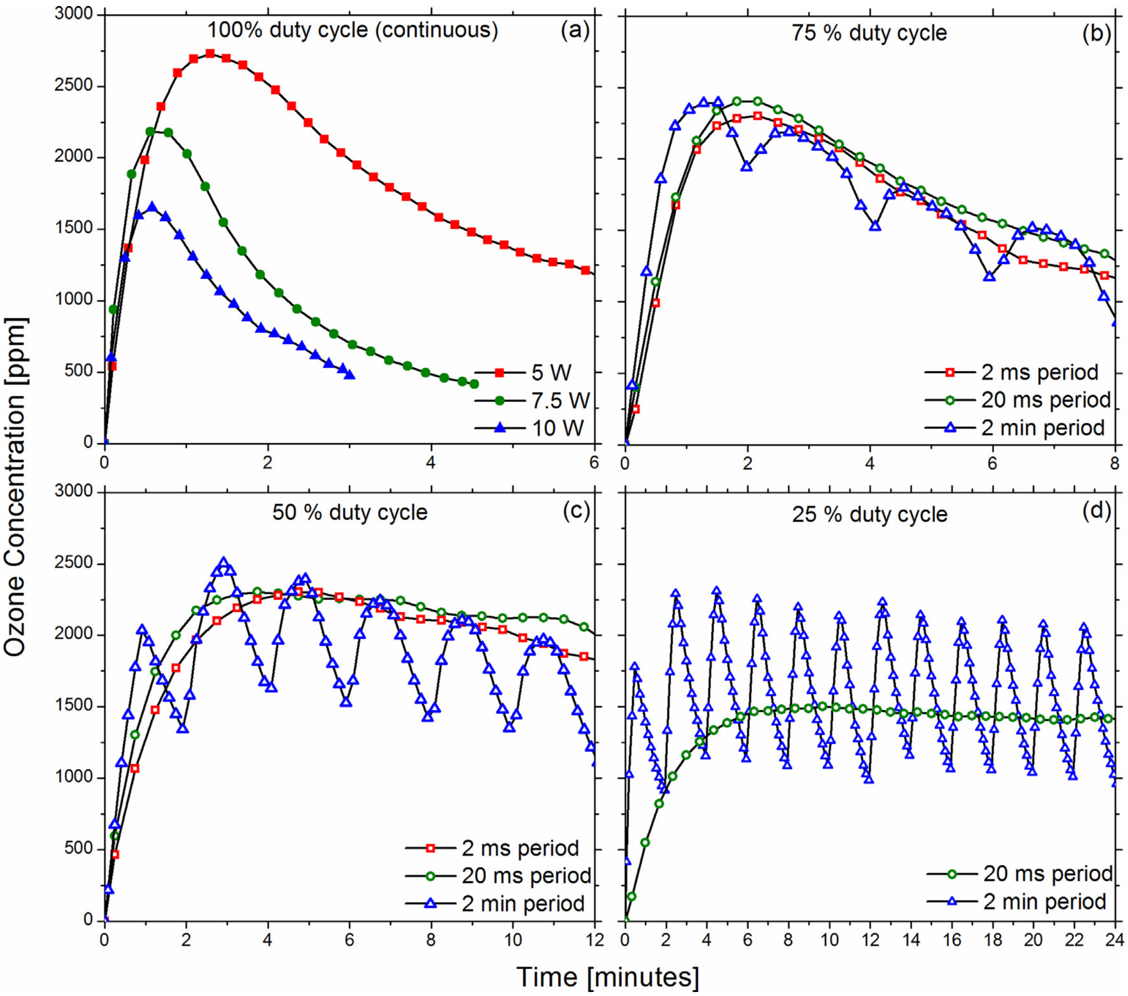

Fig. 5. Time evolution of ozone concentration in sample enclosure: (a) continuous cases; (b) 75% duty cycle cases; (c) 50% duty cycle cases and (d) 25% duty cycle cases.

molecules $N_2(v)$ and oxygen atoms (reactions (R1)–(R3)) [20], this limits the density of O available to form ozone.

$$N_2(v) + O \rightarrow NO + N \quad (R1)$$

$$O + NO + M \rightarrow NO_2 + M \quad (R2)$$

$$O_3 + NO \rightarrow NO_2 + O_2 \quad (R3)$$

As the discharge power is increased from 5 W to 10 W, the vibrational temperature of Nitrogen increases which clearly initiates the transition to an ozone-poisoning mode; these results are highly consistent with previous reports on the poisoning effect of NO on O_3 [20,21].

With low plasma power, the concentration of ozone in the gas phase is high and its flux to the liquid layer is also significant; yet, recent studies focusing on similar discharges in contact with water have indicated that the concentration of aqueous O_3 is relatively low [22]. This is due in part to the relatively low Henry's law constant of O_3 coupled with rapid reactions occurring at the gas–liquid interface. Table 2 shows the main reactions for O_3 destruction at the gas–liquid interface. Many of the products formed in these interface reactions are precursors for the production of Reactive Oxygen Species (ROS) and Reactive Nitrogen Species (RNS) in the bulk liquid that play a significant role in the decolorization process.

To assess the impact of plasma generation conditions on O_3 production, the time evolution of O_3 in the reactor was measured, as shown in Fig. 5. In the 100%, 75% and 50% duty cycle tests, the concentration of ozone in the reactor peaked after a given time (dependent on conditions) followed by a decay. In the 25% duty cycle tests the curve plateaus with no perceptible downward slope. This downwards trend is attributed to a reduction in the ozone production rate at the elevated temperatures associated with higher power operation, increased thermal decomposition of ozone and enhanced quenching by nitrogen oxides. The peak ozone concentration in the 25% duty cycle test is approximately 50% lower than that observed in the 5 W, 100% duty cycle test; however, this lower level is maintained indefinitely for the duration of the 24 min test. It is clear to see that as duty cycle increases, the peak level of ozone inside the reaction chamber increases but is accompanied with an increasingly rapid decay. Given that the 25% duty cycle test establishes a condition where the sample solution is exposed to a

Table 2
Key reactions for O_3 destruction at the gas–liquid interface.

Reaction	Rate coefficient [$M^{-1}\,s^{-1}$]	Ref.
$O_3 + OH^- \geq O_2 + HO_2^-$	40	[23]
$O_3 + OH^- \geq O_2^- + HO_2$	70	[24]
$O_3 + O^- \geq O_2^- + O_2$	5.0×10^9	[25]
$O_3 + O_2^- \geq O_3^- + O_2$	1.6×10^9	[23]
$O_3 + HO_2^- \geq O_2^- + O_2 + OH$	5.5×10^6	[23]
$O_3 + OH \geq HO_2 + O_2$	3×10^9	[23]
$O_3 + HO_2 \geq O_2 + HO_3$	5.0×10^8	[25]
$O_3 + HO_2 \geq OH + 2O_2$	1.0×10^4	[26]
$O_3 + H_2O_2 \geq OH + HO_2 + O_2$	6.5×10^{-3}	[26]
$O_3 + H \geq HO_3$	3.8×10^{10}	[25]
$O_3 + NO_2^- \geq O_2 + NO_3^-$	$5 \times 10^5 \exp(-6950/T_w)$	[26]

high level of ozone for the entire duration of the test, it is clear to see why this is the most effective test condition. A longer exposure to ozone and a decreased concentration of nitrogen oxides that would otherwise compete with dye molecules for ROS can partly explain the two-fold increase in degradation efficiency. In the 7.5 W and 10 W continuous cases, ozone generation was severely restricted compared to the 5 W case. These observations are consistent with those of the dye degradation efficiency shown in Fig. 3. Given that the reaction chamber is sealed and the lifetime of ozone is known to be significant under ambient conditions, it was predicted that the level of ozone would not decrease significantly on a minute timescale. In Fig. 5, the pulse modulated cases with a period of 2 min highlight a significant decay of ozone density (>25%) within 60 s. This decay rate is far greater than the predicted ozone decomposition under the experimental conditions used. Based on this we can conclude that Ozone is readily being lost at the liquid surface and is not simply decomposing in the gas phase.

While ozone is clearly important in the gas phase, its relatively low concentration in solution indicates that it is not the primary agent responsible for the decolorization process. In the bulk liquid, hydrogen peroxide concentration is relatively high in comparison to other ROS species thus suggesting it may play a significant role. This hypothesis is in line with the findings of other plasma-based AOP studies [27,28], and, given the relatively long lifetime of H_2O_2 in solution, it can partly explain the post-treatment decolorization observed. Consequently, it can be concluded that in an SBD reactor, ozone is a critical intermediary species and changes made to the plasma-generating waveform that enhance ozone production will translate to enhanced degradation efficiency. This finding is in line with both the measured ozone density under pulse modulated plasma generation and the observed two-fold increase in dye degradation.

3.3. Concentration of nitrogen oxides

As discussed in the previous section, NO production is undesirable due to its poisoning effect on O_3; however, in the context of an industrially-viable plasma-based AOP NO production has a second important repercussion. For real-life scenarios where treated water is released back in to the environment, strict rules are in place on the allowable level of dissolved nitrates and nitrites [29,30]. From Fig. 4, it is clear that NO_x species generated by the plasma are present in the gas phase; their concentration increases dramatically with increasing discharge power. In the liquid phase, species such as HNO_2 dissociate to form NO_2^- which reacts with O_3 to form NO_3^-.

To confirm the hypothesis that the generation of large concentrations of NO_x species in the gas phase leads to nitrate and nitrite formation in solution, the nitrate and nitrite concentration in plasma-treated DI water samples was measured. Fig. 6 shows the concentration after exposure to both pulse-modulated and continuously-generated plasma. As the plasma power was increased, the concentration of both nitrate and nitrates in solution increases; this is in-line with the FTIR results highlighted in Fig. 4. Given that the EU Nitrates Directive (91/676/EEC) indicates that nitrate concentrations of 50 ppm and above are a cause for concern in both surface and groundwater, it is clear that plasma based AOP's operating in air have the potential to produce problematic levels of contamination; pulse modulation of the discharge minimizes this hence offers a means to greatly improve the final water quality.

3.4. pH and conductivity

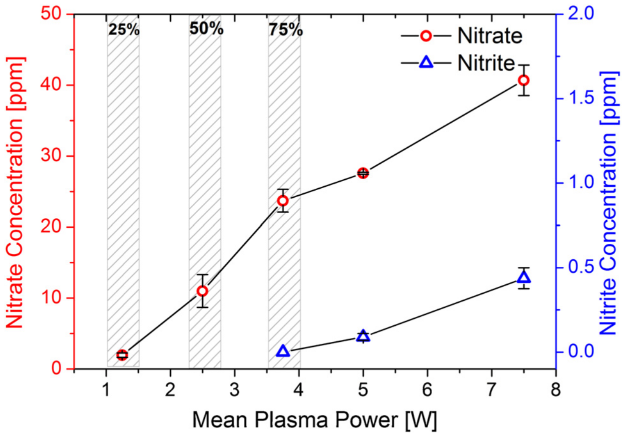

Fig. 6. Nitrate and nitrite concentration in a distilled water sample post plasma treatment with respect to mean plasma power; percentages indicate duty cycle used.

In addition to contaminating the treated water with nitrates and nitrites, plasma reactors typically generate other undesirable compounds such as acids. These ionic compounds increase conductivity and decrease the pH of the treated solution, as is depicted in Fig. 7. The decrease in pH can be partly explained by the formation of nitrogen oxides, as outlined previously, and their subsequent dissolution into water leading to nitrite NO_2^- and nitrate ions NO_3^-. These, in turn, form nitric acid HNO_3 and peroxynitrous acid ONOOH [31].

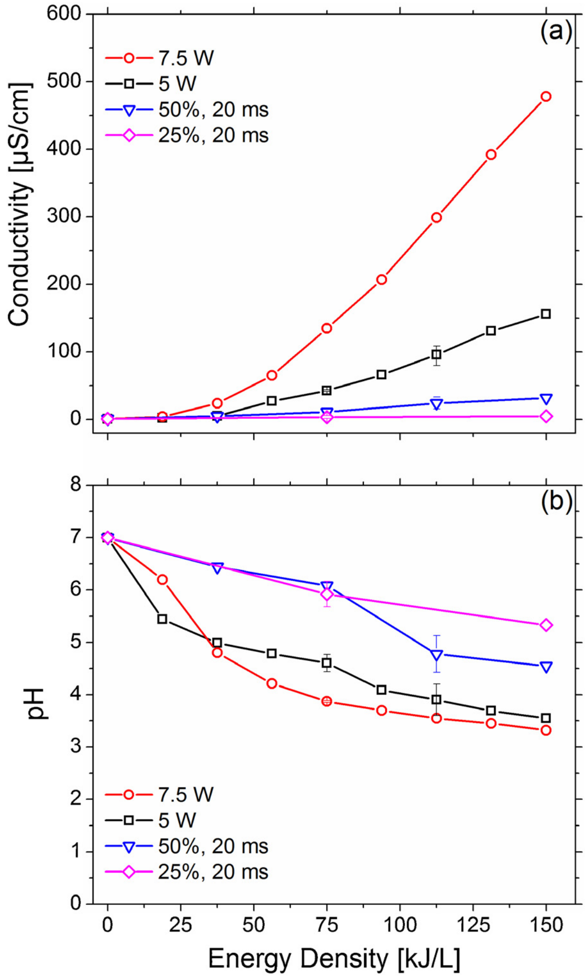

Fig. 7. Evolution of (a) conductivity and (b) pH of DI water sample, as a function of plasma energy density.

Although the SBD used in this study follows the same pattern as other plasma systems, the lowest power case (25% duty cycle) registered the smallest change in conductivity and pH despite being the most effective at degrading MO. This indicates that pulse modulation of the discharge can lead to enhanced discharge chemistry: in this case reducing the production of nitrogen oxides while maintaining ozone production.

4. Summary

Decolorization of the organic dye methyl orange was examined using a surface barrier discharge reactor at various excitation duty cycles, periods and power settings. It was found that degradation efficiency for pulse modulated cases, i.e. those with duty cycles of less than 100%, was significantly higher than cases in which continuous sinusoidal excitation was employed. It was demonstrated that dye degradation efficiency can be more than doubled when using a pulse modulation duty cycle of 25% compared to continuously generated plasma. The period of the pulse modulated signal was determined to not have a significant impact on dye decolorization efficiency.

Measurements of ozone evolution in the reactor showed that the concentration of ozone reaches a peak shortly after plasma ignition, followed by a period of decay; with the rate of decay being linked to an increase in plasma temperature and elevated NO production. Although the peak ozone concentration was found to be lower in the pulse modulated cases, the decay rate was also lower, with the 25% duty case showing only a very slight reduction over the duration of the test. In conclusion, improvements in the degradation efficiency when using pulse-modulation excitation can be attributed to: (1) the sample having a longer residence time in the reactor thus allowing for greater absorption of long-lived reactive species, (2) the reduction of gas heating leading to an increase in O_3 production coupled with reduced thermal decomposition and (3) a reduced production of NO and subsequent poisoning of the ozone formation process. Pulse modulation period did not have a significant effect on the degradation efficiency, indicating that plasma species in the reactor have already reached equilibrium within 1 ms, the shortest plasma-on time considered.

Pulse-modulated tests produced a reduced concentration of nitrites, nitrates and other ionic compounds compared with continuous-wave tests. In the best case, nitrate concentration was reduced by a factor of 22 compared to continuously-generated plasma. From the results it is clear that manipulation of the electrical excitation, specifically via pulse modulation, is an effective means to enhance the efficiency of plasma mediated breakdown of organic contamination in water. Additionally, this improvement is achieved whilst simultaneously improving the quality of water such that it is suitable for discharge without further processing. In summary, it is clear that pulse modulation introduces multiple benefits for plasma based dye degradation; however, for an industrially viable water-treatment system based on such technology a trade-off would need to be reached between the energy efficiency of the system and treatment time required to obtain sufficient degradation.

Acknowledgments

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