

# The Importance of Transport Phenomena in the Design of Gas-Liquid Electrical Discharge Plasma Reactors

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**Abstract:** This work investigates contaminant removal in three gas-liquid electrical discharge reactors: plasma spinning disc reactor, bubble column reactor and lateral flow reactor with the purpose of identifying the hydrodynamic parameter(s) relevant to designing and operating highly efficient plasma reactors. Rhodamine B dye and caffeine were used as model contaminants. The effect of discharge properties on the degradation was assessed by varying the input energy. The effect of gas-liquid contact parameters on the degradation was investigated by varying the individual reactor's operation parameters which included gas flowrate and bubble size, disc rotational speed and the characteristic reactor dimension. Results indicate that interfacial liquid renewal rate is the main predictor of the reactor performance irrespective of the type of contaminant present.

**Keywords:** bubbling, caffeine, plasma, rhodamine B, transport

## 1. Introduction

Low-temperature plasmas contacting liquids have applications in environmental remediation, medicine, and agriculture, among others [1]. The ability of the electrical discharge plasma to induce high chemical activity in the treated liquid without any chemical additives makes the technology an attractive alternative to conventional and advanced oxidation processes (AOPs) [2]. Plasmas owe their reactivity to the production of short-lived reactive species such as hydroxyl radicals and oxygen atoms, which non-selectively react with a range of organic and inorganic compounds. However, the generation of sufficient amounts of reactive species does not guarantee an effective degradation of a target compound in the liquid phase. Indeed, the target compound transport rate to the plasma-liquid interface plays a central role in the overall observed degradation kinetics [3, 4].

The primary objective of this work is to connect apparent degradation rates of several contaminants to mass transport and thus identify the phenomena relevant to designing and operating highly efficient plasma reactors. For that purpose three different gas-liquid discharge plasma reactor designs differing in hydrodynamics were used; plasma spinning disc reactor (PSDR), lateral flow reactor and bubble column reactor. The design of the PSDR maximizes the plasma-liquid contact while offering unprecedentedly high fluid renewal rates. The lateral flow reactor is a simple plasma-liquid system featuring laminar, unidirectional fluid flow in contact with the plasma. The system design allows independent control of the area of the plasma-liquid contact and the liquid flow under the plasma. The bubble column is a tubular reactor with a concentric rod-cylinder electrode configuration where plasma area enhancement is achieved by continuous sparging of a gas through a treated liquid.

## 2. Experimental

The plasma spinning disc reactor, shown in Fig. 1, consists of a circular stainless-steel disc mounted onto a hollow stainless-steel rod which acted as both the inlet for the liquid flow to the disc surface and the ground electrode.

The spinning disc was enclosed in a custom designed cylindrical acrylic chamber. The chamber was mounted on a square acrylic base which collected and directed the liquid leaving the disc to an external solution reservoir. The plasma source was an argon-driven atmospheric pressure plasma jet (APPJ) positioned 25 mm above the spinning disc and off centered ~18 mm from the liquid inlet. The entire acrylic assembly was mounted on an aluminum-reinforced acrylic box which housed the mechanism for the disc rotation. In the PSDR, liquid is introduced onto the surface of a rotating disc from its center from which it flows radially outward to the sides of the disc, as shown in Fig. 1. 0.2 mM Rhodamine B (RhB) solution with solution conductivity adjusted to 100 mS/cm using sodium chloride was introduced onto the spinning disc at various liquid flowrates from an external solution reservoir using a peristaltic pump. Total treatment volume was 250 mL. Electrical discharges were created by an AC power supply with a maximum voltage and frequency of 40 kV (peak-to-peak, VP-P) and 70 kHz, respectively.

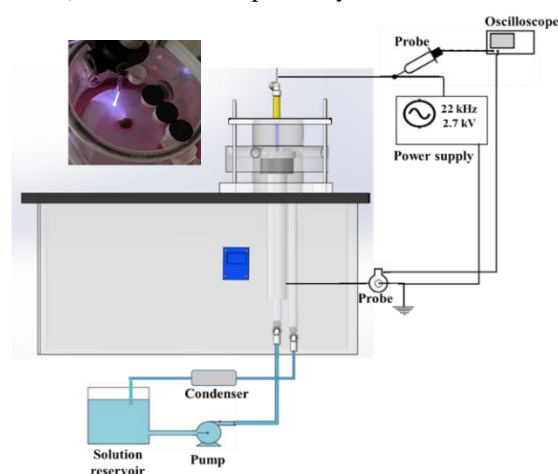


Fig. 1. Schematic of the overall PSDR experimental setup. Picture shows argon-driven atmospheric pressure plasma jet discharge contacting the surface of a RhB solution on the spinning disc.

The lateral flow reactor (Fig. 2) was a rectangular channel fabricated from scratch-resistant acrylic with a total volume of 54 mL. The solution was introduced into the reactor with a peristaltic pump at flowrates between 1 mL/s and 5 mL/s. The channel was divided into the inlet and the plasma generation zones with an acrylic sluice gate. The plasma generation zone was sealed from ambient air by a rubber gasket fitted with a gas inlet line and a high voltage (HV) electrode. Positive argon pressure was maintained in the reactor by a constant argon flow at 1.2 L/min. Electrical discharges were generated between a platinum wire HV electrode and a square platinum-coated titanium electrode. The HV electrode was positioned on the channel centerline in the gas phase 5 mm above the liquid surface. The position of the HV electrode along the reactor length was adjustable. The tested positions were 15, 30, 60, and 90 mm from the inlet sluice gate. The ground electrode was submerged in the solution at the reactor centerline within the inlet zone ~ 3.0 mm from the reactor back wall. The discharges were driven by a resistor-capacitor circuit with a 0.1 nF or 1 nF load capacitor at 40 Hz. Solutions containing 10  $\mu$ M of caffeine were treated in the plasma reactor in the semi-batch mode for 30 minutes. The total solution volume was 50 mL.

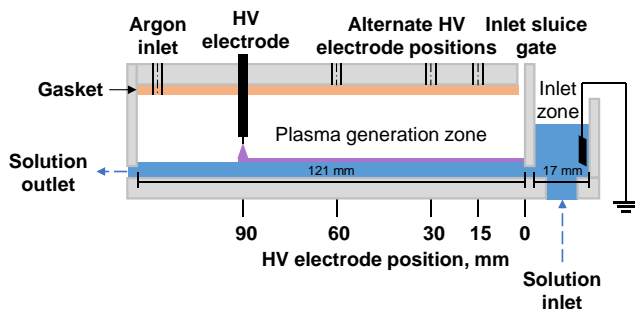


Fig. 2. Schematic of the the plasma channel semi-batch reactor with lateral solution flow.

The bubble column reactor shown in Fig. 3 consists of two sections: the bubble column and a solution overflow column. The bubble column with an internal diameter of 25.4 mm was made of three pipe segments of different materials. The top and the bottom bubble column segments were made of transparent PVC, while the middle segment was a stainless steel pipe which also served as the ground electrode. The HV electrode was a tungsten rod 3.2 mm in diameter. This electrode was situated in the middle of the bubble column, concentric to the reactor walls. The resulting interelectrode gap was 11 mm. The solution overflow column was made of transparent PVC, which was connected to the bubble column. The overflow column was used as an intermediate solution storage for experiments with constant solution recirculation and was disconnected during batch mode experiments. Argon gas (0.01–3.1 L/min) was introduced at the bottom of the bubble column through a sintered stainless-steel diffuser. The contaminant solution (10  $\mu$ M of caffeine or rhodamine B) was recirculated between the overflow column and the bubble

column with a peristaltic pump at flowrates up to 1 L/min. Pulses were formed by the same circuit used to generate plasma in the lateral flow reactor.

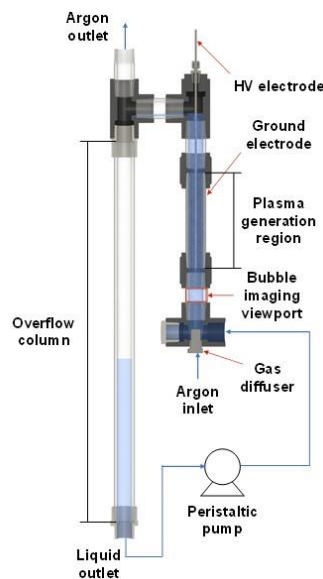


Fig. 3. Section view of the plasma bubble column reactor.

### 3. Results and Discussion

In the PSDR, RhB removal was investigated as a function of discharge power, disc rotational speed, and liquid flowrate (individual results not shown). It was noticed that changes in each of these parameters affected either the plasma area or the liquid velocity across the disc or both. Area and velocity control the residence time fluid spends under the plasma according to:

$$\tau = \frac{L_p}{v_{r,\max}} \quad (1)$$

where  $\tau$  (s) is the residence time,  $L_p$  (m) is the plasma length, obtained from images of the plasma spread on the liquid surface, and  $v_{r,\max}$  (m/s) is the surface velocity of fluid across the disc. Fig. 4 shows the removal rates of RhB dye as a function of liquid residence time derived from the variations in discharge power, disc rotational speed, and liquid flowrate. The plot reveals that regardless of the parameter used to calculate the residence time, the dye removal initially increases and then begins to plateau and even decrease with further increase in residence time. To better understand this behavior, we deconvoluted the area from hydrodynamic effects (fluid velocity) as shown in Fig. 5, by normalizing the dye removal rate with plasma area. Without the effect of the plasma area, for  $\tau > 2$  ms the removal rate is weakly dependent on residence time and we hypothesize that the degradation is limited by the rate of diffusive transport of RhB from the bulk to the interface. For  $\tau < 1.5$  ms, the removal rate increases as the flow transitions into the convection limited regime.

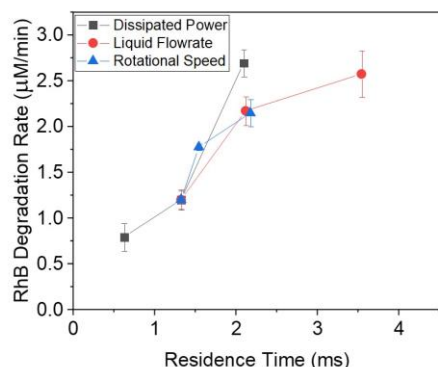


Fig. 4. PSDR degradation rates of RhB dye obtained from individual investigations into the effects of discharge power, liquid flowrate and rotational speed as a function of the residence time.

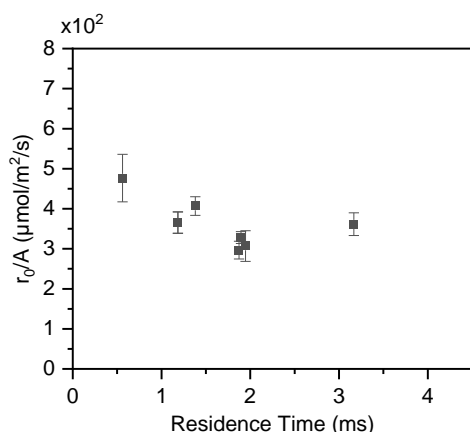


Fig. 5. PSDR degradation rates of RhB dye as a function of the residence time.

The lateral flow reactor allowed for independent investigations of the plasma area and fluid flow. Fig. 6 shows the caffeine degradation rate as a function of the contact area and the solution recirculation flowrate (surface flow speed). The contact area significantly affected the caffeine degradation rate. In contrast, the increase in the solution recirculation yielded no increase in the degradation rate for the smallest contact area. As the contact area increased, the effect of solution recirculation on degradation became apparent. For instance, at the contact area of 1271 mm<sup>2</sup>, the solution recirculation flowrate increase from 1 mL/s to 5 mL/s resulted in a 27% increase in the degradation rate. As observed for RhB removal in the PSDR, the plasma-liquid contact area effect on caffeine degradation was assumed to be closely related to the hydrodynamic effects and caffeine mass transport in the liquid phase.

Fig. 7 shows caffeine degradation rates normalized by the contact area as a function of contact time. High degradation rates up to  $6.1 \times 10^{-7}$  mol/m<sup>2</sup>/s were observed for short contact times (< 1 s). However, the rates quickly decreased with increasing contact time, and for long contact times (> 1 s), the degradation rate fluctuated around  $1.5 \times 10^{-7}$  mol/m<sup>2</sup>/s. The observed change in caffeine degradation rate suggests that the mass transport of caffeine is highly transient on a sub-second timescale.

A hydrodynamic model was developed to explain these results (details not shown). The results revealed two degradation mechanisms which depended on the characteristic plasma-liquid contact time. As suggested earlier from RhB results, for contact times < 1 s, caffeine was removed mainly from the interface by hydroxyl radicals (convection limited regime). For contact times > 1 s, the degradation rate was controlled by diffusion through the subsurface region (diffusion limited regime).

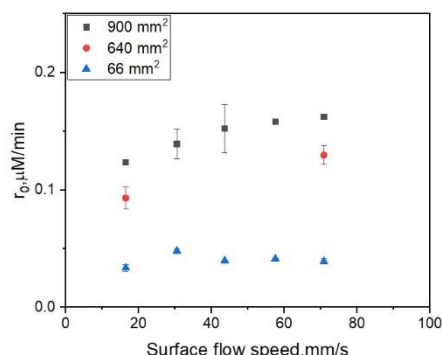


Fig. 6. Degradation rates of caffeine in the lateral flow reactor as a function of surface flow speed.

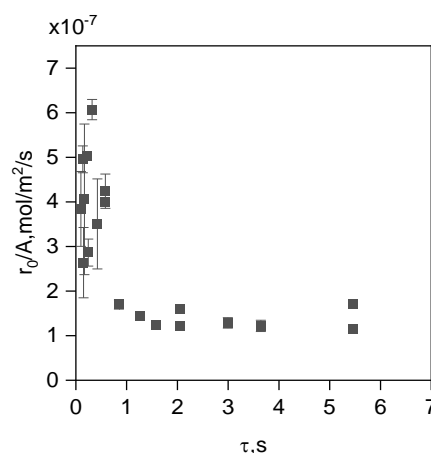


Fig. 7. Area-normalized degradation rates of caffeine in the lateral flow reactor as a function of liquid residence time.

Fig. 8 shows the removal rates (plotted as first order rate constants) of rhodamine B dye and caffeine in the bubble column reactor as a function of gas flowrate. Results reveal that for any given flowrate, the removal of rhodamine B exceeds that of caffeine. Gas flowrate ( $Q_g$ ), alongside the number of gas bubbles present ( $\varepsilon_g$ ) and bubble size ( $d$ ) all determine the liquid surface renewal rate in bubbling reactors which was hypothesized to control the removal rate of the two contaminants. Extensive bubble characterization experiments that were performed to characterize the bubbles revealed that surfactants such as rhodamine B prevent bubble coalescence, especially at high gas flowrates, which increases the total effective interfacial area. Compared to caffeine, rhodamine B bubbles were significantly smaller and were present at much higher concentrations throughout the reactor volume. Bubble imaging allowed for the calculations of  $\varepsilon_g$  and  $d$  which were used to calculate the liquid renewal rate. As shown in Fig. 9, the parameter scales almost linearly with the removal indicating that in bubbling reactors removal rates are determined by the volume and the size of the bubbles in the discharge zone, among other parameters.

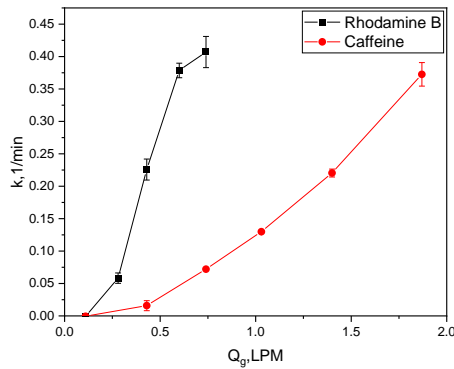


Fig. 8. Removal rate constants of caffeine and rhodamine B in the bubble column reactor as a function of gas flowrate.

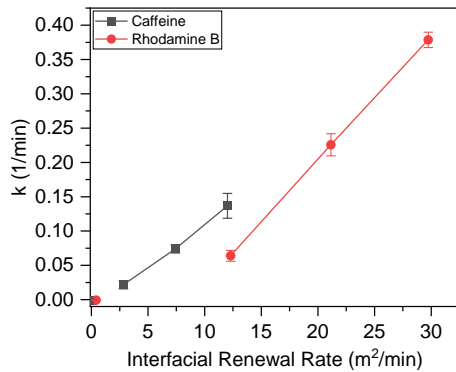


Fig. 9. Removal rate constants of caffeine and rhodamine B in the bubble column reactor as a function of interfacial renewal rate.

Fig. 10 compares the removal rates of caffeine as a function of interfacial renewal rates ( $\lambda$ ) for four different reactors. The reactor with the highest removal is the plasma spinning disc reactor which operates in the convection limited regime and allows for the fluid elements under the plasma to be rapidly renewed. Fluid renewal rates in the lateral flow square channel reactor are the lowest which decreases the contaminant removal rate.

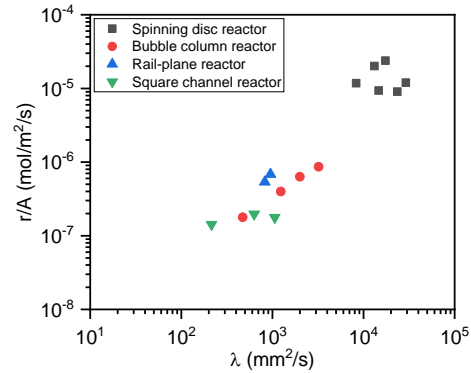


Fig. 10. Area-normalized removal rates of caffeine in four different plasma reactors as a function of interfacial renewal rate.

#### 4. Conclusions

This work has focused on determining a relationship between the contaminant removal and the liquid's surface renewal rate (flow speed). Results indicate that the contaminant removal is controlled by either the (1) fluid residence time – the time for which fluid elements contact plasma or (2) surface renewal rate – the rate at which (treated) fluid elements are replenished. In non-bubbling reactors, the highest contaminant removal rates are obtained for the lowest residence times, as those timescales do not allow for the diffusional resistances to be formed. In bubbling reactors, the removal rates are determined by the volume and the size of the bubbles in the discharge zone – the surface renewal rates. Those will be the largest for surfactant compounds.

#### 5. References

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