



Effect of recycling overhead gases on pollutants degradation efficiency in gas-phase pulsed corona discharge treatment



Vineeth Pothanamkandathil^a, Raj Kamal Singh^{b,*}, Ligy Philip^b, Sarathi Ramanujam^c

^a School of Civil and Chemical Engineering, VIT University, Vellore, Tamil Nadu, 632014, India

^b Department of Civil Engineering, Indian Institute of Technology, Madras, Chennai, Tamil Nadu, 600036, India

^c Department of Electrical Engineering, Indian Institute of Technology, Madras, Chennai, Tamil Nadu, 600036, India

ARTICLE INFO

Keywords:

Corona discharge
Reactive oxygen species
Gaseous ambiances
Recycled H₂O₂
Dye degradation
Economic comparison

ABSTRACT

In the present study, pollutant degradation efficiency was investigated by recycling of overhead gases from gaseous phase to aqueous phase in gas-liquid interface pulsed corona discharge reactor. Methylene blue (MB) was used as a model pollutant and its degradation was compared by recycling and non-recycling of oxygen, air and argon gases. The degradation rate constants of MB were 0.28 and 0.23 min⁻¹ in recycled condition which was decreased to 0.22 and 0.21 min⁻¹ in non-recycled condition in oxygen and argon gas, respectively. On contrary, in air medium, comparatively higher MB degradation rate (0.21 min⁻¹) was achieved in non-recycled condition compared to recycled condition (0.11 min⁻¹). The long-lived reactive oxygen species (ROS) such as hydrogen peroxide and ozone were quantified in both conditions. We observed that the concentration of ozone present in the aqueous solution was slightly higher in recycling conditions as compared to that of non-recycled condition in all the gases. Moreover, higher hydrogen peroxide concentration was detected in recycled condition (185 and 168 mg/L) compared to non-recycled condition (112 and 40 mg/L) in the presence of oxygen and argon, respectively, and vice-versa in air medium. The economic comparison revealed that up to 33% of electrical energy could be saved by recycling overhead oxygen gas.

1. Introduction

Water pollution is garnering major attention not only for its impact on water availability and quality, but also for its adverse effects on humans and aquatic ecosystem. Apart from microbiological contamination, the voracious consumption and introduction of new chemicals discharged by various industries such as textile, pharmaceutical manufacturing, tannery, paint, printing, cosmetics manufacturing etc, are on rise. Various chemical laden effluent by industries causes significant environment damage and human diseases [1–4].

Several conventional methods such as coagulation/flocculation [5], adsorption [6], biological treatment [7], and different advanced oxidation processes (AOPs) like ozonation [8], fenton oxidation [9], photofenton [10] and photo-catalytic degradation [11,12] have been implemented to treat the various organic pollutants from industrial effluent. However, many of these techniques are having some limitations. Conventional treatment methods are not effective in removing complex organic pollutants from industrial wastewater. Also, many pollutants are resistant to biological degradation, which results in the membrane fouling/damage (due to deposition and reactivity of the

pollutants on the surface or within the pore of the membrane) and incomplete mineralization [13]. Though AOPs have the potential to remove these pollutants from industrial wastewater, the treatment costs of these technologies are relatively higher and required large consumption of chemicals/catalysts [14,15]. Hence, researchers worldwide are still trying to find an optimized technique to reduce the impact of industrial discharges to the environment.

In recent time, plasma technology has emerged as one of the new advanced oxidation processes (AOP) for the treatment of organic compounds in water, sterilization of water, synthesis materials and nanoparticles, energy generation and application in medicines [16–27]. Corona discharge is one such method, which is widely being used recently by various researchers for the plasma generation to treat various organic pollutants and pathogens from water [28–33]. Typical corona discharge requires two asymmetrical electrodes; first, the electrode having very high curvature (such as needles and wires) and the second electrode having lesser curvature such as a plate. This configuration creates a very high electric field and very sharp voltage pulse in duration of nanoseconds to microseconds. Plasma can be generated either by high voltage electric discharge directly inside the water

* Corresponding author.

E-mail address: rsingh@clarkson.edu (R.K. Singh).

(electrohydraulic discharge) or as a discharge in the air above the water. High voltage corona discharge in air or water generates plasma, which is a mixture of highly reactive oxygen species (ROS) like hydroxyl radical, ozone, hydro peroxy, hydrogen peroxide and atomic oxygen, which then reacts with the organic contaminants and breaks them into innocuous compounds [16,34,35].

Direct corona discharge (electrohydraulic discharge) has its own pros and cons; direct interaction of the reactive species to the pollutants is advantageous whereas the concentration gradient that forms due to the low rate of transport in the liquid phase stands as the disadvantage [36,37]. Similarly, diffusion of reactive species from gas phase to bulk liquid is the major limitation of gas phase electrical discharge [38] and this shortcoming was avoided by developing hybrid gas-liquid reactor [39–42]. In hybrid system, high voltage reactor is submerged in the liquid and ground electrode is suspended in the gas phase. The benefit of this reactor is that the discharge could also happen in gas phase and liquid phase, intensifying the reactive species formation and thus resulting in an efficient pollutant removal by dissolving reactive species in the liquid. However, in hybrid gas-liquid discharges, a part of ROS generated in gaseous phase discharge may not diffuse and react with the pollutants present inside liquid. The recycling of ROS from overhead gaseous phase to liquid phase would increase the degradation efficiency of the corona discharge based plasma reactors.

Therefore, the objective of the present study is to recycle the ROS present in overhead gaseous phase to aqueous phase in order to further improve the pollutant degradation. Methylene blue (MB) was used as a model pollutant and its degradation was compared by recycling and non-recycling of overhead gases in the reactor. Though, some of the studies have discussed about the MB degradation in gas phase plasma treatment [32,42–46], the insight into efficient utilization of gas-phase ROS for the MB degradation is lacking. Thus, in this study an attempt was made for the efficient utilization of overhead gas-phase ROS for the MB degradation in gas phase corona discharge reactor. An economic comparison between recycling and non-recycling condition of the pulsed corona discharge treatment was also performed.

2. Materials and methodology

2.1. Reagents and apparatus

Methylene blue (99% purity, Paxmy chemicals, India) was used as a model organic pollutant. Titanium(IV) Oxysulfate-sulfuric acid (Sigma Aldrich, India) and Ozone kit (Prerna Laboratory, Pune, India) was used for the analysis of H_2O_2 and O_3 , respectively.

2.2. Experimental set up and reactor configuration

The experimental set up used in the present study is as shown in Fig. 1. For generation of high voltage an AC source was used, which consisted of a discharge-free test transformer (100 kV, 5 kVA) and the AC source was converted to a DC source using a high voltage diode (140 kV, 20 mA, 100 k Ω). The continuous DC source was converted to pulse by means of a Rotating Spark Gap (RSG), wherein the shape of the pulse was recorded by using an oscilloscope (HP 54645A, 100 MHz). The pulse voltage and injected current in the reactor was recorded using a voltage probe (EP-50 K, PEEC, Japan) and current probe (Pearson Electronics, USA, model no – 101), respectively.

The corona discharge was produced by using a multiple-needle and plate arrangement. The reactor consists of an electrode made of iron with nine streamers attached to a circular plate and the tip of each streamer needle had a radius of curvature of 50 μ m. The electrode was connected to the high voltage DC source. The bottom of the reactor was a plane electrode, which was grounded. The high voltage electrode was also adjustable in its pitch using a screw arrangement so that the electrode distance can be adjusted (increased or decreased) from the water surface. One pitch rotation was equivalent to 1 mm distance.

Therefore, the distance between tip of the needles and water surface can be adjusted 1 mm by one rotation of screw rod. The reactor chamber was formed using cylindrical glass of diameter 4.5 cm and height of 6 cm. The two electrodes were provided with ports and valves to facilitate the entry and exit of required gases (Ar, O_2 and Air), recycling of gases as well as for sample collection. Gas was recycled as forced system. Fresh gases were continuously introduced during the experiment, which could develop pressure in the head space above the liquid inside the reactor. A tube was connected from the head space to the bottom part of the electrode for the recycling. Due to the pressure gradient developed between the head space and liquid, the gases were recycled through bottom part of the reactor. A hole was provided at the center of the ground (bottom) electrode, through which recycled gas was introduced to the reactor. The reactor was provided with a water jacket in order to maintain constant temperature during the span of the experiment. The reactor was filled with 50 mL of sample solution methylene blue (MB) or water. The tip of the streamer was maintained at a height of 5 mm from the surface of the sample solution for the production of surface corona discharge. The reactor was sealed properly to prevent leaks of gases using a gasket and septum. The hard-flexible tube made up of teflon was used for the recycling experiments. The extra built pressure was released during each sampling (after 2 min of treatment time). There no condensation in the tube was observed during the experiment. The length, diameter and thickness of the tube was 10 cm, 6 mm and 1 mm, respectively. The temperature of the tube was around 30–40 °C.

2.3. Experimental procedure

Different batch experiments were performed for the degradation of MB and to measure the concentration of H_2O_2 and O_3 in recycled and non-recycled conditions. In recycled condition, the headspace gases were recycled back to aqueous phase by opening valve. For MB degradation, 50 mL sample solution of MB with 50 mg/L concentration was used as the sample and was treated in the reactor for a total duration of 10 min. Samples were collected at intervals of 2 min to measure the residual MB concentration in both recycling and non-recycling conditions. Similarly, various experiments were carried out in deionized water (50 mL) and concentrations of H_2O_2 and O_3 were measured. A constant flow rate of 50 mL/min of different gases (Oxygen, pure air and Argon) was purged during the experiments. Gases were introduced perpendicular to the liquid surface above 3 cm of the plasma region. The uniform gaseous environment can be expected due to 3 cm air gap. The system was purged for 5 min with a very high flow rate of gases before experimentation. All the batch experiments were performed at an applied voltage of 16 kV with a pulse frequency of 25 Hz. The solutions were manually mixed during each sampling (after each 2 min) in both recycling and non-recycling condition. All the experiments were performed in deionized water of initial pH 7 and conductivity of 18 μ S/cm. The MB degradation efficiency and energy consumption for the present treatment method were determined using Eqs. (1) and (2) [18,19].

$$\% \text{ Degradation } (\eta) = \left(1 - \frac{C_t}{C_0}\right) \times 100 \quad (1)$$

$$W_p = \int_{t=0}^{t=T} U(t)I(t)dt \times f \quad (2)$$

where C_0 (mg/L) was the initial MB concentration and C_t (mg/L) was the MB concentration at treatment time 't'. W_p is the input power (kW), which was calculated by recording instantaneous voltage, $U(t)$; and current $I(t)$ over the one cycle. 'f' was the applied pulsed frequency in Hz.

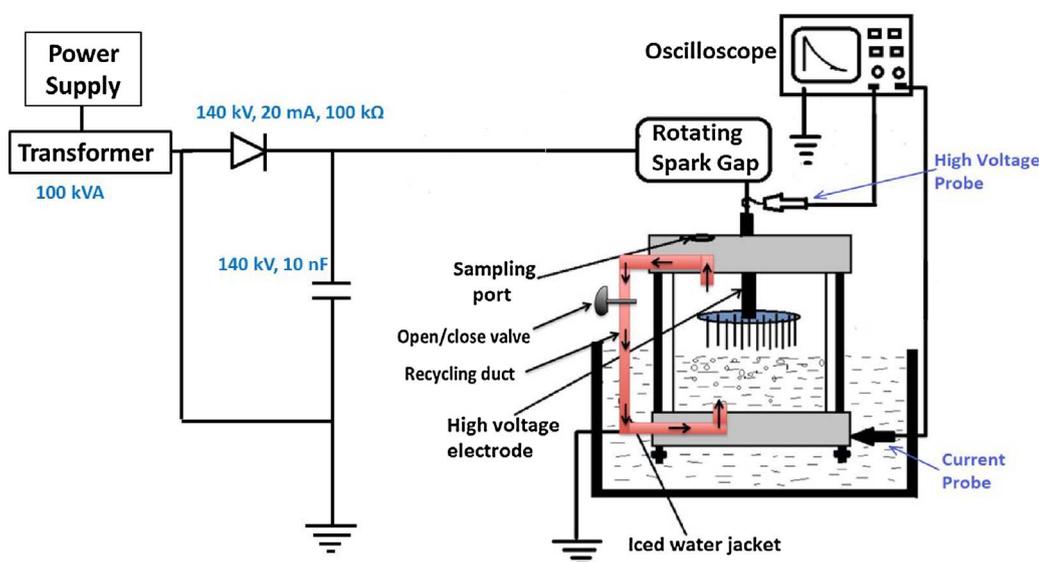


Fig. 1. Schematic of experimental set-up.

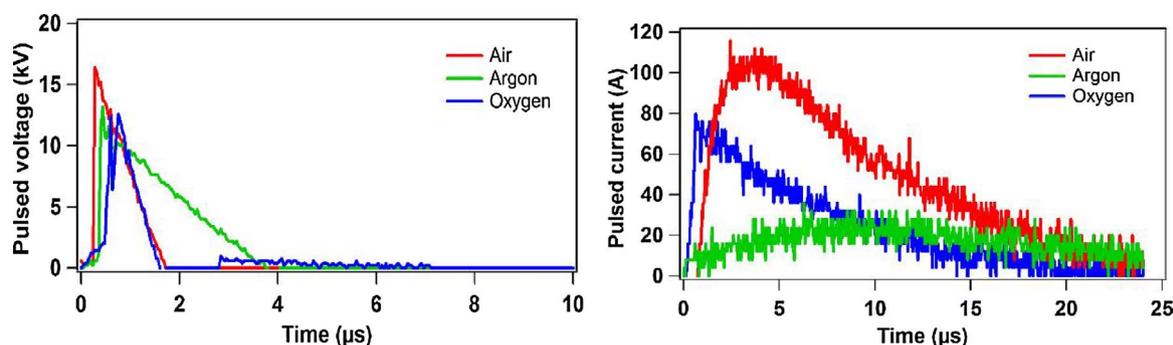


Fig. 2. Typical waveforms of discharged voltage (left) and discharged current (right) in presence of different gases.

2.4. Analytical procedures

2.4.1. Analysis of methylene blue (MB)

The concentrations of MB in the collected samples were measured using an UV spectrophotometer (Schimadzu, Japan) at maximum absorbance of 668 nm wavelength.

2.4.2. Analysis of hydrogen peroxide concentration

The concentration of H_2O_2 was determined by colorimetric method, where 2 mL of aqueous solution of reactor sample was mixed with 1 mL of titanium (IV) oxy sulfate-sulfuric acid solution to form perititanic acid complex. The complex formed gives a yellow colored solution whose concentration was determined by using an UV spectrophotometer at 410 nm wave length. The minimum hydrogen peroxide concentration measured was 1 mg/L.

2.4.3. Estimation of ozone (O_3)

An ozone kit (Prerana laboratories, Pune, India) based on DPD (*N,N*-diethyl-*p*-phenylenediamine) method was used to determine the concentration of dissolved O_3 in deionized water. The ozone reacts with DPD in the presence of potassium iodide to produce pink color. The intensity of color is proportional to the dissolved ozone concentration and was measured by comparison against standard color indicated on a comparator. The ozone kit could measure a minimum dissolved ozone concentration of 0.1 mg/L.

2.4.4. Total organic carbon analysis

The total organic carbon (TOC) content of the treated and non-treated samples was analyzed in TOC analyzer (Shimadzu, Japan). The

instrument was equipped with non-dispersive infrared analyzer. The purified air was used as the carrier gas. The blank experiments with deionized water were also performed. In order to minimize experimental errors, the TOC value of blank was subtracted from the TOC values of samples.

2.4.5. Estimation of nitrate concentration

Nitrate ion concentration in liquid samples was measured using AS11 (4×250 mm) column in ion chromatography (DX-100, Dionex, USA), equipped with electron conductivity detector. 3 mM methane sulfonic acid and 12 mM NaOH was used as eluent.

3. Results and discussion

3.1. Discharge characteristics

Pulsed voltage and current waveforms were recorded in different gases and is shown in Fig. 2. Pulse voltage of amplitude 16 kV and pulse frequency of 25 Hz were used in this experiment. The pulse width in air and oxygen was similar ($\sim 2 \mu\text{s}$). However, amplitude of pulse in oxygen medium was slightly lower than that of amplitude in air medium. In presence of argon, the pulse width was $4 \mu\text{s}$. The peak discharge current and area of the pulse in case of air medium, was found to be the highest followed by oxygen and argon. The average power dissipated in the discharge was 26.18, 22.23 and 21.75 W in air, oxygen and argon gas, respectively. We did not observe any significant variation in current profile in recycling and non-recycling conditions in different gases.

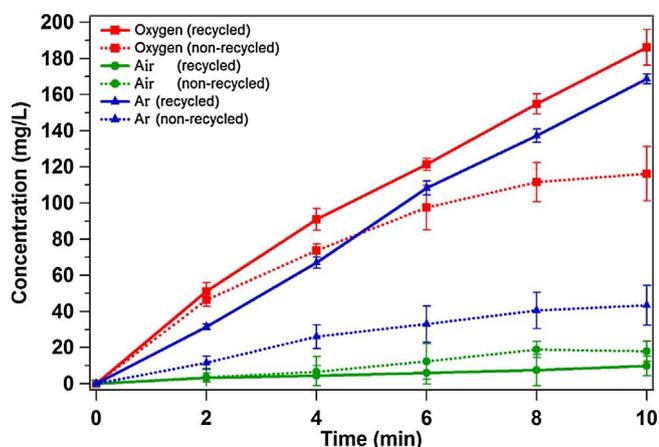


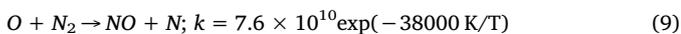
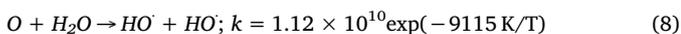
Fig. 3. Concentration of hydrogen peroxide in recycled and non-recycled condition; Initial pH of the solution = 7, gas flow rate = 50 mL/min, pulsed voltage and frequency was 16 kV and 25 Hz respectively.

3.2. Hydrogen peroxide concentration in recycled and non-recycled condition

The ROS such as $\cdot\text{OH}$, O , H_2O_2 and O_3 are responsible for the degradation of organic compounds in the water. In the presence of different gases, the ROS such as H_2O_2 and O_3 were quantified in recycled and non-recycled conditions in de-ionized (DI) water. The short-lived species such as $\cdot\text{OH}$, O , H and e^-_{aq} were not quantified as the residence time of ROS (2.4 s) in recycling duct is much higher than the lifetime of these short-lived species (in nano seconds). Therefore, these short-lived species would die-off or get converted to their stable form such as H_2O_2 before reaching to the aqueous solution. The results of the quantification of hydrogen peroxide in liquid phase are shown in Fig. 3. The result clearly shows a higher concentration of hydrogen peroxide in the recycling condition as compared to that of the non-recycling condition with oxygen and argon gases. This could be due to the dissolution of gas-phase H_2O_2 in water in recycled condition, which otherwise would not have been dissolved in the water (in case of non-recycling condition). The reactive species such as e^- , O , O_3 and $\cdot\text{OH}$ are responsible for the formation of H_2O_2 in the presence of water molecule in both gas-phase and aqueous solution (Eqs. (3)–(7)) [47]. The dissolution of additional gas-phase H_2O_2 increased the total H_2O_2 concentration in liquid-phase.

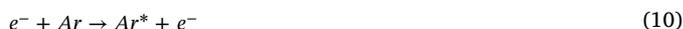


On contrary, a relatively higher concentration of H_2O_2 was detected in non-recycled condition compared to recycled condition in air medium. The lesser production of H_2O_2 in recycled condition could be due to the lesser production of ROS such as O and $\cdot\text{OH}$, and comparatively higher production of NO (Eqs. (8) and (9)). It is evident that the rate constant of Eq. (8) [48] is one order of magnitude lesser than the rate constant of Eq. (9) [49]. Therefore, the formation of NO by reaction between O and N_2 causes the depletion of O atoms in recycled condition and hence leading to a lesser H_2O_2 formation.



Hydrogen peroxide formation was also compared at different gaseous environments. The rate of H_2O_2 formation was found to be higher

in the presence of oxygen followed by argon and air. The value of the hydrogen peroxide and ozone concentration is comparable to the values reported in the plasma treatment processes [18,30,45]. The formation rate of main oxidative species during plasma generation under different ambient gases was discussed earlier in various literatures [39,50,51]. In the oxygen environment, the atomic oxygen gets generated by the bombardment of highly excited electrons in the plasma region (Eq. (3)). Atomic oxygen generates $\cdot\text{OH}$ after reaction with water molecules, which further gets converted to hydrogen peroxide (Eqs. (5) and (7)). The $\cdot\text{OH}$ also get formed by the dissociation of water molecules caused by the impaction of electrons (Eq. (6)). In argon environment, $\cdot\text{OH}$ can be formed only by the dissociation of water molecules caused by the excited Ar atoms (Eqs. (10) and (11)) [52]. In case of argon, the concentration of O and O_3 is negligible, which again leads to the lesser H_2O_2 production. However, it is worth to mention that a large increase (3.2 times) of H_2O_2 was observed in recycled condition compared to non-recycled condition. The probable reason could be the rate limiting step of Eq. (11), where the reaction between Ar^* and vapour phase H_2O droplets is more favourable (due to high interfacial mass transfer) compared to reaction between Ar^* and bulk H_2O .



In air, although excited nitrogen molecules can form the $\cdot\text{OH}$ by reaction with water molecules (Eq. (12)) [53], the formation of NO (Eq. (9)) leads to the depletion of available O atoms, which is required for the H_2O_2 formation. However, the measurement for NO in gas phase was not performed in the study.



Nitrate and pH of the treated aqueous solution in the different gaseous medium is presented in Table 1. It can be noted that the nitrate concentration in air medium is significantly higher compared to oxygen and argon. Therefore, in air medium, NO_3^- and NO_2^- formed by the dissolution of NO in water can also react with H_2O_2 , which could further reduce the H_2O_2 concentration in water.

3.3. Effect of recycling on ozone formation

The quantification of ozone was performed at pulsed voltage of 16 kV and the results obtained are shown in Fig. 4. The production of ozone in case of the recycled condition as compared to that of the non-recycled condition in all the gases. The fastest rate of production of ozone was observed in recycled condition in the oxygen environment followed by air and argon environment. This is a predictable observation as the abundance of oxygen present in the reactor facilitates higher production rates of ozone (Eqs. (3) and (4)). The ozone concentration was also detected in case of argon. This may be due to the dissolved oxygen present in the water, which could react with atomic oxygen and form ozone molecules in the water. However, the detected ozone concentration was very less ($\leq 1 \text{ mg/L}$) in all the gases. Similar trend have been reported in earlier studies [18,32,54].

3.4. Effect of recycling of gases on MB degradation

For the MB degradation experiment, 50 mL of MB sample was

Table 1
Nitrate concentration and pH in deionized water after 10 min of plasma treatment in presence of different gases.

	Oxygen	Argon	Air
Nitrate (mg/L)	8.62 ± 3.05	9.31 ± 3.28	134 ± 14.46
pH	2.95 ± 0.02	3.05 ± 0.02	2.64 ± 0.03

*Initial pH of solution was 6.9.

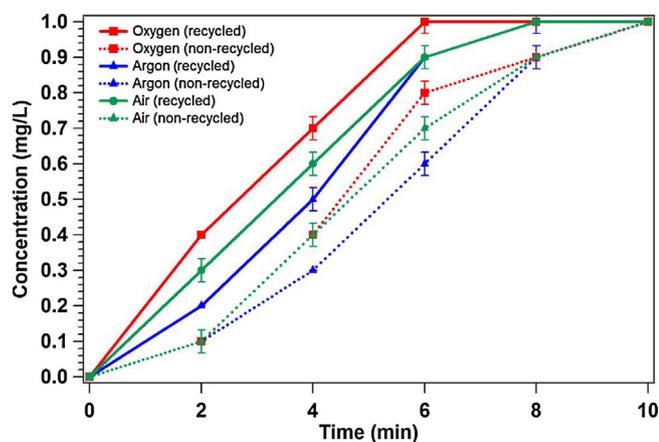


Fig. 4. Concentration of ozone generated in recycled and non-recycled condition; Initial pH of the solution = 7, gas flow rate = 50 mL/min, pulsed voltage and frequency was 16 kV and 25 Hz, respectively.

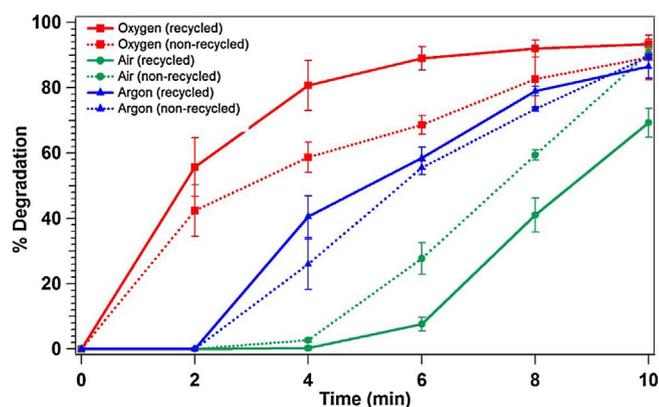


Fig. 5. Methylene blue degradation in recycled and non-recycled condition; Initial pH of the solution = 7, gas flow rate = 50 mL/min, pulsed voltage and frequency was 16 kV and 25 Hz respectively.

treated in the reactor first with oxygen followed by argon and finally with air supplied at 50 mL/min in order to study the difference in degradation of MB in the three ambient conditions. The results of the experiment are as shown in Fig. 5. A figure representing the validation of pseudo-first order kinetics is also shown in Fig. 1S of Supplementary material. In ambient oxygen, a faster degradation rate of MB was observed in the recycling condition compared to that in the non-recycling condition. In case of argon, a similar trend was observed, however, a delay of 4 min was observed during starting of the degradation process. However, in presence of air, the MB degradation in non-recycled condition was higher than that of the recycled condition, which could be correlated with the H_2O_2 production in the reactor (Fig. 3). The concentration of H_2O_2 in water is the indirect representation of higher $\cdot OH$ concentration in aqueous solution, as indicated in Eqs. (13) and (14). However, dissociation of water vapor molecules due to direct electron impact is the common source of $\cdot OH$ formation in all the gases as shown in Eq. (15) [55]. The formation of oxidizing species such as $\cdot OH$ in different gaseous environment is responsible for the pollutant degradation and their concentrations is the indirect indication of the pollutant degradation efficiency [32,40,50,56]. Also, recycling may cause bubbles, which help in interfacial mass transfer and in turn increases the pollutant degradation.



Table 2
TOC reduction in recycled and non-recycled conditions in presence of different gases after 12 min of treatment time; Applied pulsed voltage = 16 kV and frequency = 25 Hz.

	Oxygen	Argon	Air
Recycled	72%	62%	45%
Non-recycled	66%	61%	56%

Also, it is noted that, after 10 min, the difference in% degradation is not significant in case of oxygen and argon gas. After 10 min of treatment, the concentration of MB is low (< 10 mg/L) and hydrogen peroxide concentration is too high (168–185 mg/L). Therefore, the concentration of oxidants would not be limiting for MB degradation. Hence, an insignificant difference in MB degradation was observed in recycling and non-recycling condition.

The mineralization of the MB in recycled and non-recycled condition was further evaluated using TOC analysis and the results are shown in Table 2. TOC reduction results are in consistent with the results of MB degradation (Fig. 5 and Table 2). From, Table 2, it is evident that the higher TOC reduction was obtained in oxygen gas followed by argon and air. TOC reduction in recycled oxygen gas was 72%, which was higher than that of in non-recycled oxygen gas (66%). On contrary, a higher TOC reduction was obtained in non-recycled air medium compared to recycled air medium. Nonetheless, the difference in TOC in recycled and non-recycled argon was insignificant. A good TOC removal was achieved in the system. The reactor volume was very low (50 mL) and power deposition was very high (21.75–26.18 W). Due to higher energy deposition in small volume of aqueous solution, a high pollutant mineralization can be expected. Some of the previous studies reported the TOC removal in the range of 20–70% by utilizing power of 1–70 W under the different plasma treatment process [30,32,44,45].

3.5. Economic comparison between recycled and non-recycled condition

Comparison of treatment cost is very important aspects for the implementation of any technology. An attempt was made to compare the operation cost of the present treatment system in recycling and non-recycling conditions. The operating cost was evaluated in terms of consumption of electrical energy (EE), which was expressed in kWh required per m^3 of water treated. The treatment level was fixed for 50% and 90% degradation efficiency. The pseudo first order kinetic constants (k) and treatment times ($t_{0.5}$ and $t_{0.9}$) were also compared in recycled and non-recycled conditions. From Table 3, it is evident that the treatment cost in recycling condition is significantly lower than that in non-recycling condition in all the gases except air. Similarly, the treatment time required in recycled conditions was much lower than that of non-recycled conditions, as the rate constants were higher in recycled conditions. For the 50% MB degradation with recycling, 33.34 and 9.1% electrical energy can be saved in oxygen and argon gas, respectively. Also for the 90% MB degradation, the electrical energy can

Table 3

A brief comparison of pulsed corona discharge treatment in recycling and non-recycling condition of ROS; where k = first order kinetic constant, $t_{0.5}$ = Time required for 50% MB degradation, $t_{0.9}$ = Time required for 90% MB degradation, $EE_{0.5}$ and $EE_{0.9}$ are the electrical energy required for 50 and 90% MB degradation, respectively, at an initial concentration of 50 mg/L.

Parameters	Recycled			Non-recycled		
	Oxygen	Argon	Air	Oxygen	Argon	Air
k (min^{-1})	0.28	0.23	0.11	0.22	0.21	0.21
$t_{0.5}$ (min)	2.00	5.00	9.00	3.00	5.50	5.50
$t_{0.9}$ (min)	7.00	10.50	11.50	10.50	10.50	10.50
$EE_{0.5}$ (kWh/m^3)	14.82	36.25	78.54	22.23	39.88	48.00
$EE_{0.9}$ (kWh/m^3)	51.87	76.12	100.36	77.78	76.12	91.62

Table 4

A brief economic comparison across various studies use plasma treatment for MB degradation.

Types of discharge	Electrode configuration	Treatment efficiency (%)	Energy yield (g/kWh)	References
DBD	Wire-to-cylinder	73–94	13.1–67.0	[45]
DC Diaphragm discharge	Two electrodes separated by a pin-hole diaphragm	50	0.042	[60]
RF plasma	Pipe-to-rod	50	0.037	[61]
Microwave discharge	–	50	0.16	[62]
PCD	Needle-to-plane	50	0.34	[63]
DBD	Rod-to-cylinder	95	57	[58]
DBD	Multiple wire-to-plane	50	1.30	[59]
PCD	Multiple pin-to-plane	90	7.64–28.65	Present study

DBD – Dielectric Barrier Discharge, PCD – Pulsed Corona Discharge.

be remarkably reduced by 33.31 and 2.1% in oxygen and argon gas, respectively. Thus, it is evident that the operating cost of gas-phase pulsed corona discharge processes can be significantly reduced by recycling overhead gases.

Regarding energy efficiency, various studies have reported varied efficiency in terms of g/kWh of pollutant degradation. The reported energy efficiency in literature varied between 0.1 and 57 g/kWh depending on the types of electrical discharges and initial pollutant concentration [43,57–59]. In the present study, the energy efficiency obtained was in the range of 7.64–28.65 g/kWh under various conditions as mentioned. A brief economic comparison for the removal of recalcitrant pollutants from above reported literature is summarized in Table 4. In general, it is observed that the energy efficiency is good for higher pollutant concentration in plasma reactor. Also, it is noted that the energy efficiency is generally higher for the dielectric barrier discharge compared to corona discharge processes.

Different experimental conditions, variable pollutant concentrations employed in various water treatment technologies makes it difficult to compare the treatment cost. However, considering different experimental conditions some recent review paper reported the cost involved in the various AOPs and adsorption process. Deng et al., reported the treatment cost range between \$66 to \$206/m³ in UV assisted AOPs [64]. Mahamuni et al., extensively reviewed the cost involve in ultrasonication, UV, ozone, photocatalysis and hydrogen peroxide assisted process and reported the treatment cost in the range of \$5 and \$4105/m³ treatment of various types of pollutants in wastewater [65]. In this study, we achieved the treatment cost as low as \$52/m³ for 90% MB removal in recycling conditions which is comparable to other AOPs, however, higher than the adsorption process. Adsorption processes uses activated charcoal, clay, zeolites and biomass material, whose market price are very cheap as \$0.03–\$0.12/kg [66]. However, mineralization of pollutants, recovery and disposal of adsorbents causes an extra environmental and economic burden. In the present scenario, though plasma processes require comparatively higher cost for the removal of recalcitrant pollutants from wastewater, it has obvious advantages such as clean, no requirement of chemical additives and high mineralization capabilities of recalcitrant chemicals.

4. Conclusion

A gas-liquid interface pulsed corona discharge reactor with recirculation of overhead gases was successfully designed and used for the MB degradation from aqueous solution. In the oxygen environment, the hydrogen peroxide, ozone concentration and dye degradation were improved significantly by recycling gaseous phase ROS into aqueous phase. H₂O₂ concentration increased by 65 (73 mg/L) and 320% (128 mg/L) by recycling overhead oxygen and argon gas, respectively. However, the H₂O₂ concentration was decreased marginally in recycling air due to scavenging of reactive atomic oxygen by NO species. By recycling, the electrical energy require for 50% MB degradation efficiency was significantly reduced by 33.34 and 9.1% in the presence of oxygen and argon gases, respectively. Higher degradation efficiency

was observed in presence of oxygen followed by argon and air. TOC reduction also improved from 66 to 72% by recycling overhead oxygen gas. This study could help in improve the degradation efficiency and minimize energy cost by recycling gases. The approach of the present study can be implemented in the design of continuous flow reactor also. The multiple tubes can be used for the recycling of gases from head space plasma region to the flowing liquid region. However, this study provides the first-hand information for the designing a big-scale plasma treatment system with the provision of recycling of head space gases. Further study needed for the implementation of this recycling design aspects in plasma reactors.

Acknowledgement

The authors acknowledge the financial support received from Department of Science and Technology (DST), Government of India, for this study.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.jece.2018.01.029>.

References

- [1] A.J. Sipos, H. Urakawa, Differential responses of nitrifying archaea and bacteria to methylene blue toxicity, *Lett. Appl. Microbiol.* 62 (2015) 199–206.
- [2] Y. Yang, Y. Sik, K. Kim, E.E. Kwon, Y. Fai, Occurrences and removal of pharmaceuticals and personal care products (PPCPs) in drinking water and water/sewage treatment plants: a review, *Sci. Total Environ.* 596–597 (2017) 303–320.
- [3] S. Kuppasamy, P. Thavamani, K. Venkateswarlu, Remediation approaches for polycyclic aromatic hydrocarbons (PAHs) contaminated soils: technological constraints, emerging trends and future directions, *Chemosphere* 168 (2017) 944–968.
- [4] G. Galezowska, M. Chraniuk, L. Wolska, In vitro assays as a tool for determination of VOCs toxic effect on respiratory system: a critical review, *TrAC – Trends Anal. Chem.* 77 (2016) 14–22.
- [5] A.K. Verma, R.R. Dash, P. Bhunia, A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters, *J. Environ. Manag.* 93 (1) (2012) 154–168.
- [6] A.A. Kadam, H.S. Lade, S.M. Patil, S.P. Govindwar, Low cost CaCl₂ pretreatment of sugarcane bagasse for enhancement of textile dyes adsorption and subsequent biodegradation of adsorbed dyes under solid state fermentation, *Bioresour. Technol.* 132 (2013) 276–284.
- [7] W. Przysaś, E. Zabłocka-Godlewska, E. Grabińska-Sota, Biological removal of azo and triphenylmethane dyes and toxicity of process by-products, *Water Air Soil Pollut.* 223 (4) (2012) 1581–1592.
- [8] K. Turhan, I. Durukan, S.A. Ozturkcan, Z. Turgut, Decolorization of textile basic dye in aqueous solution by ozone, *Dye Pigm.* 92 (3) (2014) 897–901.
- [9] N.P. Tantak, S. Chaudhari, Degradation of azo dyes by sequential Fenton's oxidation and aerobic biological treatment, *J. Hazard. Mater.* 136 (3) (2006) 698–705.
- [10] M.M. Alnuaimi, M.A. Rauf, S.S. Ashraf, Comparative decoloration study of Neutral Red by different oxidative processes, *Dye Pigm.* 72 (3) (2007) 367–371.
- [11] N. Talebian, M.R. Nilforoushan, Comparative study of the structural, optical and photocatalytic properties of semiconductor metal oxides toward degradation of methylene blue, *Thin Solid Film* 518 (8) (2010) 2210–2215.
- [12] R. Salazar, E. Brillas, I. Sirés, Finding the best Fe²⁺/Cu²⁺ combination for the solar photoelectro-Fenton treatment of simulated wastewater containing the industrial textile dye Disperse Blue 3, *Appl. Catal. B Environ.* 115–116 (2012) 107–116.
- [13] A. Asghar, A. Aziz, A. Raman, W. Mohd, A. Wan, Advanced oxidation processes for in-situ production of hydrogen peroxide/hydroxyl radical for textile wastewater

- treatment: a review, *J. Clean. Prod.* 87 (2015) 826–838.
- [14] N. Klammerth, S. Malato, M.I. Maldonado, A. Agüera, A.R. Fernández-Alba, Application of photo-fenton as a tertiary treatment of emerging contaminants in municipal wastewater, *Environ. Sci. Technol.* 44 (5) (2010) 1792–1798.
- [15] A.R. Ribeiro, O.C. Nunes, M.F.R. Pereira, A.M.T. Silva, An overview on the advanced oxidation processes applied for the treatment of water pollutants defined in the recently launched Directive 2013/39/EU, *Environ. Int.* 75C (2014) 33–51.
- [16] B.R. Locke, M. Sato, P. Sunka, M.R. Hoffmann, J.-S. Chang, Electrohydraulic discharge and nonthermal plasma for water treatment, *Ind. Eng. Chem. Res.* 45 (3) (2006) 882–905.
- [17] B. Jiang, J. Zheng, S. Qiu, M. Wu, Q. Zhang, Z. Yan, Q. Xue, Review on electrical discharge plasma technology for wastewater remediation, *Chem. Eng. J.* 236 (2014) 348–368.
- [18] R.K. Singh, V. Babu, L. Philip, S. Ramanujam, Disinfection of water using pulsed power technique: effect of system parameters and kinetic study, *Chem. Eng. J.* 284 (2016) 1184–1195.
- [19] R.K. Singh, L. Philip, S. Ramanujam, Disinfection of water by pulsed power technique: a mechanistic perspective, *RSC Adv.* 6 (2016) 11980–11990.
- [20] X. Chen, L. Liu, F. Huang, Black titanium dioxide (TiO₂) nanomaterials, *Chem. Soc. Rev.* 44 (2015) 1861–1885.
- [21] S.G. Kumar, K.S.R.K. Rao, Comparison of modification strategies towards enhanced charge carrier separation and photocatalytic degradation activity of metal oxide semiconductors (TiO₂, WO₃ and ZnO), *Appl. Surf. Sci.* 391 (2017) 124–148.
- [22] K.-D. Weltmann, T.V. Woedtke, Plasma medicine –current state of research and medical application, *Plasma Phys. Control. Fus.* 59 (2016) 014031.
- [23] W. Liu, T. Wang, X. Chen, C. Ma, Characteristics and applications of diffuse discharges of water electrodes in air, *Plasma Sci. Technol.* 20 (2018) 014003.
- [24] J.E. Foster, Plasma-based water purification: challenges and prospects for the future, *Phys. Plasmas* 24 (2017) 055501.
- [25] C.M. Du, J.M. Mo, H.X. Li, Renewable hydrogen production by alcohols reforming using plasma and plasma-catalytic technologies: challenges and opportunities, *Chem. Rev.* 115 (3) (2015) 1503–1542.
- [26] X. Wang, M. Zhou, X. Jin, Application of glow discharge plasma for wastewater treatment, *Electrochim. Acta* 83 (2012) 501–512.
- [27] E. Tatarova, N. Bundaleska, J. Ph Sarrette, C.M. Ferreira, Plasma for environmental issues: from hydrogen production to 2D materials assembly, *Plasma Sources Sci. Technol.* 23 (2014) 063002.
- [28] H. Krause, B. Schweiger, J. Schuhmacher, S. Scholl, U. Steinfeld, Degradation of the endocrine disrupting chemicals (EDCs) carbamazepine, clofibric acid, and iopromide by corona discharge over water, *Chemosphere* 75 (2) (2009) 163–168.
- [29] D. Gerrity, B.D. Stanford, R.A. Trenholm, S.A. Snyder, An evaluation of a pilot-scale nonthermal plasma advanced oxidation process for trace organic compound degradation, *Water Res.* 44 (2) (2010) 493–504.
- [30] D. Dobrin, C. Bradu, M. Magureanu, N.B. Mandache, V.I. Parvulescu, Degradation of diclofenac in water using a pulsed corona discharge, *Chem. Eng. J.* 234 (2013) 389–396.
- [31] J. Zeng, B. Yang, X. Wang, Z. Li, X. Zhang, L. Lei, Degradation of pharmaceutical contaminant ibuprofen in aqueous solution by cylindrical wetted-wall corona discharge, *Chem. Eng. J.* 267 (2015) 282–288.
- [32] R.K. Singh, V. Babu, L. Philip, S. Ramanujam, Applicability of pulsed power technique for the degradation of methylene blue, *J. Water Process Eng.* 11 (2016) 118–129.
- [33] R.K. Singh, L. Philip, S. Ramanujam, Rapid removal of carbofuran from aqueous solution by pulsed corona discharge treatment: kinetic study, oxidative, reductive degradation pathway, and toxicity assay, *Ind. Eng. Chem. Res.* 55 (26) (2016) 7201–7209.
- [34] R.K. Singh, L. Philip, S. Ramanujam, Rapid degradation, mineralization and detoxification of pharmaceutically active compounds in aqueous solution during pulsed corona discharge treatment, *Water Res.* 121 (2017) 20–36.
- [35] R.K. Singh, L. Philip, S. Ramanujam, Removal of 2, 4-dichlorophenoxyacetic acid in aqueous solution by pulsed corona discharge treatment: effect of different water constituents, degradation pathway and toxicity assay, *Chemosphere* 184 (2017) 207–214.
- [36] S.M. Thagard, K. Takashima, A. Mizuno, Chemistry of the positive and negative electrical discharges formed in liquid water and above a gas–liquid surface, *Plasma Chem. Plasma Process.* 29 (6) (2009) 455–473.
- [37] B.R. Locke, S.M. Thagard, Analysis and review of chemical reactions and transport processes in pulsed electrical discharge plasma formed directly in liquid water, *Plasma Chem. Plasma Process.* 32 (5) (2012) 875–917.
- [38] W.F.L.M. Hoeben, E.M. van Veldhuizen, W.R. Rutgers, C.A.M.G. Cramers, G.M.W. Kroesen, The degradation of aqueous phenol solutions by pulsed positive corona discharges, *Plasma Sources Sci. Technol.* 9 (2000) 361–369.
- [39] H. Kusic, N. Koprivanac, B.R. Locke, Decomposition of phenol by hybrid gas/liquid electrical discharge reactors with zeolite catalysts, *J. Hazard. Mater.* 125 (2005) 190–200.
- [40] P. Lukes, B.R. Locke, Degradation of substituted phenols in a hybrid gas – liquid electrical discharge reactor, *Ind. Eng. Chem. Res.* 44 (2005) 2921–2930.
- [41] M. Sahni, B.R. Locke, Degradation of chemical warfare agent simulants using gas –liquid pulsed streamer discharges, *J. Hazard. Mater.* 137 (2006) 1025–1034.
- [42] F. Holzer, B.R. Locke, Multistage gas – liquid electrical discharge column reactor for advanced oxidation processes, *Ind. Eng. Chem. Res.* 47 (3) (2008) 2203–2212.
- [43] F. Huang, L. Chen, H. Wang, Z. Yan, Analysis of the degradation mechanism of methylene blue by atmospheric pressure dielectric barrier discharge plasma, *Chem. Eng. J.* 162 (1) (2010) 250–256.
- [44] L.O.D.B. Benetoli, B.M. Cadorn, V.Z. Baldissarelli, R. Geremias, I.G. de Souza, N.A. Debacher, Pyrite-enhanced methylene blue degradation in non-thermal plasma water treatment reactor, *J. Hazard. Mater.* 237–238 (2012) 55–62.
- [45] P. Manoj Kumar Reddy, B. Rama Raju, J. Karupiah, E. Linga Reddy, C. Subrahmanyam, Degradation and mineralization of methylene blue by dielectric barrier discharge non-thermal plasma reactor, *Chem. Eng. J.* 217 (2013) 41–47.
- [46] K. Hsieh, H. Wang, B.R. Locke, Analysis of a gas-liquid film plasma reactor for organic compound oxidation, *J. Hazard. Mater.* 317 (2016) 188–197.
- [47] P.J. Bruggeman, et al., Plasma-liquid interactions: a review and roadmap, *Plasma Sources Sci. Technol.* 25 (2016) 053002 (59pp).
- [48] A. Lifshitz, J.V. Michael, Rate constants for the reaction O + H₂O → OH + OH over the temperature range 1500–2400 K, by the flash photolysis-shock tube technique, *Proc. Combust. Inst.* 23 (1991) 59–67.
- [49] J.B. Heywood, *Internal Combustion Engine Fundamentals*, McGrawHill, Inc., 1988.
- [50] M. Magureanu, N.B. Mandache, V.I. Parvulescu, Degradation of organic dyes in water by electrical discharges, *Plasma Chem. Plasma Process.* 27 (2007) 589–598.
- [51] M. Magureanu, N.B. Mandache, V.I. Parvulescu, Chlorinated organic compounds decomposition in a, *Plasma Chem. Plasma Process.* 27 (2007) 679–690.
- [52] C. Hibert, I. Garand, O. Motret, J.M. Pouvesle, [OH(X)] measurements by resonant absorption spectroscopy in a pulsed dielectric barrier discharge, *J. Appl. Phys.* 85 (1999) 7070–7075.
- [53] P. Lukes, M. Clupek, V. Babicky, V. Janda, P. Sunka, Generation of ozone by pulsed corona discharge over water surface in hybrid gas-liquid electrical discharge reactor, *J. Phys. D: Appl. Phys.* 38 (3) (2005) 409–416.
- [54] C. Wang, Y. Wu, G. Li, Inactivation of E coli with plasma generated by bipolar pulsed discharge in a three-phase discharge plasma reactor, *J. Electrostat.* 66 (1–2) (2008) 71–78.
- [55] M.A. Malik, A. Ghaffar, S.A. Malik, Water purification by electrical discharges, *Plasma Sources Sci. Technol.* 10 (1) (2001) 82–91.
- [56] S.G. Kumar, K.S.R.K. Rao, Comparison of modification strategies towards enhanced charge carrier separation and photocatalytic degradation activity of metal oxide semiconductors (TiO₂, WO₃ and ZnO), *Appl. Surf. Sci.* 391 (2017) 124–148.
- [57] M.A. Malik, Water purification by plasmas: which reactors are most energy efficient? *Plasma Chem. Plasma Process.* 30 (2010) 21–31.
- [58] M. Magureanu, D. Piroi, N.B. Mandache, V. Parvulescu, Decomposition of methylene blue in water using a dielectric barrier discharge: optimization of the operating parameters, *J. Appl. Phys.* 104 (2008) 103306.
- [59] M. Magureanu, C. Bradu, D. Piroi, N.B. Mandache, V.I. Parvulescu, Pulsed corona discharge for methylene blue degradation in water, *Plasma Chem. Plasma Process.* 33 (2013) 51–64.
- [60] Z. Stará, F. Krčma, Nejezchleb, J.D. Skalný, Organic dye decomposition by DC diaphragm discharge in water: effect of solution properties on dye removal, *Desalination* 239 (2009) 283–294.
- [61] T. Maehara, I. Miyamoto, K. Kurokawa, Y. Hashimoto, A. Iwamae, M. Kuramoto, H. Yamashita, S. Mukasa, H. Toyota, S. Nomura, A. Kawashima, Degradation of methylene blue by RF plasma in water, *Plasma Chem. Plasma Process.* 28 (2008) 467–482.
- [62] T. Ishijama, H. Hotta, H. Sugai, M. Sato, Multibubble plasma production and solvent decomposition in water by slot-excited microwave discharge, *Appl. Phys. Lett.* 91 (2007) 121501.
- [63] M.A. Malik, U.-U. Rehman, A. Ghaffar, K. Ahmed, Synergistic effect of pulsed corona discharges and ozonation on decolorization of methylene blue in water, *Plasma Sources Sci. Technol.* 11 (2002) 236–240.
- [64] J. Deng, Y. Shao, N. Gao, S. Xia, C. Tan, S. Zhou, X. Hu, Degradation of the anti-epileptic drug carbamazepine upon different UV-based advanced oxidation processes in water, *Chem. Eng. J.* 222 (2013) 150–158.
- [65] N.N. Mahamuni, Y.G. Adewuyi, Advanced oxidation processes (AOPs) involving for wastewater treatment: a review with emphasis on cost estimation, *Ultrason. Sonochem.* 17 (2010) 990–1003.
- [66] M. Rafatullah, O. Sulaiman, R. Hashim, A. Ahmad, Adsorption of methylene blue on low-cost adsorbents – a review, *J. Hazard. Mater.* 177 (2010) 70–80.