Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2020.25409

185 (2020) 344–354
May

Non-thermal atmospheric pressure plasma jet-assisted degradation of azo dye–acid orange 7 (AO7): influence of operating parameters and toxicity evaluation

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Received 16 July 2019; Accepted 26 December 2019

ABSTRACT

The present investigation describes the effect of various plasma operating parameters on the degradation efficiency of azo dye acid orange 7 (AO7) molecules in wastewater using a non-thermal atmospheric pressure plasma jet. The de-coloration and degradation of argon plasma-treated AO7-containing solutions were investigated using UV-Vis spectroscopy and high-performance liquid chromatography (HPLC). Information on the reactive species involved during the plasma treatment was examined in detail by optical emission spectroscopy (OES). The species such as $OH^\bullet$ and H_2O_2 generated during the treatment processes were also investigated by means of spectroscopy. The change in pH and total organic carbon (TOC) of plasma-treated AO7-containing aqueous solutions were also investigated. The toxicity of plasma-treated AO7-containing aqueous solution was estimated by antibacterial analysis using agar well diffusion method against two different bacteria's such as *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) bacteria. The OES results confirmed the generation of various reactive species such as $OH^\bullet$ radicals, O, $NO^\bullet$ and other exciting species of argon (Ar) during the treatment and these reactive species are responsible for the degradation of AO7 dye molecules in aqueous solution as confirmed by UV-Vis spectroscopy and HPLC. Furthermore, this investigation confirmed that the degradation process of the AO7 solution is highly dependent on the plasma operating parameters, which is further confirmed by TOC and pH analysis. The bacterial analysis demonstrated that the plasma-treated AO7 water did not show any considerable antibacterial activity against the bacterial, that is, plasma-treated AO7 unveiled non-toxicity against *S. aureus* and *E. coli* bacteria.

Keywords: Non-thermal atmospheric pressure plasma jet; AO7 wastewater; Degradation; Non-toxicity

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1944-3994/1944-3986

1. Introduction

Over the past few decades, textile industries have been facing major problems related to the disposal and treatment of effluents generated during the various phases of dyeing processes. These effluents are characterized by the presence of a high amount of toxic dye components, suspended solids, salts and varying pH [1–5]. The removal of these dyes from wastewater is a major environmental challenge because of their complex molecular structures, non-negligible toxicity, low biodegradability, carcinogenicity and discoloration of dye wastewater. Upon chronic exposure, this wastewater can lead to tumors, cancers, and allergies in humans and pose a severe threat to the aquatic environmental system. Numerous effluent treatment methods such as advanced oxidation treatment (ozone, hydrogen peroxide, photo-Fenton, UV/H_2O_2), biodegradation, photocatalysis, atmospheric pressure plasma treatment, and electrochemical degradation methods, etc. have been extensively employed to decompose toxic dye components from the effluents [6–9]. Nevertheless, physicochemical, photochemical and biological treatment methods have certain limitations; for instance, the loss of effectiveness of oxidation, undigestible carbon, unidentified product transformation and transfer of the toxin to another phase that minimizes the anticipated mineralization. There has been a growing interest in recent years in employing atmospheric pressure plasma for textile effluent treatment as non-thermal plasma technology enables the decomposition of a variety of dyes with greater efficiency than other treatment methods. Moreover, the plasma process is very simple, cost-effective and the technology can easily be scaled up to industrial scale and does not involve any destructive and harmful chemical agents during the process.

A major advantage of the use of plasma for textile effluent treatment is simultaneous in situ production of primary reactive species such as $OH^•$, $H^•$, $O^•$, $N^•$, $NO^•$ and ions in a gaseous and aqueous environment. These reactive species induce oxidation and mineralization, converting organic toxic compounds to non-toxic compounds, avoiding the need for secondary treatment. Furthermore, the interaction of primary active species with gaseous and aqueous molecules leads to the generation of secondary reactive species such as NO_x, O_3, HNO_2, HNO_3 which facilitate reactions in the aqueous medium, resulting in decomposition of target molecules in the aqueous medium. UV radiation, shock waves and local high temperature that are generated by the plasma could also be involved in the destruction of a target molecule in the effluent [10–14]. The efficiency of an effluent treatment depends on the discharge power supplied to generate plasma, gas flow rate and nature of plasma forming gases used, the location where plasma is generated (i.e. the distance between the plasma and liquid surface), and treatment time. In the present work, we have chosen acid orange 7 (AO7) dye-containing water as a model effluent for plasma treatment. It is a mono-azo acidic dye that is soluble in water and is often present as a pollutant in wastewater produced by various industries such as textiles, dyestuffs, paper, leather, etc. The global production of the dye is about 800 K tons per year, constituting nearly half of the overall azo dye production [15–17]. Many researchers reported that this azo dye molecule is mutagenic, carcinogenic; it prevents biodegradation and also is a great threat to the aquatic environment because of their complex chemical structure, creating a major risk for environment safety [18–21]. The current investigation intends to optimize the non-thermal atmospheric pressure plasma jet operating parameters for the effective degradation of azo dye AO7 molecules in the wastewater. Various characterization techniques such as UV-Vis spectroscopy, total organic carbon (TOC) and high-performance liquid chromatography (HPLC) were used to examine the de-coloration and degradation of the azo dye. The information of reactive spices in the plasma during in situ treatment was observed using optical emission spectroscopy (OES). Finally, the toxicity of plasma-treated azo dye water towards *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) bacteria was examined *in vitro*.

2. Materials and methods

2.1. Materials

AO7 (Molecular weight (MW): 350.33 g/mol) was acquired from Merck, India. Argon gas (99% purity) was supplied by Jayam Gas, Coimbatore. *S. aureus* and *E. coli* were obtained from Bioline, Coimbatore. Nutrient agar and nutrient broth were purchased from Hi-Media, India.

2.2. Methodology

The degradation study of AO7 molecules in the AO7 water sample was done in an alternating current (AC) excited (40 kV and 30 kHz) atmospheric pressure plasma effluent treatment reactor, schematically shown in Fig. 1. The major component of the reactor is the plasma torch, which consists of a rod-type live electrode and ring-type ground electrode. The live electrode is made of copper, 20 cm in length and 0.5 cm in diameter with a hemispherical-shaped tip. The electrode is encapsulated in a dielectric material like quartz to prevent transition to arc discharge mode. The ring-type ground electrode is made of copper, whose inner and outer diameter is 1.6 and 2.5 cm, respectively and is positioned symmetrically around the quartz tube. The distance between the live and ground electrodes is adjustable and this inter-electrode gap was kept constant at 6 mm throughout the experimental studies. The entire torch unit is covered by a Teflon enclosure to prevent electric induction during the experiment. The plasma torch has provision for gas feeding, which is controlled by a mass flow controller. An aqueous solution of AO7 was taken in a glass container, which was placed beneath the plasma torch, at the end of the orifice of the quartz tube (Fig. 1). Before treatment, 50 ml of the AO7 solution (10^{-4} mole concentration) was taken into a beaker and was positioned underneath the plasma torch and the distance between the water surface and the plasma exit (orifice of glass tube) was fixed at 6 mm. After the initial arrangement, argon gas was permitted to flow between the two electrodes with a prescribed gas flow rate of 7 lpm. Thereafter, an AC (30 kHz) voltage was applied between the two electrodes and plasma was generated. The plasma was ejected out via the orifice of the glass tube and emerged as a jet. Eventually, the dye solution was treated by homogeneous non-thermal atmospheric pressure plasma under different

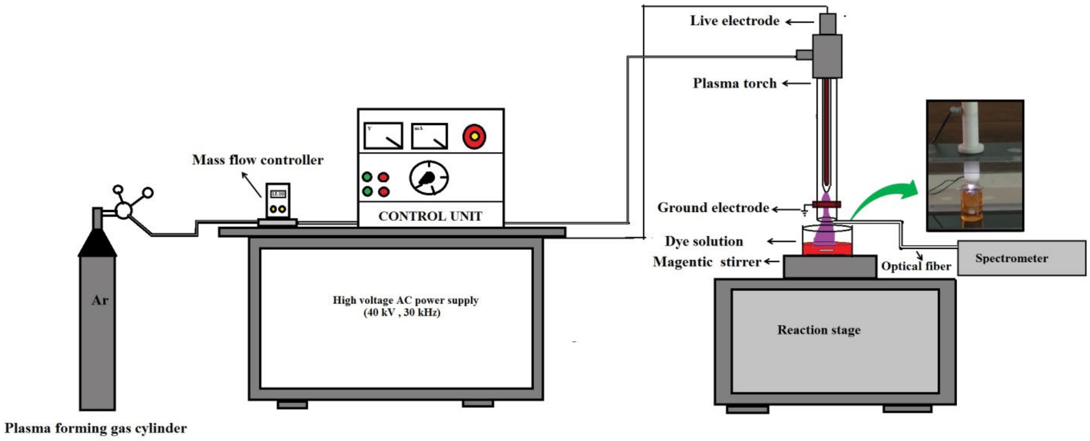

Fig. 1. Schematic diagram of non-thermal atmospheric pressure plasma jet reactor for wastewater treatment.

operating parameters such as treatment time and discharge potential. Moreover, the processing cost for the degradation of AO7 is about 6–7 USD/m^3 (approx. 600 Indian Rupees). The characteristic operating parameters for the treatment of an aqueous solution of AO7 are listed in Table 1.

The presence of reactive species during the plasma treatment of the AO7 solution was analyzed using an optical emission spectrometer (Ocean Optics HR4000CG UV-NIR spectrometer). The emission spectra were recorded in the wavelength region of 200–1,100 nm with a resolution of 1 nm. An optical fiber cable (QP400-2-SR-BX) was used to capture the optical signals during the OES measurements. In the current work, an optical fiber cable was placed near the plasma-water interface and the spectra were obtained using a collimating lens located perpendicular to the axis of plasma. The spectra were examined using OceanView spectroscopy software with the graphical user interface.

Degradation of the AO7 dye was investigated via a UV-Vis spectrophotometer and the percentage of degradation was calculated from the reduction in the absorbance peak (λ_{max}) at 484 nm after plasma exposure using the following equation [22]:

$$\% \text{ of degradation} = \frac{A_{bt} - A_{at}}{A_{bt}} \times 100 \tag{1}$$

where A_{bt} and A_{at} are the maximum absorbance at λ_{max} of the AO7 before and after treatment.

The pH of untreated and plasma-treated AO7 was measured by a digital pH meter (pHep, Hanna Instruments, USA). The variations of TOC in the untreated and plasma-treated AO7 containing water were examined by a Shimadzu TOC-LPH TOC analyzer (Japan). The degradation of AO7 molecules due to interaction with plasma was analyzed by HPLC system (Agilent 6125B SQ LC/MSD, mass detector with LC Stack for OpenLAB ChemStation, USA) using 4.6 × 100 mm 2.7-micron C18 column and 5:95 water:methanol is used as a mobile phase with a flow rate of 0.5 mL/min and the chromatogram was followed at 484 nm.

The presence of OH$^\bullet$ radicals in the AO7 aqueous solution was examined by chemical dosimetry using terephthalic acid (TA). Initially, TA was mixed with AO7 aqueous solution and the pH of the solution was maintained 10 using NaOH. After that 30 ml of solution was transferred to a 50 ml beaker and was treated by plasma jet. After the plasma treatment color of the solution was changed to yellowish green. This indicates that OH$^\bullet$ radicals produced in the aqueous solution, that is, terephthalic acid (TA) is converted in to hydroxyterephthalic acid (HTA). The experiments were carried out as a function of various operating conditions. Thereafter the plasma exposed AO7 solution was further exposed by 310 nm UV light source resulting HTA molecules emits fluorescence emission line at 400 nm which was detected by spectrophotometer using optical fiber cables [23]. The concentration of OH$^\bullet$ radicals in the AO7 aqueous solution was obtained by determining the intensity of the fluorescent emission since the intensity of fluorescent emission is proportional to the concentration of OH$^\bullet$ radicals in the solution. Subsequently H_2O_2 in the plasma exposed AO7 was investigated via spectrophotometric method involving potassium titanium oxalate. Primarily, potassium titanium oxalate, $K_2TiO(C_2O_4)$ $2H_2O$ (3.54 g) was mixed to 27.2 ml of con. H_2SO_4 and 30 ml of H_2O. The mixer was further made up to 100 ml using deionized (DI) water. The obtained Ti-reagent was used to find the concentration of H_2O_2. For measurement, 10 ml of titanium reagent and 10 ml of the AO7 dye solution were taken into a calibrated flask and made up to 25 ml. The solution was treated by the plasma as a function of applied potential and treatment time. Finally, the absorbance of the mixed solution of titanium reagent and

Table 1
Plasma processing parameters for degradation of AO7

Treatment time	0–60 min
Distance between electrodes	6 mm
Distance between the plasma jet and water surface	6 mm
Plasma forming gas	Ar
Gas flow	7 lpm
Discharge potential	11, 13, and 15 kV

AO7 dye solution was measured using a spectrophotometer at 400 nm [24].

The following expression was used to calculate the concentration of H_2O_2:

$$\left[H_2O_2\right] = \frac{\left(A_{pt} - A_{ut}\right)}{37.4\,xl} \tag{2}$$

where A_{ut} and A_{pt} are the absorbance spectra of unexposed and plasma exposed solutions respectively. x and l are the volume of the solution and path length of the spectrophotometer cuvette (cm).

Toxicity of plasma-treated and untreated AO7 containing water towards *S. aureus* and *E. coli* bacteria was evaluated by agar well diffusion method. To identify and analyze the zone of inhibition against bacteria growth, 10 mcg of *E. coli* bacteria were spread over the nutrient agar and nutrient broth in the Petri dish tissue plates whereas, for the *S. aureus*, 30 mcg of *S. aureus* bacteria were spread over the Petri dish plates. After that, five wells were punched in each Petri dish tissue plates using a sterile glass plate. Subsequently, 20 µl of untreated and various plasma-treated AO7 solution was added in each well. Here, an untreated AO7 solution was considered as the control. Finally, all the plates were incubated for 24 h at 37°C in the bacterial incubator and then, the formation of the inhibition zone around the water samples was noted. To investigate the reproducibility of the plasma effect, each set of experiment was done in triplicate [25].

3. Results and discussions

3.1. Reactive species analysis: OES results

Fig. 2a shows the OES spectrum of Ar-plasma jet emerging out of the plasma torch and Fig. 2b is the OES spectrum recorded during the experiment on plasma treatment of the AO7 water sample for various discharge potentials.

The OES spectrum of the Ar plasma generated at 11 kV exhibits emission lines at 697.32, 738.00, 751.69, 763.27, 810.84, 826.70, and 842.81 nm due to Ar emission and also shows one peak at 308.6 nm due to $OH^{\bullet}$ radicals [26,27]. The presence of $OH^{\bullet}$ radical in Ar plasma may be attributed to the presence of oxygen and moisture in the atmosphere near the plasma jet. After extending the discharge potential to higher values, no substantial amendments in the shape and position of the emission peaks could be observed. However, the intensity of the peak increases with increasing applied potential. Since the intensity of emission is proportional to the concentration of the species, which are responsible for the generation of various primary and secondary reactive species during plasma treatment (Fig. 2a), OES spectra observed during the treatment conditions [28] will confirm the reaction path and reaction dynamics. Fig. 2b shows the OES spectra observed during the treatment of AO7 at 11 kV showing five additional peaks at 270.16, 336.10, 356.18, 379.15, and 774.59 nm attributed to $NO^{\bullet}$, N_2 (Second positive system (SPS)) and O (Fig. 2b) [26,27]. Formation of nitrogen species may be caused by decomposition of dye molecules and was further excited by acquiring energy from plasma species. Another reason could be excitation of nitrogen in vicinity of plasma jet. The intensity of the spectral lines due to $OH^{\bullet}$ radical was found to be higher during plasma treatment compared to its intensity in the offline process. Besides, it was observed that the intensity of the peaks due to $NO^{\bullet}$, N_2 (secondary positive system), O, $OH^{\bullet}$ radicals and Ar lines increased with increasing applied potential. This may be due to an increased degree of ionization and increased number density of energetic plasma particles in the plasma column at higher applied potential, which facilitate the generation of various primary and secondary species at the air/liquid interface by electron impact phenomena [28,29]. The species that are generated during plasma treatment play a vital role in the effluent treatment process due to their direct chemical reaction with organic pollutant molecules and thus are responsible for decomposition of dye molecules in the aqueous solution of AO7.

3.2. De-coloration and degradation of AO7: spectroscopic analysis

The de-coloration and degradation of plasma-treated AO7 water were examined by the UV-Vis spectrometer. It is

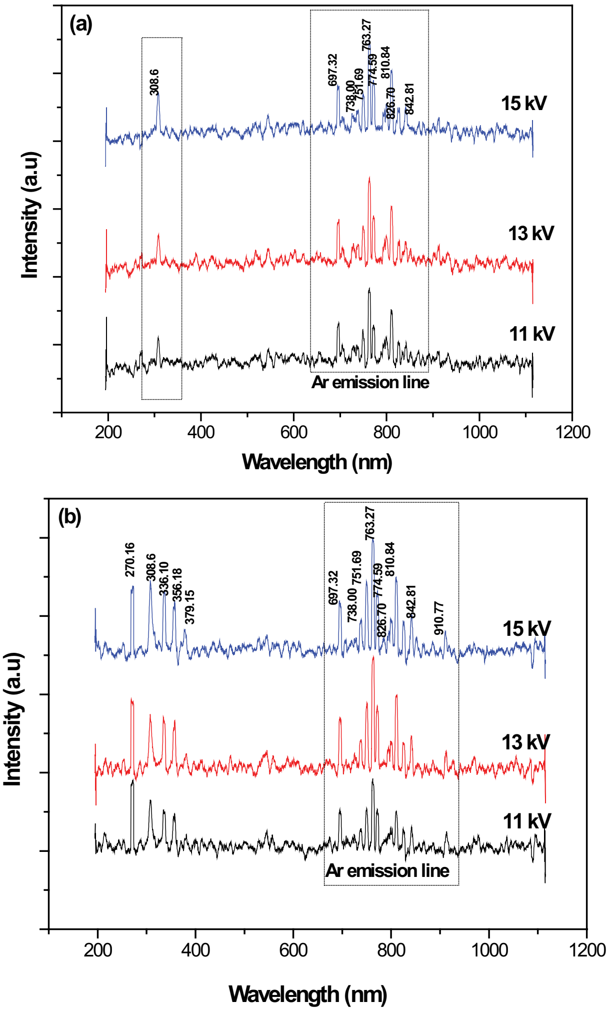

Fig. 2. OES spectra of argon plasma jet (a) emerging from the plasma torch and (b) during plasma treatment of the AO7 water sample.

important to note that the de-coloration process involves a multi-step reaction that includes a breakdown of dye molecules into various simpler intermediates and extensive interaction of these intermediates among themselves as well as with the primary and secondary reactive species generated in the plasma. Furthermore, the de-coloration process also depends on the chemical structure of the dye and the concentration of dye present in the medium. Fig. 3 depicts the absorbance spectra of the plasma-treated AO7 water as a function of treatment time for different applied potentials. It is seen from the results that the absorbance spectra of the untreated AO7 water exhibit clear peaks at 227, 262, 307, 415, and 484 nm. The peak corresponds to 227, 262, and 307 nm due to the $\pi \rightarrow \pi^*$ transition of benzene and naphthalene ring respectively. The 484 nm due to $n \rightarrow \pi^*$ transition of the hydrazine form which is a so-called characteristic absorption peak of AO7 dye. The shoulder peak at 415 nm is due to the N–N group of the azo form [5,9,30]. After 15 min of plasma treatment time, at 11 kV discharge potential, the intensity of the characteristic absorbance peak (484 nm) and its shoulder peak slightly decreased. The other peaks at 227, 262, and 307 nm were also found to decrease. Surprisingly, the intensity of the characteristic absorbance and other peaks decreased abruptly for the AO7 sample treated at 30 min and thereafter the intensity of the peak decreased gradually with increasing treatment time and finally, the peak disappeared after 60 min of treatment time (Fig. 3a). This effect may be attributed to the longer duration of exposure of the AO7 sample to the plasma jet at higher treatment time that causes the generation of increased concentration of various primary and secondary species at liquid-plasma interface leading to the destruction of the chromophore of the dye molecules and consequent de-coloration of the AO7 sample. The de-coloration caused by plasma treatment for different treatment times at higher applied potentials also exhibits a similar trait. However, the time required for complete de-coloration was found to be decreased with increasing discharge potential (Figs. 3b and c).

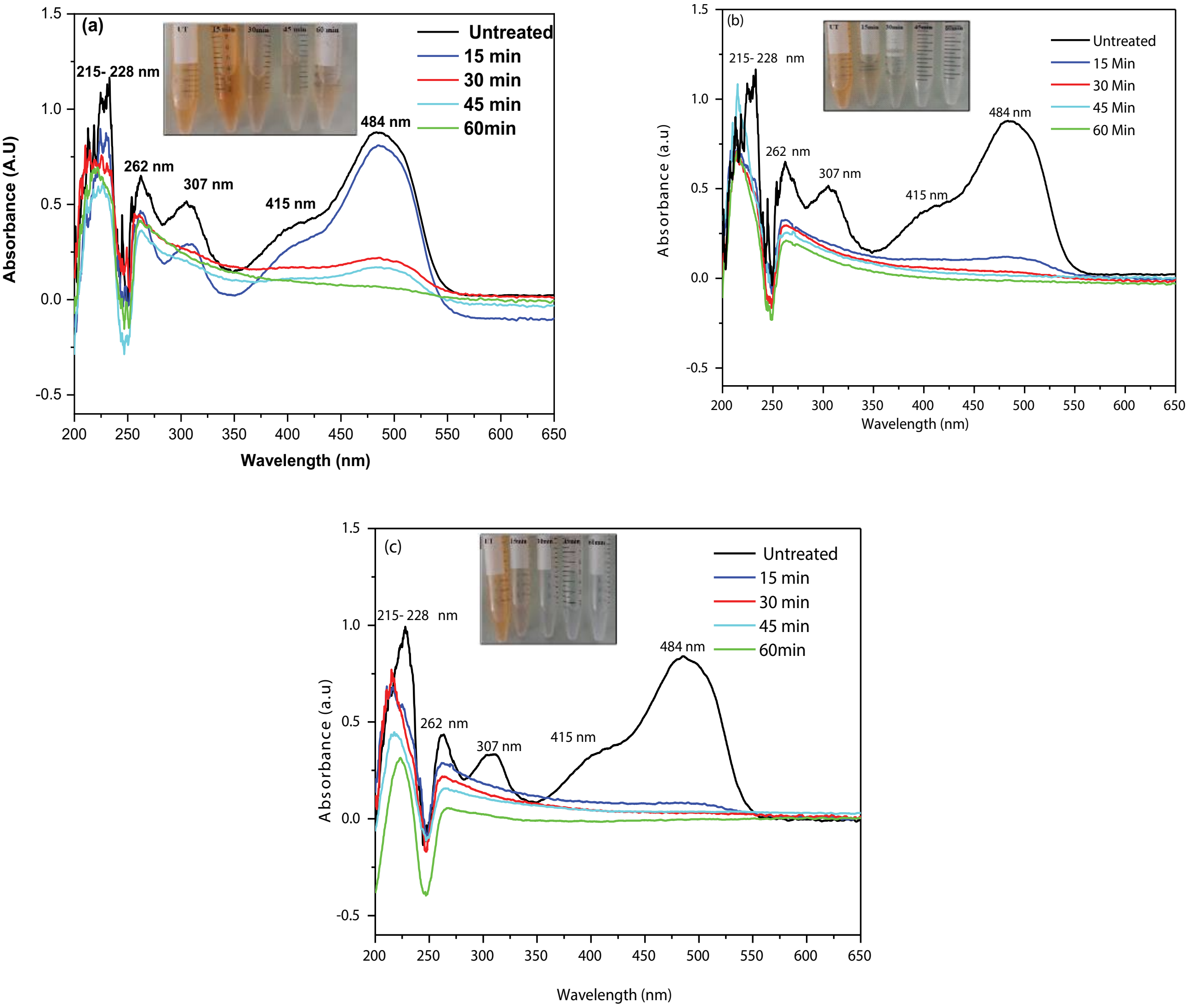

Fig. 3. UV-Vis absorption spectra of plasma-treated AO7 aqueous solution as a function of treatment time (a) 11, (b) 13, and (c) 15 kV.

Fig. 4 exhibits the correlation between the degradation rate of AO7 dye molecules in the water sample and various plasma operating parameters. It can be seen that the degradation of the AO7 water sample exposed to plasma at 11 kV applied potential for 15 min was only 14%. There was a sharp increase in degradation (%) after 30 min of plasma treatment. Extending the treatment time further resulted in a gradual increase in the degradation % and reached 90% after 60 min of plasma exposure, as can be perceived from Fig. 4. After increasing the discharge potential to 13 kV, the degradation (%) was found to be 93.8% even for a shorter treatment time of 30 min and thereafter, increased gradually with increasing time. A similar observation was found when the AO7 water sample was treated at a higher discharge potential of 15 kV; 99% of the dye was found to be degraded after plasma treatment for 60 min at 15 kV. Moreover, it was observed that as the applied potential increased, the time required for complete degradation decreased. For instance, the percentage degradation after 60 min of plasma treatment at 11 kV was found to be 90%, which could be obtained in 15 min exposure time for the sample treated at 15 kV. The above changes may be attributed to the intensification of the degree of ionization and generation of higher concentration of energetic primary oxygen species such as O_3, O, $NO^\bullet$, NO_2, etc. as well as the higher intensity of UV radiation in the gas phase at higher applied potential. These reactive species interact with water surface producing secondary reactive species, that is, reactive oxygen species (ROS) including $OH^\bullet$ radicals and long-lived hydrogen peroxide (H_2O_2) and reactive nitrogen species (RNS) (NO_2^- and NO_3^-). The formation ROS is mainly caused by decomposition O_3 at the liquid–gas interface and reaction of oxygen radicals with water molecules and RNS is due to the interaction of $NO^\bullet$ and NO_2 with water molecules. Furthermore, UV radiation produced in the plasma region also contributed to generate reactive species like $OH^\bullet$ radicals by decomposition of O_3. The intensity of UV radiation generated is proportional to the applied potential and hence the degradation of dye molecules is faster and more extensive at a higher applied potential. Thus, the concentration of reactive primary and secondary species generated in the plasma zone and the solution is higher at a higher applied potential of 15 kV and this facilitates the faster decomposition of the dye molecules compared with the AO7 water samples treated at lower applied potential. The above results confirm that the conceivable improvement of degradation and de-coloration of AO7 preciously depend on operating conditions and the presence of reactive species [31,32].

The energy consumed for removal of AO7 during the plasma treatment was evaluated using following energy yield (Y) expression [33].

$$Y\left(\frac{g}{\text{kWh}}\right)=\frac{C\left(\frac{g}{L}\right)\times V\left(L\right)\times\frac{1}{100}\times\text{degradation}\left(\%\right)}{P\left(\text{kW}\right)\times t\left(h\right)} \tag{3}$$

where C is initial concentration and V is the volume of AO7, solution, t, and P are the treatment time and power, respectively. As observed in Fig. 5, at a certain applied potential of 11 kV, it could be perceived that Y decreased marginally with increasing the treatment time attributed to expended more energy to destruction of AO7 molecules in aqueous solution at longer treatment time which leads to decreasing the Y. A similar tendency was observed for the sample treated at higher discharge potentials (Fig. 5). Nevertheless, the lowest Y value obtained for the exposed AO7 aqueous was for a maximum applied voltage of 15 kV and a treatment time of 60 min. The results showed that the sample treated at higher applied potential led to higher consumed energy to decompose the pollutants in the solutions and caused a decrease in the energy yield. The percentage of degradation and energy yield of various methods are depicted in Table 2. It was observed that most of the other degradation methods require additional catalytic material and energy sources for the degradation of pollutants [34–40]. Moreover, the degradation processes in those methods are more time consuming and lead to the production of secondary solid wastes.

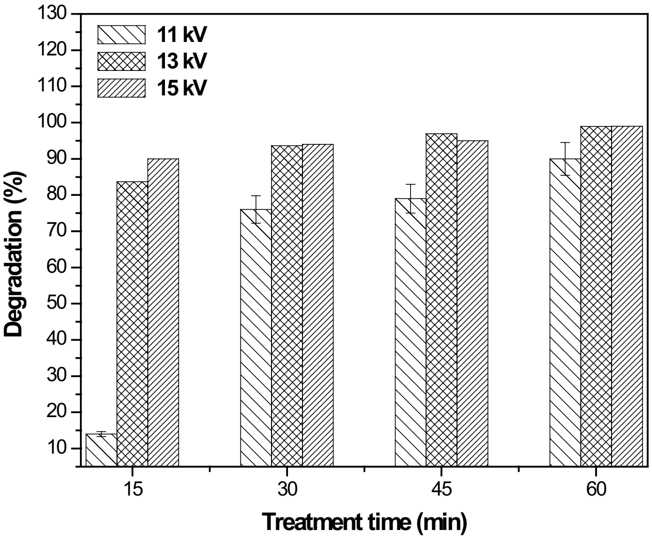

Fig. 4. Degradation (%) plasma-treated AO7 aqueous solution as a function of treatment time and applied potential.

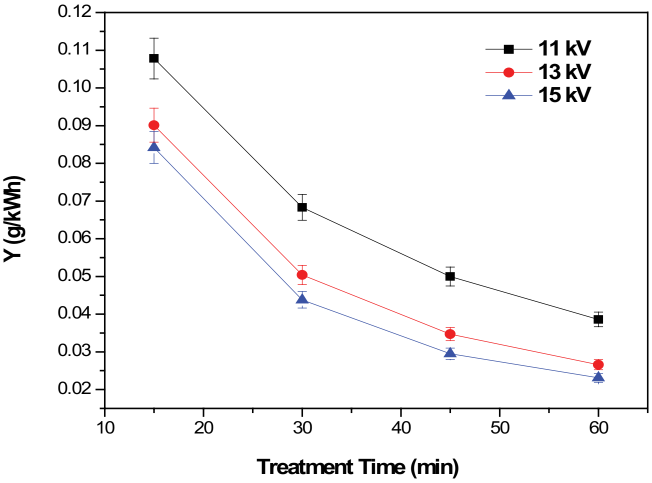

Fig. 5. Variation of energy yield (Y) as a function treatment time and applied potential.

Table 2
Comparison of degradation of azo dye by this method and other methods

Treatment method	Catalysis	Pollutants	Sample volume (ml)	Power (W)	Yield (g/kWh)	Removal (%)	Time (min)	Reference
Photocatalysis	TiO_2	Acid orange 7	200	1,000	–	70	240	[34]
Fenton	Chalcopyrite	Acid orange 7	230	–	0.54	98	360	[35]
UV	H_2O_2	Acid red 88	250	120	–	90	120	[36]
Corona	–	Acid orange 7	600	51	0.308	98.3	45	[37]
Ultrasonic	Zero-valent aluminum (ZVAl) (6 g/L) high catalytic dosage	Acid orange 7	50	300	–	96	30	[38]
Ultrasonic	Fe_3O_4 high catalytic dosage	Acid orange 7	250	200	–	95	30	[39]
Gliding arc	–	Acid orange 7	500	320	–	98	125	[40]
Plasma jet	–	Acid orange 7	50	300	0.023	99	45	

However, the plasma treatment is a catalyst-free treatment process and consuming little energy during a very short degradation process.

3.3. Evaluation of $OH^•$ radicals and H_2O_2

Fig. 6a depicts the intensity of fluorescence emission of HTA solution as a function of various treatment time and applied potential. It was found that the intensity of fluorescence emission gradually increases with an increase in treatment time at the fixed applied potential of 11 kV. After extending the discharge potential, a similar tendency was observed for various treatment times. However, the higher concentration of $OH^•$ radicals, that is, emission intensity, was observed maximum at a higher discharge potential of 15 kV and treatment time of 60 min as shown in (Figs. 6a and b). The above changes may be attributed to the increase in the concentration of energetic plasma species when the plasma is excited at higher discharge potential. Furthermore, when treatment time is increased, the reactive species interact for a longer time with the reactive column that induces a higher concentration of $OH^•$ radicals.

The presence of H_2O_2 in the plasma treated AO7 aqueous solution was quantitatively examined spectrophotometrically using potassium titanium(IV) oxalate [14,17]. Fig. 7a exhibits changes in the concentration of H_2O_2 in plasma exposed AO7 aqueous solution as a function of different operating parameters such as treatment time and applied potential. It shows that the concentration of H_2O_2 linearly increases with increasing treatment time at an applied potential of 11 kV. A similar trend was observed for the samples treated at higher discharge potentials of 13 and 15 kV. Among the various operating parameters, a higher concentration of H_2O_2 was obtained at 15 kV and 60 min treatment time as shown in Figs. 7a and b. The above results may be attributed to the generation of $OH^•$ radicals in the aqueous solution due to the interaction of energetic plasma species with molecules of the aqueous solution which recombined to form H_2O_2. The above results confirm that the plasma operating parameters play a significant role in the formation of $OH^•$ radicals and H_2O_2 species.

3.4. pH and TOC measurements

The vulnerability of interaction between plasma and AO7-water can be further investigated by pH measurement which is also an indicator of oxidation of organic dye molecules by plasma treatment. Fig. 8 shows the influence of operating parameters on the change in pH value of the AO7 aqueous solution. It was observed that the pH value of the untreated AO7 was 7. After 15 min of plasma treatment at 11 kV of discharge potential, the pH value of the plasma-treated AO7 decreased to 5.6; the pH further decreased with increasing treatment time. pH values of AO7 water treated at various times for higher discharge potential (13 and 15 kV) also exhibited a similar trend. It was observed that the lowest pH value (pH = 3) was perceived for AO7 treated at an applied potential of 15 kV and 60 min. The decrease in pH value of AO7 is due to the formation of a strong acid caused by the oxidation of $NO^•$ species by ozone resulting in the formation

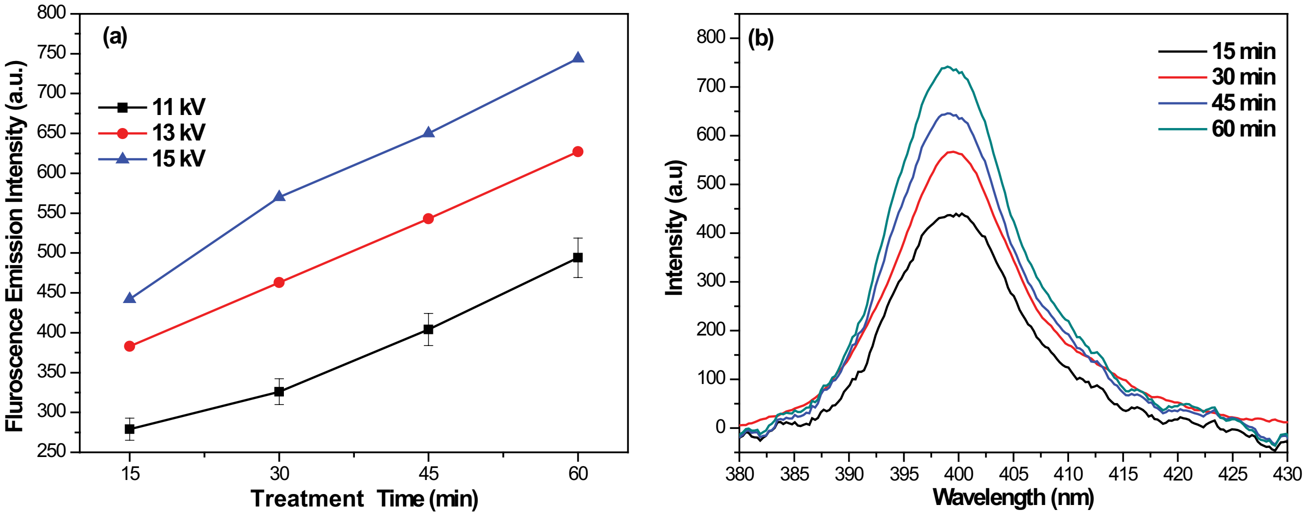

Fig. 6. Fluorescence analysis of OH$^\bullet$ radicals as a function of (a) treatment time and potential and (b) fluorescence spectra of plasma-treated AO7 solution as a function of treatment time at 15 kV.

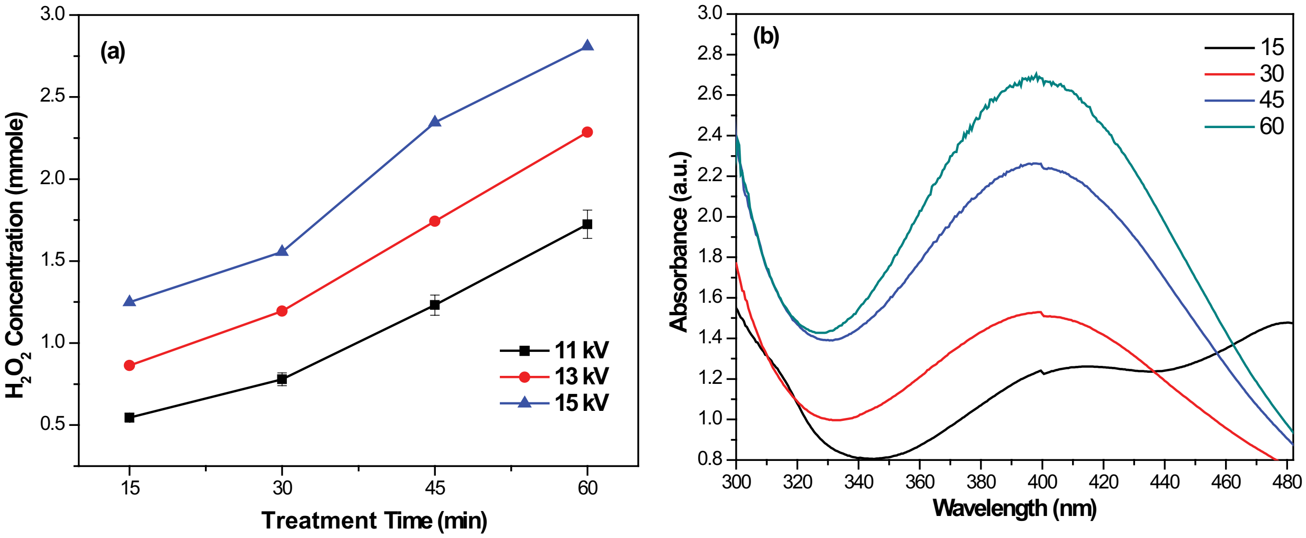

Fig. 7. The concentration of hydrogen peroxide (H_2O_2) as a function of (a) treatment time and potential (b) absorbance spectra of plasma-treated AO7 solution as a function of treatment time at 15 kV.

of HNO_3. The fragmentation of the dye molecules and oxidation of the dye molecules in water also leads to reduce the pH value of the aqueous solution [32,41].

Fig. 9 shows the variation of TOC in aqueous solution of AO7, plasma-treated at various treatment time and applied potential. It was noted that the TOC of untreated AO7 water was 13.7 ppm. After plasma treatment at 11 kV, the TOC value of the AO7 solution was seen to decrease; further, the decrease in TOC was found to be higher with increasing treatment times. After extending the discharge potential to 13 kV, a similar trend was observed. In the case of samples treated at a higher discharge potential of 15 kV, the TOC value significantly decreased after a shorter treatment time of 15 min to 8.72 ppm and thereafter, no significant change was observed. The decrease in the amount of TOC indicates the degradation of AO7 molecules by the plasma reactive species and for complete mineralization, longer treatment time is required [42,43].

3.5. HPLC results

The decomposition of AO7 was further examined using HPLC. Fig. 10 portrays the HPLC chromatogram of untreated and argon plasma-treated AO7 solution (applied potential of 15 kV). The HPLC chromatogram of untreated AO7 discloses one major peak with retention time at 13.60 min, which may be attributed to the chemical components found within AO7 molecules (Fig. 10). On the other hand, the HPLC chromatogram of the AO7 water sample, after plasma treatment for 30 and 60 min at 15 kV, showed no characteristic peak due

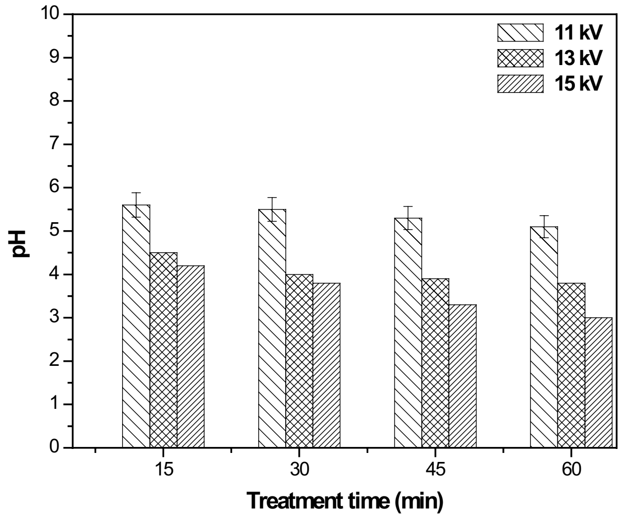

Fig. 8. Variation of pH of plasma-treated AO7 aqueous solution as a function of treatment time and deposition time.

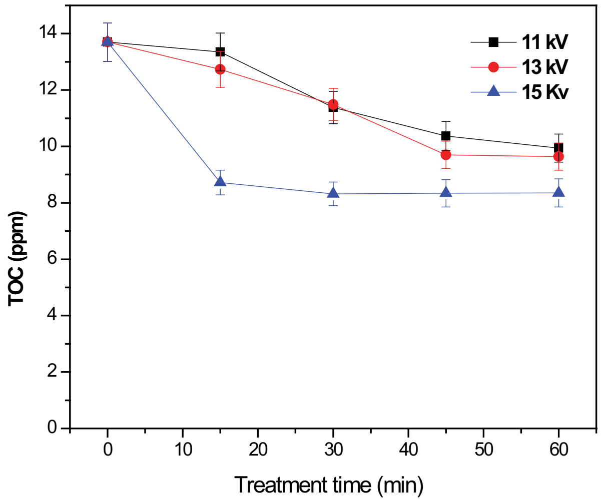

Fig. 9. Variation of TOC of plasma-treated AO7 aqueous solution as a function of treatment time and applied potential.

to the complete degradation of AO7 components. The above HPLC results confirm that the degradation of AO7 in the wastewater using atmospheric pressure non-thermal plasma treatment. The latter is in good agreement with the UV-Vis spectroscopic results.

3.6. Toxicity analysis: antibacterial results

Plasma degradation in the dye AO7 water sample was further evaluated by studying the growth of *S. aureus* as well as *E. coli* bacteria in the AO7 water sample before and after argon plasma treatment. The experiments were carried out for various plasma exposure times at a fixed applied potential of 15 kV, which was found to be the most effective in dye decomposition. Fig. 11 displays photographs of *S. aureus* and *E. coli*-bacterial growth in untreated and plasma-treated AO7 water samples. It can be seen from Fig. 11 that well-defined inhibition zone of *S. aureus* and *E. coli* was established around the untreated AO7 solution and the same was found to considerably decrease in the argon plasma-treated AO7 water medium even after 15 min of treatment time. Bacterial inhibition was not perceived when the bacteria were allowed to grow in AO7 water samples exposed to plasma for a longer duration time. In other words, the plasma-treated solution exhibits non-toxic behavior (Figs. 11a and b) towards the growth of bacteria. The non-toxic behavior of plasma-treated AO7 was unswervingly correlated to the decomposition of the toxic AO7 molecules in the AO7 sample. Finally, as revealed by the toxicity analysis, we conclude that plasma-treated AO7 water sample revealed a non-toxic behavior, confirming the degradation of toxic AO7 dye by plasma exposure.

4. Conclusion

Degradation of azo dye AO7 by cold atmospheric plasma jet and the effect of various operating parameters on the degradation efficiency have been reported. The percentage of degradation of AO7 was found to increase with increasing applied potential and treatment time whereas the energy yield Y decreased with increasing applied potential. The maximum percentage of degradation 99% was obtained at high treatment time (60 min) and applied potential (15 kV).

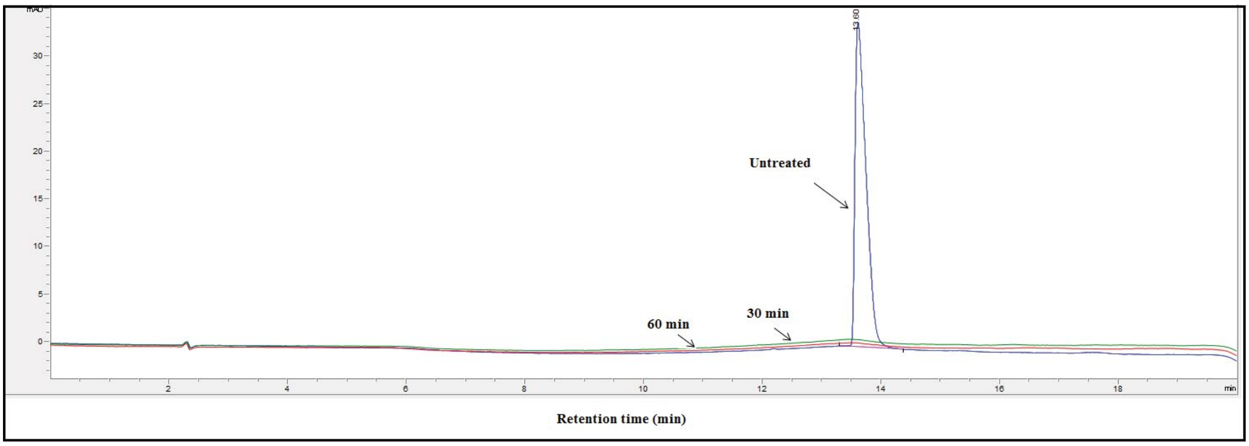

Fig. 10. HPLC of plasma-treated AO7 aqueous solution as a functions of treatment time (at 15 kV).

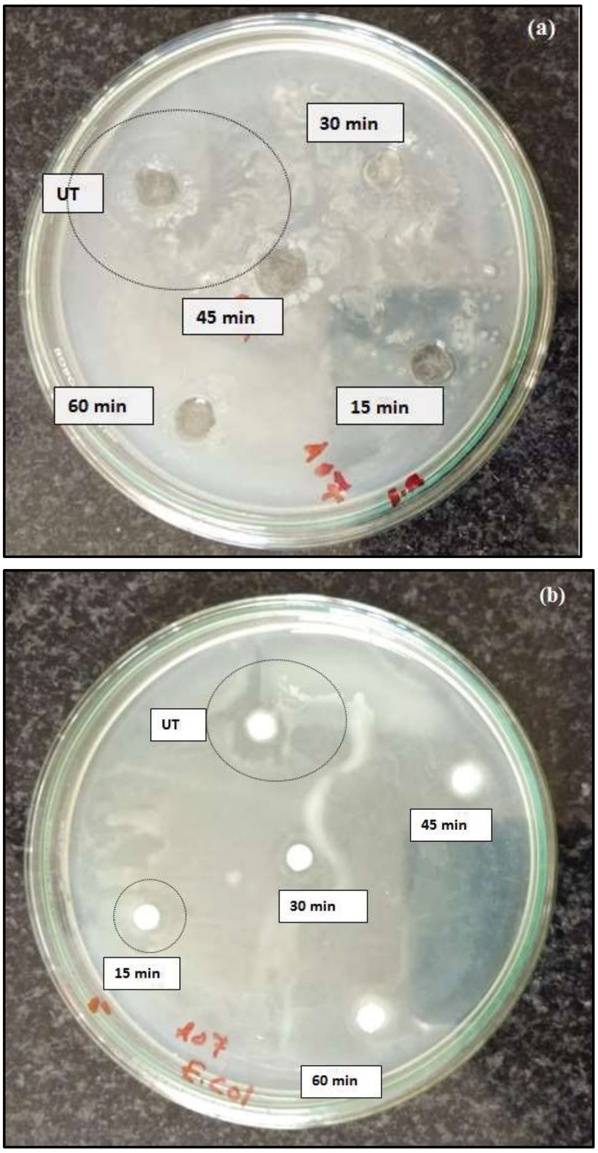

Fig. 11. Photographic images of Petri plates for estimation of antibacterial effect of AO7 aqueous solution as a function of treatment time (V = 15 kV) against (a) *E. coli* and (b) *S. aureus* strains.

The above results confirm degradation of AO7 may be attributed to generation various reactive species such as ROS (O, $OH^\bullet$ radicals and H_2O_2) and RNS ($NO^\bullet$, N_2 SPS) during the treatment. These were confirmed by OES. Furthermore, the formation of $OH^\bullet$ radicals and H_2O_2 was confirmed using spectroscopic analysis and their formation was highly dependent on the operating parameters. HPLC, TOC and pH measurements suggested a complex reaction mechanism involving fragmentation of the dye molecule and oxidation with consequent mineralization and conversion of the dye molecule into non-toxic materials. Moreover, the plasma-treated AO7 aqueous solution unveiled non-toxicity against *E. coli* and *S. aureus* bacteria. This was attributed to the decomposition of the toxic AO7 molecules in the AO7 sample. Finally, from the above-obtained results, we conclude that the proposed plasma-assisted technique is an alternative technique for the effective degradation of pollutants from the effluents since this method does not require any catalyst or other light sources.

Acknowledgments

The corresponding authors (Dr.K. Navaneetha Pandiyaraj) wish to express his honest gratefulness to Science & Engineering Research Board (SERB), Department of Science and Technology (DST), Government of India for providing the financial support (EMR/2016/006812 Dated: 02-Nov-2017).

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