

Water treatment by the AC gliding arc air plasma

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Abstract In this study, the effects of gliding arc (G Arc) plasma system on the treatment of water have been investigated experimentally. An AC power supply of 15 kV potential difference at 50 Hz frequency was employed to generate plasma. Plasma density and temperature were measured using spectroscopic method. The water was contaminated with staphylococcus aureus (Gram-positive) and salmonella bacteria (Gram-negative), and Penicillium (mold fungus) individually. pH, hydrogen peroxide, and nitride contents of treated water were measured after plasma treatment. Decontamination of treated water was determined using colony counting method. Results indicate that G Arc plasma is a powerful and green tool to decontaminate water without producing any byproducts.

Keywords G Arc discharge system · Removing bacteria · Complete sterilization · Spectroscopy · Salmonella · Penicillium (mold fungus) · staphylococcus aureus

Introduction

There are different types of microorganisms which pollute water. For this reason, different physical and chemical methods are applied for removing these pollutants, such as the process of filtration, chlorination, UV irradiation, and ozonation, but these methods have several disadvantages.

Therefore, researchers tried to employ new methods for inactivation of decontaminants in water [1]. Producing harmful byproducts in the nature and water as well as immunity of several microorganisms to such treatments are some disadvantages of convenient water treatment methods, which force researchers to look for new methods for treatment of polluted water. In the recent two decades, the use of plasma as an effective method for removing bacteria has been introduced and extensive research in this area has been done. Applying an electrical discharge in the water to sterilize is one of the new methods of decontamination, which has fixed many of the problems of the convenient methods [1].

It is more than two decades that plasma is used for removing the bacteria; however, sterilization with plasma systems is a new approach for removing all kinds of microorganisms. These systems on the contrary to other chemical methods are free of any biocides and toxic chemicals and remove all kinds of microorganisms in a short time in a very low temperature. Inactivation of microorganisms is relevant to the presence of various reactive plasma species, such as OH·, H·, O·, and HO₂ and molecular species such as H₂O₂, H₂, and O₂. Electric field, ultraviolet radiation, and shock waves are other parameters of plasma which may have different positive effects on the treatment of water [2–7].

In this experimental study, the G Arc plasma has been used in contact with water by inputting compressed air gas for inactivation of two kinds of bacteria and also one type of fungus. Staphylococcus aureus and Salmonella are Gram-positive and Gram-negative bacteria, respectively, and fungus is Penicillium (mold fungus). Staphylococcus is one of the toughest and most resistance spherical Gram-positive bacteria. The cell wall of these bacteria is very thick and grows large on a rich medium. Staphylococcus

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aureus is responsible for a wide range of diseases such as mild skin infections (impetigo, folliculitis, etc.). Salmonella is a Gram-negative, non-spore-forming rod-shaped bacterium which can be transferred by eating or drinking contaminated food or water, in particular. Salmonella enters into the body through ingestion and easily makes its way through the stomach acid to its intestines and also is responsible for many diseases including vomiting and fever [8]. Both of these bacteria grow in water and may transfer to body from water. Recently, researches show that the fungal-like Penicillium spores grow better with water, especially in tap water, damp or water-damaged buildings, and in pool waters and create many problems. Damp or water-damaged building materials are in danger of fungal growth (mold growth) and endanger the health of building occupants and damages to the buildings. Other problems of fungal growth are blockage of water pipes, organoleptic deterioration, and pathogenic fungi [9, 10].

Experimental details

Plasma

The schematic and pictorial view of the plasma G Arc generator are shown in Fig. 1a, b. Air plasma was generated by a G Arc discharge setup. Electrodes were two half circular aluminum plates of 4 cm radius and 2 mm thickness. The gap between two electrodes was 2.5 cm in maximum case and 0.5 cm in minimum for producing plasma. There was 1 cm gap between the electrodes and the output part. The discharge was done using a 15 kV, AC power supply at 50 Hz frequency which was plugged into 220 V. The output voltage of power supply is shown in Fig. 2. Plasma was made with compressed air which was flown at 18 ml/min between electrodes. A container of water was placed on the stirrer. Using a sterile magnet in water, the output plasma could be covered and the plasma acted more effectively on the large area of the liquid. The volume of polluted water was 50 ml. Experiment was carried out at a room temperature of 24 °C. Plasma was diagnosed by a CCS200 Thorlabs spectrometer. Plasma spectrum is presented in Fig. 3.

Microbiological preparation

Microorganisms

Distilled water was polluted separately with two types of bacteria named staphylococcus aureus and Salmonella. Their features are different. Staphylococcus aureus is Gram-positive and Salmonella is Gram-negative. Water

was also polluted by one type of fungus named Penicillium (mold fungus).

Suspension preparation

First of all, the bacteria were cultured on nutrient agar medium (Merck, Germany) and fungi were cultured on Sabouraud Dextrose Agar (SDA) (Merck, Germany). Then bacteria were incubated for 24 h at 36 °C and fungi were incubated for 1 week at 25 °C. For preparing the suspension of bacteria and fungi, 10 ml of distilled water was pipetted in a test tube and few colonies of bacteria and spores of fungi were added to it by loop until reaching a density of 0.5 McFarland standards which is equal to 1.5×10^8 CFU/mL. This suspension was used as a reference to adjust the turbidity of bacterial and fungal suspensions. Then 1–9 ml of suspension and distilled water were diluted for two times. Again 5 cc of polluted suspension were mixed with 45 cc distilled water for the last dilution. The final sample was 50 ml of solution with density of 1.5×10^5 CFU/ml polluted agent. The prepared bacterial solution was treated under G Arc plasma for 2–10 min. In the case of fungal pollution the time of treatment was 4–16 min. Then 100 µl of the controlled and treated samples in different mentioned times was cultured on said mediums. At last the mediums were incubated for 24 h at 36 °C and 1 week at 25 °C for bacteria and fungi, respectively.

The number of CFU which grew on the medium after incubating was counted by BZG 30 colony counter. Furthermore, the pH of water was measured using pH meter 8686 pH, AZ Instrument. SEM imaging was done employing AIS2100 together with gold coating by SC7620 device, hydrogen peroxide of treated water was measured using MQuant™ Peroxidase Test Kit and nitrate of treated environment was measured by DR5000 Spectrophotometer.

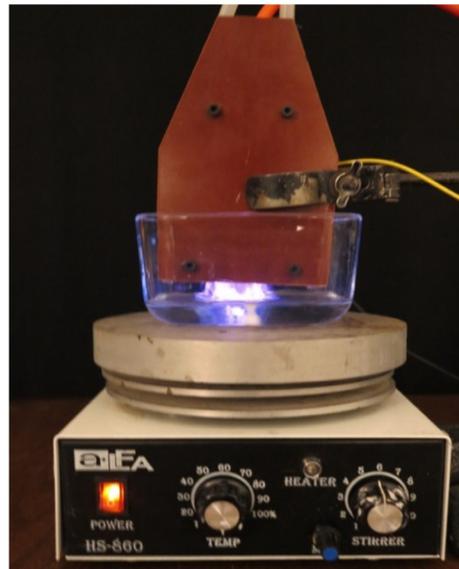
Results and discussion

Spectroscopy of G Arc plasma

Spectroscopy was used to determine the density and temperature of G Arc air plasma in the wavelength range of 200–1100 nm. The air plasma spectrum was sketched through the origin software (Fig. 3). The spectrum shows some reactive species like N_2 , O, H_α , H_β (486.1 nm), H_γ (410.2 nm) in plasma. Different species of hydrogen were generated in the collision of water molecules with electrons ($H_2O + e \rightarrow H + OH + e$). N_2 and O lines arise from air gases which were excited in the discharge process. Considering Fig. 3 there is no

Fig. 1 The experimental setup of gliding arc plasma (a) with its schematic view (b)

A



B

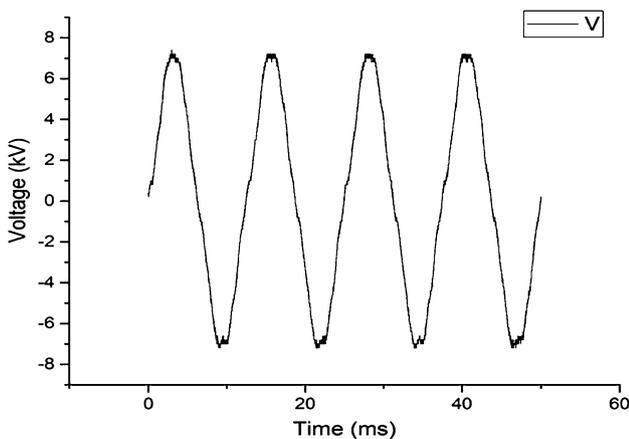
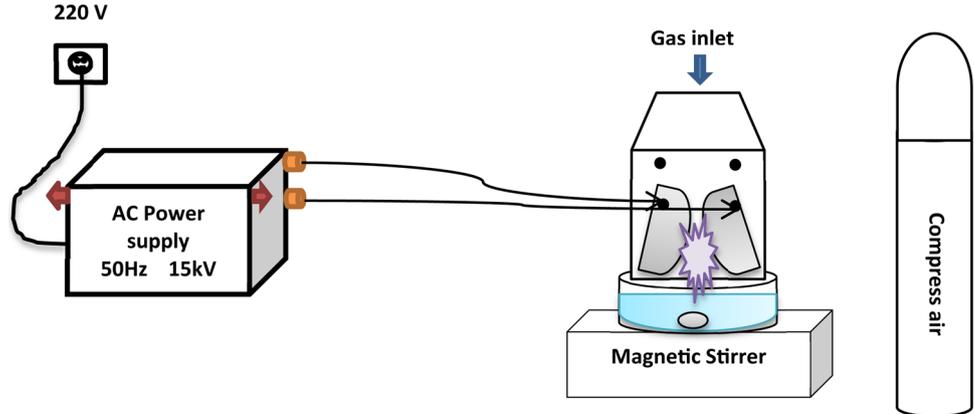


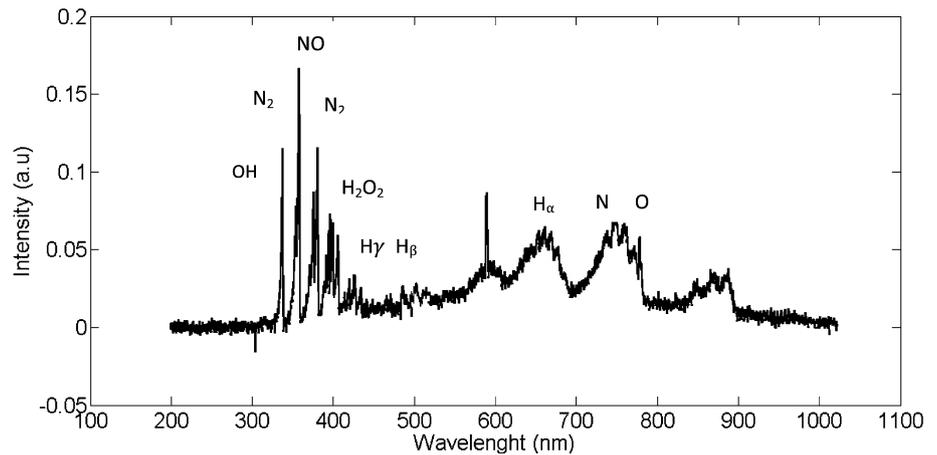
Fig. 2 Waveform of the power supply voltage with peak-to-peak-voltage 15 kV

emission in the interval of 200–300 nm wavelengths. Reactive oxygen species radiates at 777 nm. Generally, oxygen species is one of the most important materials for

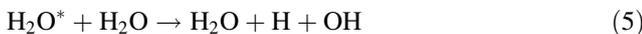
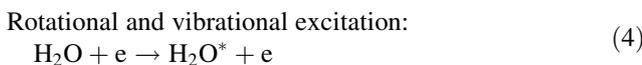
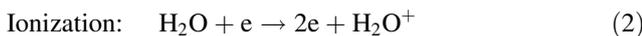
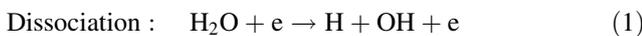
sterilization which has been mentioned in many reports on plasma sterilization. Atomic nitrogen radiates at 745 nm and N_2 as the other important reactive particle is detected in the range of 320–400 nm [11, 12]. Ultraviolet peaks are at 364.5, 388.5, 388.9, and 397 nm and the peaks of NO are at 296, 357.7, and 378.9 nm [13]. Such waves are radiated due to collisions between electron and neutral species. Ultraviolet radiation destroys organic components and dissolves hydrogen peroxide and ozone from each other to finally produce hydroxyls in plasma which removes the pollutants and increases the internal electrical energy efficiency.

When the water molecules are under the effect of electrical discharge, OH and H radicals are produced due to decomposition, ionization, rotational, and vibrational excitation reactions. Typical wavelength of OH radical emission is between 309 and 317.8 nm [13]. They are one of the most effective elements in the sterilization process because they can easily penetrate into the membrane of the

Fig. 3 The emission spectrum of G Arc plasma



fungus and bacteria to destroy them. Following reactions are the processes of OH and H production. The lifetime of hydroxyl is very short.



One of the interesting ways for analyzing the spectrum of plasma is measuring electron density, which may be obtained from H_α line in the spectrum. This type of atomic hydrogen is sensitive to stark broadening, which contains useful information such as electron density [14]. Stark broadening is obtained from the following equation:

$$\Delta\lambda_{\text{stark}} = 2.5 \times \alpha_{1/2} \times (n_e)^{2/3} \quad (8)$$

where $\alpha_{1/2}$ is a constant and n_e is the density of plasma electrons [15].

$\Delta\lambda_{\text{stark}}$ may be extracted from the equation

$$\Delta\lambda_L = \Delta\lambda_{\text{stark}} + \Delta\lambda_{\text{vanderwaals}} \quad (9)$$

where $\Delta\lambda_L$ is the width of H_α line. This line is shown by dots in Fig. 4, which is fitted by a Voigt curve using Origin software. $\Delta\lambda_{\text{vanderwaals}}$ is a kind of Lorentzian broadening which is obtained from $\Delta\lambda_{\text{vanderwaals}} = \frac{1.82}{T_g^{0.7}}$ (T_g is gas temperature) by taking van der Waals broadening, one can find $\Delta\lambda_{\text{stark}} = W = 31.6529$ and taking $\alpha_{1/2} = 2 \times 10^{-11}$ plasma density is found to be $5.03 \times 10^{16} \text{ 1/cm}^3$. Regarding the point that $n_e \geq 10^{20} \text{ m}^{-3}$ is the density of thermal plasma and $n_e \cong 10^{10} \text{ m}^{-3}$ is the density of non-

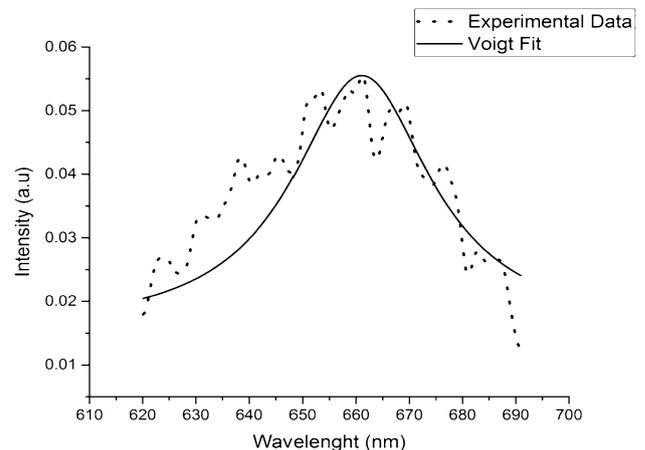


Fig. 4 Broadening Voigt for simulating the line of H_α

thermal plasma, the used G Arc plasma in this experiment is between thermal and non-thermal plasmas.

Plasma temperature is one of the considerable elements in sterilization which directly affects the biochemical reactions of bacteria [16]. Electron temperature of G Arc plasma was obtained by limiting the wavelength between 370 and 382 nm to SpecAir software for fitting which is shown in Fig. 5. Plasma temperature was calculated as follows:

$$T_e = 3000 \text{ K} = 0.2 \text{ eV}$$

During the experiment the temperature of water was checked. The maximum temperature of polluted water was 29°C during the plasma treatment.

Results of colony counting

Results show that the numbers of CFU decreased proportionally with time under the treatment with the G Arc plasma. Number of CFU for Staphylococcus and Salmonella bacteria and Penicillium are shown in Figs. 6, 7, and 8 respectively. These data are plotted in Fig. 9. Colonies of bacteria were counted on nutrient agar after

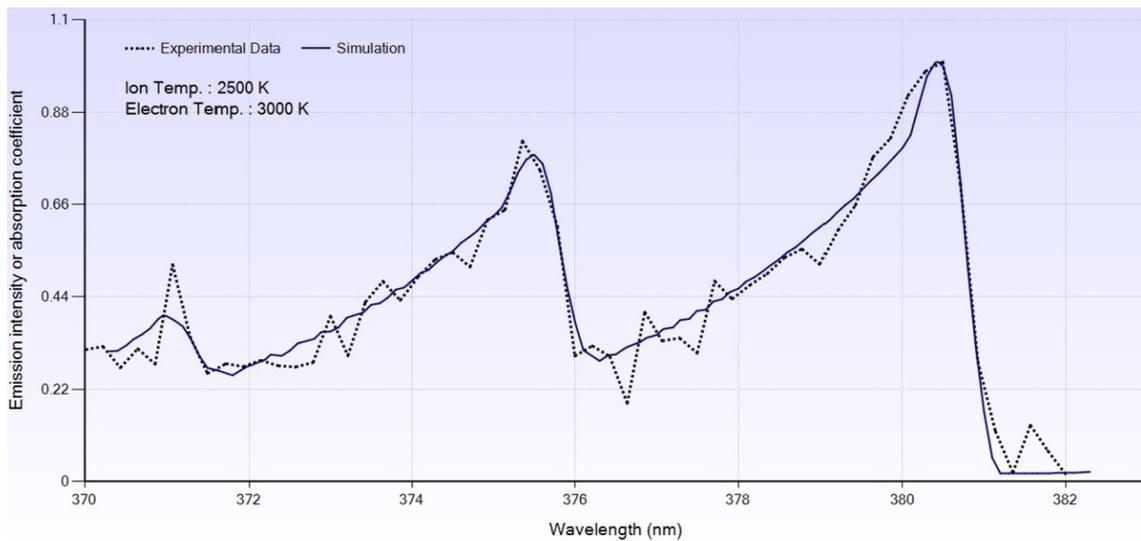


Fig. 5 Fitting for measuring ion and electron temperature of G Arc plasma using SpecAir software

Fig. 6 Results of G Arc plasma on the Staphylococcus bacteria (Gram-positive) after 24-h incubation at 36 °C

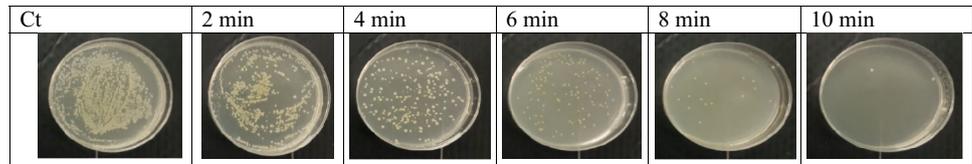


Fig. 7 Results of G Arc plasma on the Salmonella bacteria (Gram-negative) after 24-h incubation at 36 °C

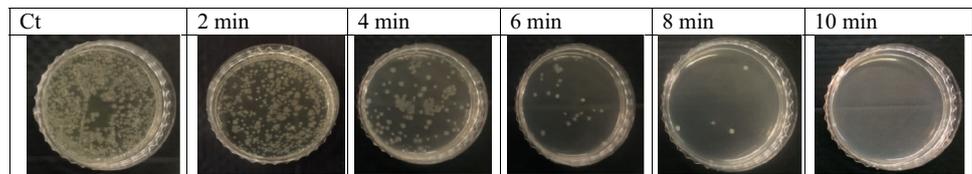
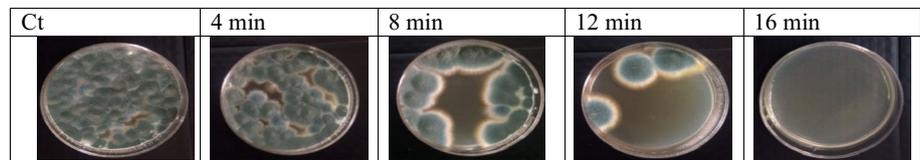


Fig. 8 Results of G Arc plasma on the Penicillium (mold fungus) after 1-week incubation at 25 °C



24-h incubation at 36 °C and colonies of Penicillium were counted on SDA after 1-week incubation at 25 °C. In this experiment, 10 min was enough for decontamination of bacteria but for the case of Penicillium, decontamination was completed in 16 min. In the case of Salmonella, the survival curve consists of two lines while for the case of Staphylococcus the survival curve consists of three lines. The first line of survival curve with very soft slope introduces the destruction of the shield of bacteria by the UV photons of plasma [1, 17]. Figure 3 shows that in comparison with other references, the number of UV photons is very large in our G Arc plasma. In this case, the slope of the first line is steep. In the case of Gram-negative bacteria, because the bacteria shield is thinner than the Gram-

positive one, the first and second lines of survival curve have almost the same slope. In the case of Gram-positive bacteria, because of their thicker shield, the slope of the first line is smaller. The second stage of decontamination occurred between minutes 2 and 4 of plasma exposure. At this stage the DNA and RNA of bacteria react chemically with reactive species of plasma. This stage occurred faster for the Gram-positive bacteria. Finally, in 10 min decontamination was completed for both bacteria.

Among these three microorganisms, the time for decontamination of Penicillium (mold fungus) was longer than others. The survival curve of this fungus consists of two stages. It is more similar to the survival curve of Salmonella which is a Gram-negative bacterium. First

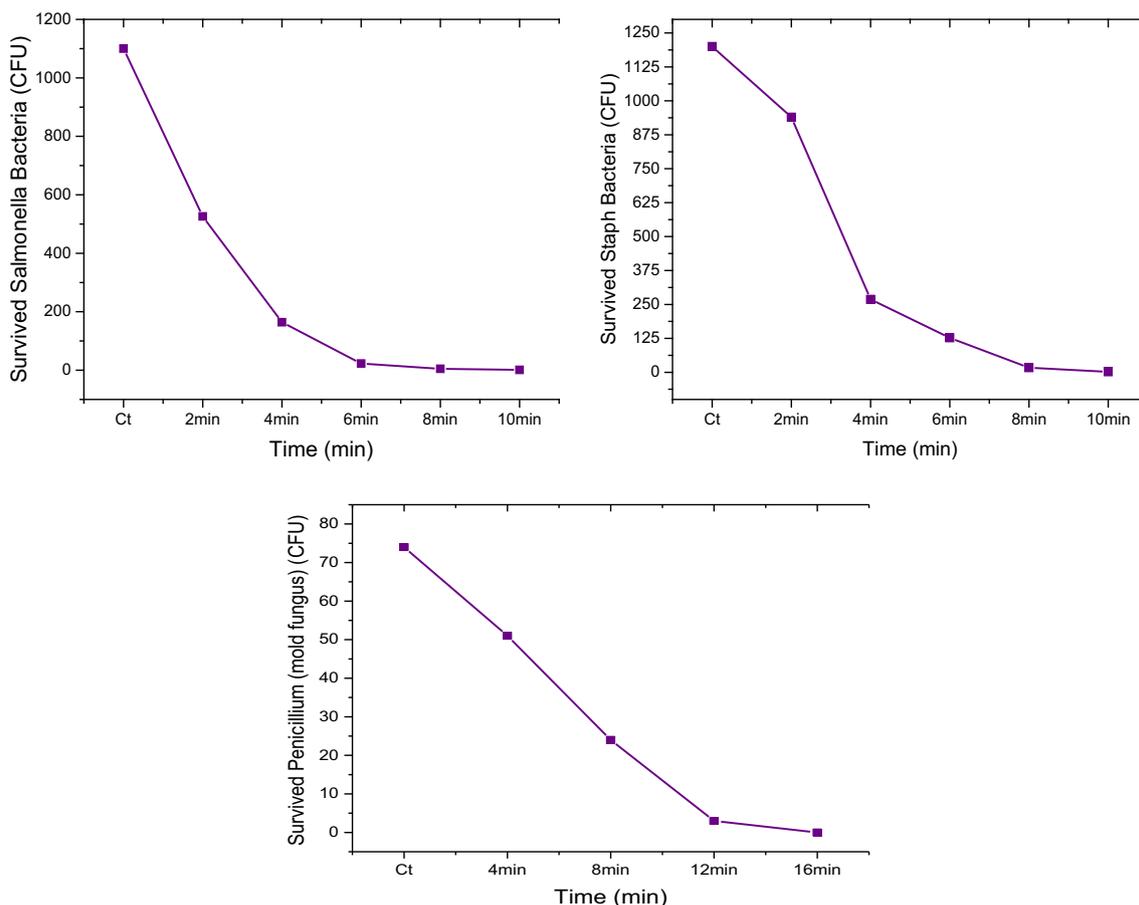


Fig. 9 Results of G Arc plasma on the *Penicillium*, *Staphylococcus*, and *Salmonella* bacteria

stage took 12 min while the second stage took only 3 min. It seems that the shield of this fungus is tighter against the UV radiation in comparison with two other agents. Thus, it took a longer time for destroying the shield of this fungus. This process occurred uniformly and in the first 12 min the slope of the survival curve is constant. Results show that after shielding destruction, this fungus dies down very fast and in only 3 min we do not have noticeable amount of them in the medium.

Results of scanning electron microscopy analysis (SEM)

Results were also checked using SEM images. Performing SEM images, at first, 1 cc of water sample before and after treatment was pipetted into a small container. Samples were centrifuged for 15 min till all the spores and bacteria were deposited. Then instead of water, glutaraldehyde 2% was added to the deposited part. After 24 h of fixing with glutaraldehyde, samples were centrifuged again until spores and bacteria sedimented. Then glutaraldehyde was drained. Again samples were

centrifuged with 95, 70, 50, 30, and 100% ethanol for 15 min, respectively. At this step samples were dehydrated. Finally, dried samples on aluminum foil were coated with gold to perform SEM images.

In Fig. 10 the effect of 10-min G Arc plasma treatment on the *Staphylococcus* bacteria is shown. All bacteria were affected by plasma treatment. Before treatment (Fig. 10a) bacteria are spherical with about 800 nm diameter. The shell of bacterial is shiny in the scanning electron probe beam. After treatment, the shell of the bacteria was deformed. They were not spherical anymore. Some holes and cracks appeared on the body of bacteria. Their shells were not shiny and the edge of bacteria was deformed to a sawtooth-like structure. According to images in the case of *Staphylococcus* bacteria, the shell of bacteria was destroyed by plasma agents.

Effect of 6 and 10 min plasma treatment on the *Salmonella* bacteria is shown in Fig. 11. After 6-min treatment the shell of bacteria was destroyed. Some parts of its body were destructed. After 10-min treatment the shell of bacteria was removed completely. Their cores and internal parts of their bodies may be seen in the SEM image.



Fig. 10 Results of scanning electron microscopy on the staphylococcus aureus bacteria: control sample are completely spherical and symmetric (a) after 10-min treatment by G Arc plasma; the staph bacteria got deformed (b)

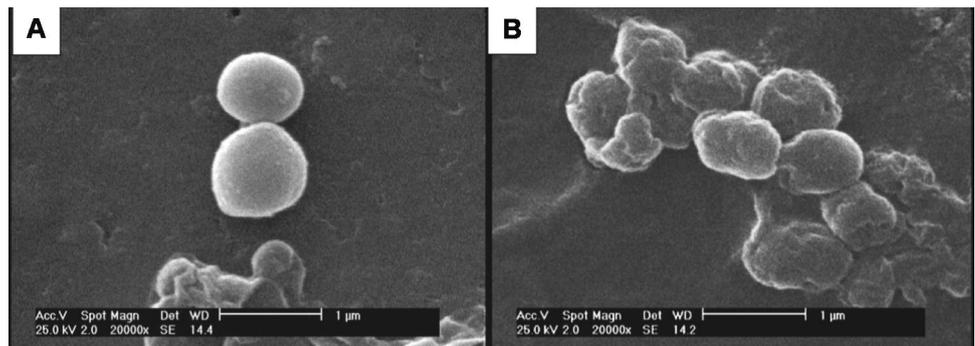


Fig. 11 Results of scanning electron microscopy on the *Salmonella* bacteria: control sample is of bacillus form (a) after 6-min treatment by plasma (b) after 10-min treatment by G Arc plasma (c)

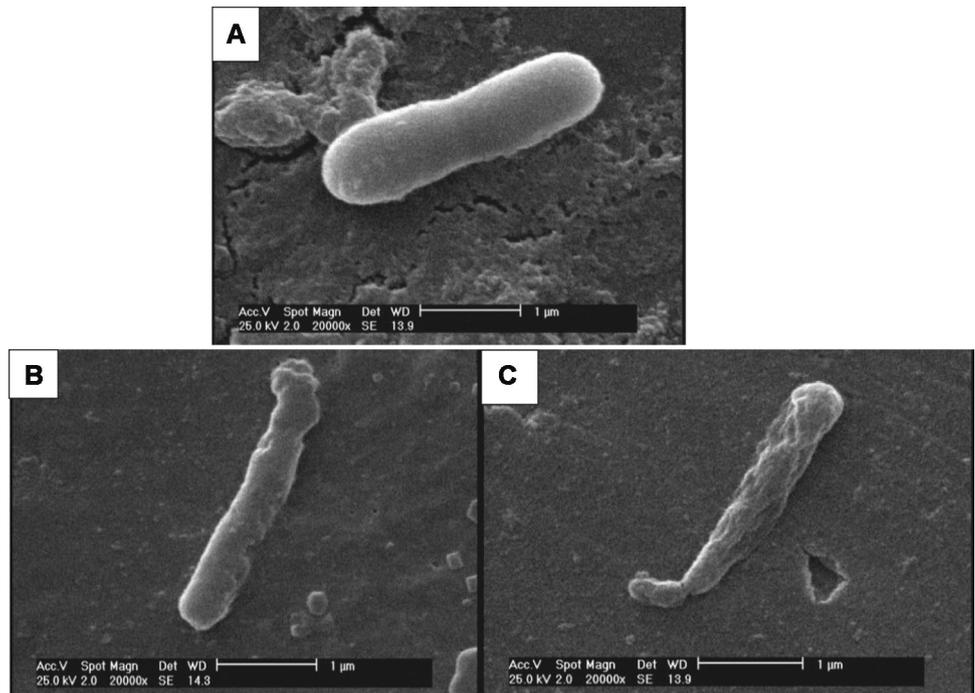


Fig. 12 Results of scanning electron microscopy on the Penicillium Green (mold fungi): spores in control sample are like chain or cluster (a) after treated by G Arc plasma, spores got deformed (b)

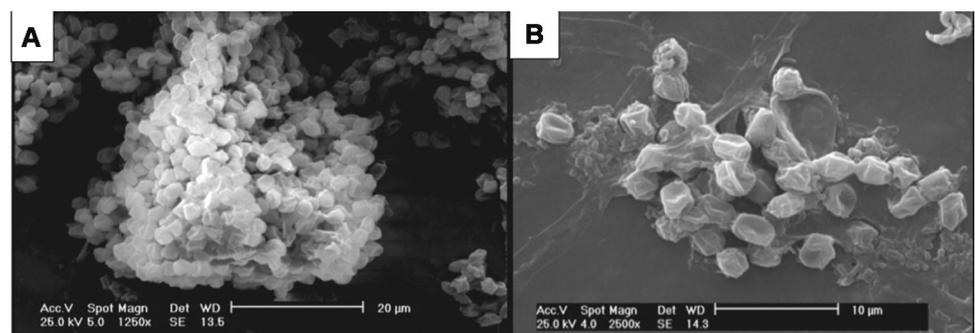


Figure 12a, b shows the evolution of Penicillium (mold fungus) after G Arc plasma treatment. Many spores of fungi were removed completely after plasma treatment. It seems that they have been squished and crushed because of plasma treatment. The numbers of remaining parts of spores are much smaller after the treatment and they got separated from

each other, while they were like a chain or cluster before treatment. There are some holes in their cell shells and some parts of their internal organisms penetrated out. It is known that plasma, especially G Arc discharge, can produce shockwave in water which plays an important role in the detachment of fungal spores [18, 19].

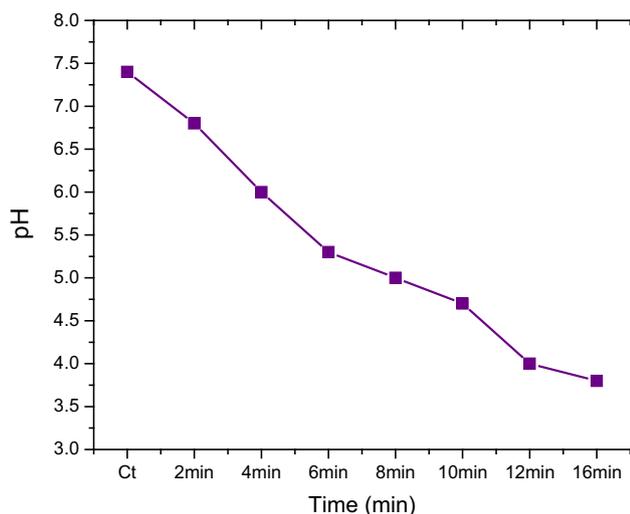


Fig. 13 Results of pH of water before and after using G Arc plasma

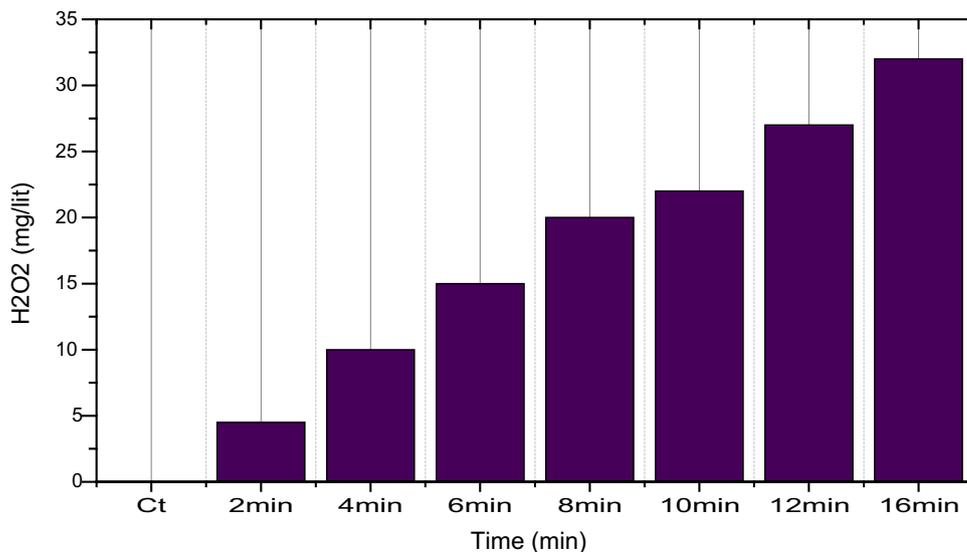
Results of measuring pH in water

pH of water before and after treatment was measured gradually during the plasma treatment process. Results are shown in Fig. 13. Within 16 min, the pH of water was decreased from 7.4 to 3.8. In other words the plasma treatment led to acidification of water.

Results of producing H_2O_2 (hydrogen peroxide) by G Arc plasma in water

Using the special kits (peroxide test) for measuring H_2O_2 (hydrogen peroxide) through the inserted directives on it and comparing with color change, the target numbers were obtained. Results are shown in Fig. 14. Hydrogen peroxide may be produced by combination of hydroxyl

Fig. 14 Results of producing H_2O_2 (hydrogen peroxide) in water by G Arc plasma



radicals and also can increase the ability of acidity of plasma, and the wavelength is approximately in the range of 379–430 nm [20, 21]. By increasing hydrogen peroxide as indicated in Figs. 13 and 14 the pH was increased.

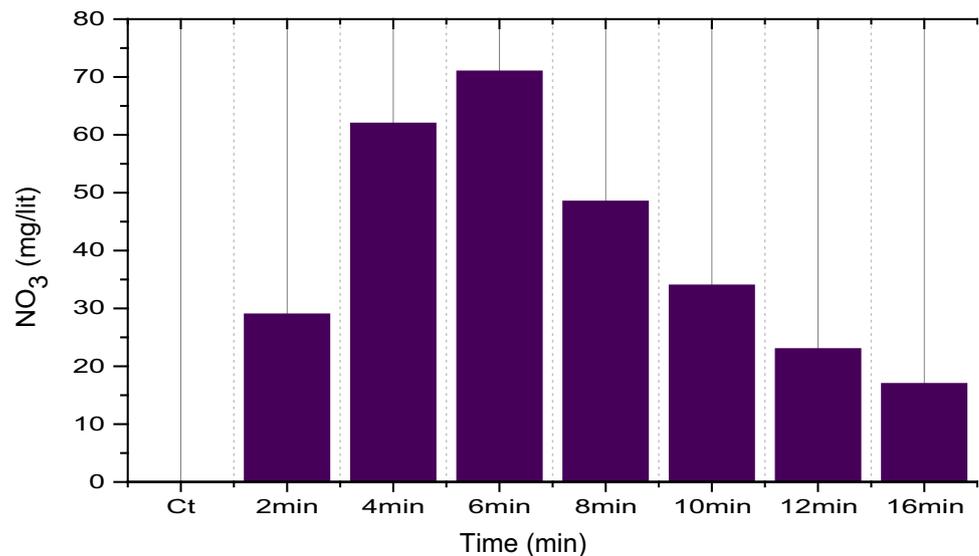
Results of measuring NO_3 (nitrate) in water before and after plasma

The amount of nitrate in treated water during the treatment process is shown in Fig. 15. Results show that this amount was increased in the treated water in the first 6 min and was gradually decreased in the next 10 minutes. However, we still had about 10 mg/l NO_3 in the water after the treatment. Comparing the pH measurement with NO_3 results shows that in the plasma treatment process in the second part of the experiment because of H radical production, NO_3 molecules were changed to HNO_3 molecules.

Conclusion

The present study presents the effects of air plasma which was generated by G Arc discharge system for reducing microorganisms in water using different physical conditions. A power supply of 15 kV at 50 Hz frequency was employed to perform discharge with compressed air flow. Characteristics of plasma were measured using spectroscopic method. During this study important parameters of water including pH, H_2O_2 , and NO_3 were measured. Effect of plasma discharge, especially on two different kinds of bacteria (*Staphylococcus aureus* and *Salmonella*) and a type of fungus [*Penicillium* (mold fungus)] were studied. Results show that G Arc is one of the most considerable

Fig. 15 Results of measuring NO₃ (nitrate) in water before and after using G Arc plasma



systems with more efficiency compared to the advanced oxidation techniques because of low equipment and energy costs [22, 23]. Comparing to other plasmas, G Arc plasma is more applicable and appropriate to the industry [22, 24]. Another feature of G Arc plasma comes from its plasma temperature. G Arc plasma in this working regime generates thermal plasma but it did not increase the temperature of water during the experiment. All useful plasma species, such as hydrogen peroxide, H radicals, ultraviolet radiations, nitrogen, and oxygen, may generate in this plasma, which makes it an efficient tool to treat polluted water.

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