

Improvement of water quality using dielectric barrier discharge plasma

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Abstract. The improvement of water quality using by atmospheric plasma produced from a dielectric barrier discharge (DBD) was studied. An experiment was set-up with a 4 mm diameter pipe, which contains 2 electrodes and has an air flow with the rate of 15 liters per minute. Surface water, domestic wastewater and DI water were treated with the DBD plasma for some period of time. Electricity was supplied at 3.5 kV with the frequency of 5.5 kHz. Some key parameters of water quality includes the level of chemical oxygen demand (COD), total suspended solid (TSS), color, and odor are measured before and after. The result showed that strong acid with pH below 2 was observed after 60 minutes plasma treatment for the DI water, while the surface water and wastewater needs about 120 minutes to pH below 2 even though the pH value are about the same at the beginning. Moreover, It was formed that the COD, TSS microorganism was noticeably decreased, therefore the increasing of transparency level. This result confirms that atmospheric DBD plasma generated acidity in water as reduce amount of organic and suspended solid in water.

1. Introduction

Waste water treatment is one of crucial issues in many cities around the world, required a balance between economic development and environmental protection. Traditional sewage and water treatment technologies can be specifically classified into three categories: biological, chemical and physical processes. Biological methods often use to treat both municipal and industrial waste waters, but they are generally not successful at degrading many toxic organic compounds. Chemical processes typically involve adding a chemical substance to a system to initiate a transformation. Some commonly added chemicals, such as chlorines, can cause negative effects on both human and environmental health. Physical processes are generally served as removing contaminants from the bulk fluid phase by concentrating them in a liquid or sludge phase. Many drinking water systems are challenged with difficult to treat target compounds such as organics (e.g., NDMA) and pathogens (e.g., Cryptosporidium, viruses, etc.)[6]. In fact, due to some properties of atmospheric plasma, it has been used in many applications, such as cleaning or modifying material surface. It is interesting to know the effectiveness of atmospheric plasma to improve the water quality, especially for waste water.



In order to adapt to sustainable development, the improving water resource management typically refers to recycling wastewater. This has been set as the first priority in many countries around the world. Plasma technology was suggested as the most promising technique to solve this task. The use of plasma processes was known as environmental friendly technique, safety and cost- effective alternatives. Recent studies about plasma technology in water treatment almost focus on direct plasma and thermal plasma because they require complex equipment as plasma reactor and small scale or apply plasma as additional method such as using UV, Ozone to disinfection [6 -7, 10-12]. This study is presenting a simple, comprehensive and large- scale method using indirect atmospheric dielectric barrier discharge (DBD) plasma.

Plasma technology based on applying electrical current, ions, high-reactive short-lived radicals are generated in plasma from ambient air or atmospheric oxygen such as oxygen and nitrogen reactive radicals, ozone, H^+ , etc. Hence, reactive particles are generated during discharge and rapidly react with dissolved pollutant in water due to their high reactivity. The oxidation processes of ozone and oxygen radicals are major factors to reduced pollutant in water and they are commonly using techniques. Alternatively, they were called as advantaged oxidation processes (AOP). However, the reaction between reactive oxygen species, nitrogen species and water were strongly supposed to acidify in water. The acidification of deionized water under direct exposure to dielectric barrier discharge (DBD) plasma was demonstrated in Natalie et.al. and Oehmingen et.al. Natalie's research shown that deionized water has $pH \approx 2$ after 90 minutes treat with DBD plasma [1-2]. So, the control acidity in water during plasma treatment is important in using plasma technology to water treatment.

This study observed indirect DBD plasma system working as a comprehensive water treatment. The sewage, surface water and DI water were used in the experiment. Some key parameters were observed, especially total suspended solid (TSS), pH, chemical oxygen demand (COD), and microorganism. Treatment mechanism of system based on dynamic gas moving in water tank and the advantage of oxidation processes. In plasma phase, there are the strong energy electrons, ions, UV rays and advanced oxidation such as HO^* , O^* , H^* , O_3 , H_2O_2 (hydrogen peroxide). When water contacted to plasma, the ionic bonds, covalent linking of organic, inorganic and bacteria are broken down and killed by advanced oxidation. Moreover, acidification in water has strong effect on inactive bacteria. Therefore, the quality of wastewater is improved and then it might be pumped out.

2. Experimental

The experiment setup is shown in Figure 1. The power supply is a laboratory-made free running oscillator which was set at frequency of 5.5.kHz, and Voltage was set at 3.5 kV. This system works at the atmosphere pressure and using air as carrier gas. A glass tube (2) with one inner copper electrode and aluminum external electrode wrap around will be used as dielectric barrier. The distance between two electrodes is approximately 1 mm. This tube also connected to a gas pump with an attached valve control (4). Gas speed was supplied at 15 litter/ minutes. The high-voltage was supplied to two electrodes and created a plasma, the gas passed through a glass tube and get energy from high voltage electricity and then it went down into a water tank (5). When the air passed the glass tube, they are excited and jumped into water. Reactive oxygen species (ROS) and reactive nitrogen species (RNS) are usually found in exhaust stream. Represents for these species are O_2^* , O^* , O_3 , OH^* , NO^* , NO_2^* , etc.

[15, 16, 17]. These compounds can react with water in the tank.

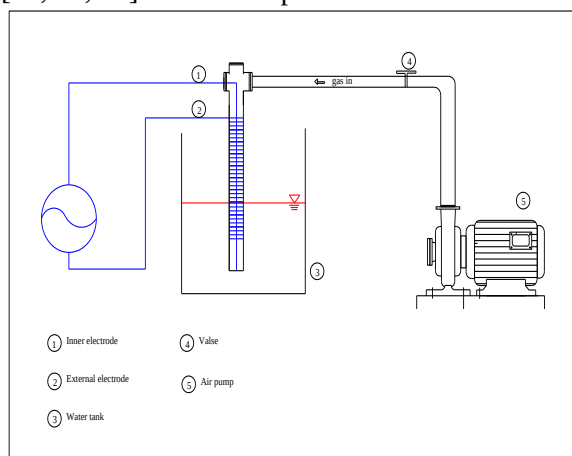


Figure 1. Experiment schematic

3. Results and discussion

The first observation of water after the plasma treatment is the improvement of organoleptic quality. They have almost non-color and odorless. It indicates that a large amount of organic matter has decomposed. Total suspended solid of water has noticeably reduced.

Total suspended solids (TSS) is the most visible indicator of water quality. TSS are particles which sizes are greater than 2 microns found in the water column. In another hand, TSS are total quantity measurements of solid material per volume of water though most suspended solids. These suspended solids are made up of inorganic materials, bacteria and algae can also contribute to the total solids concentration. TSS affect to water turbidity and water clarity also. TSS can be used to calculate sedimentation rates.

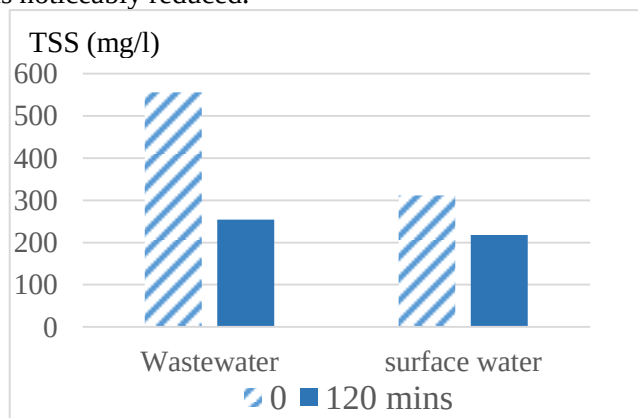


Figure2. Total suspended solid of wastewater and surface water before and after plasma treated.

In our study, the values of TSS were recorded in both wastewater and surface water (Figure 2). TSS of wastewater and surface water reduced to 54.32% and 30.12%, respectively. These superoxide radicals generated in plasma phase play an important role to removed organic compound in wastewater (normally >50%), which is main reason cause the color of water [7, 18, 19]. Moreover, visual inspection recorded the reduced of large-size solids. It seems treatment process causes a breakdown in large-size solids without any additional physical methods. However, the mechanism should be detailed explain.

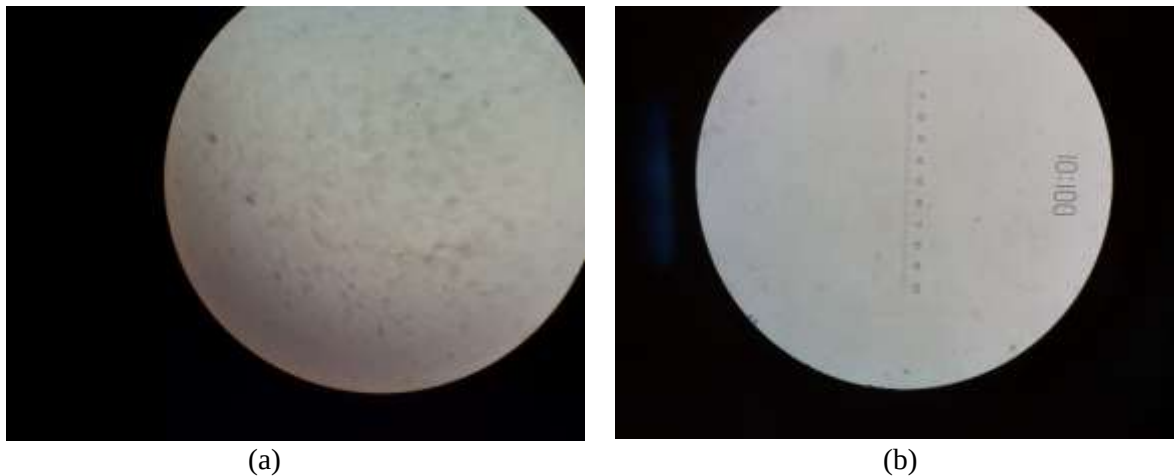


Figure 3. Microscope picture of surface water before(a) and after treated (b)

Figure 3 shows the decreasing of microorganism in surface water that was observed in a microscope. Wastewater has not made a clear difference. Before plasma treatment, surface water samples have many algae and planktons, and most of them were killed during plasma treatment. Algae and bacteria, plankton in water might be killed by oxidation and acidity in water. When oxidants such as ozone contacts with bacteria cell, which keep bacteria in shape and protect bacteria, a reaction called an oxidative burst occurs which literally creates a tiny hole in the cell wall. A newly created hole in the cell wall has injured the bacterium, after thousands of ozone collisions in a few seconds, the bacterial wall can no longer maintain its shape and the cell got killed. Moreover, the acidification in water during working of plasma system also killed bacteria by reaction of reactive oxygen species. Superoxide and hydrogen peroxide (H_2O_2) are produced while generating plasma. Both O_2^- and H_2O_2 can damage a variety of biomolecules and enzyme. These types of damage result in metabolic defects, including auxotrophy for aromatic, branched-chain, and sulfur-containing amino acids. Superoxide cannot damage membranes in bacteria but they destroyed bacteria through damage DNA and enzyme of bacteria [1,2,14]. Results of increase acidity in water also support this opinion.

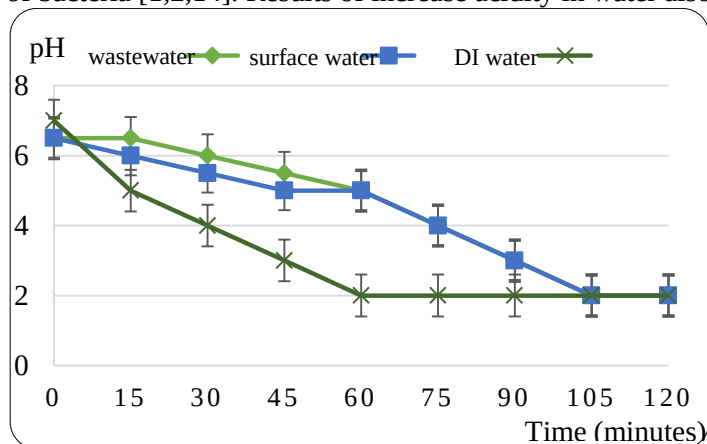


Figure 4. The change of pH value of different type of water during experiment.

The detected of nitrate/ nitrous acid was confirmed in both Natalie *et al.* and Oeminhem *et al.* study. Atmospheric plasma causes some chemical reactions in the air, typical creation ozone (O_3) and oxidize nitrogen, then dissolve in water and cause chemical change. Although the formation of nitrate/nitrous acid in water was confirmed, they still do not have strong acidity, which indicated by $\text{pH} \approx 2$. The other important things are superoxide radicals, which were the result of reaction between ozone and water. This result and mechanism also explained in Natalie *et al.* and others study [1,3]. The acid, which from superoxide O_2^- , and H^+ radical was called plasma acid. Figure 4 shows pH

In this experiment, the system is indirect system, which has the same principle with Oeminhem *et al.* experiment. Indirect plasma technologies generate plasma in a location away or near to but not direct within sample to be treated. In this case, the main source of the pH change in the liquid is a chemical change – HNO_3 , HNO_2 , O_2 radical and O_3 that are created by the plasma in the air are reaching the liquid and becoming dissolved there.

dependence on time of four types of water: deionized (DI) water, surface water, and wastewater. It clearly shows a rapid increase in the acidity of all types of water. Although the time to achieved strong acid is different, the strong acid which has $\text{pH} \approx 2$ was detected in all types of water. In other words, DBD plasma created acidity in all types of water. The similar results with DI water were reported in Natalie *et al.* and Oeminhem *et al.* [1, 2]. DI water achieved $\text{pH} \approx 2$ after 60 minutes treated and keep it stable in a long time later while wastewater and surface water need 135 minutes to gain $\text{pH} \approx 2$.

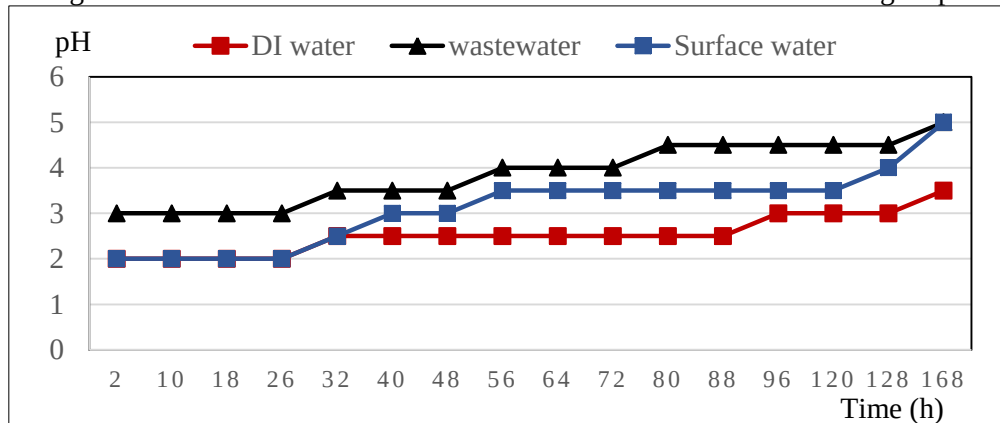


Figure 5. The increases of pH values of DI water, wastewater and surface water after treatment without plasma exposure.

Figure 5 show the sustainability of water when leaving them without addition of plasma. Plasma acid is stable in a long time after plasma treatment, water sample was kept in 7 days without additional plasma. The pH values of water show that plasma acid, which was created in treating time stable for 26 hours and slowly increase after that. After 7 days without addition plasma treatment, pH value of wastewater and surface water are 5 while DI water has $\text{pH} \approx 3.5$. Although $\text{pH} \approx 5$ is not recommended, the output water is not dangerous affect to human. These results suggest that plasma can use as chemical method to kill bacteria line chlorine. However, it also suggests that keeping treated water in tank or raceway system at least 7 days is necessary when we use plasma treatment as wide method.

The slow increase of acidity in wastewater and surface water suggested that the influence of other compounds in water to increasing of acidity. The most suspicious element is organic compounds, which has a large part in both wastewater and surface water and be easily oxidized by ozone and reactive oxygen radicals. Chemical oxygen demand (COD) of wastewater and surface water were measured before and after treatment to observe the effect of plasma system to dissolve pollutants in water.

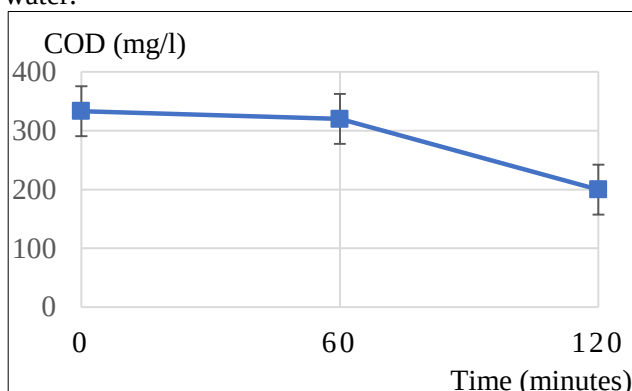
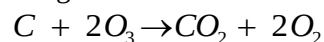


Figure 6. COD of waste water during treated.

The impression results in terms of sensory were also recorded in this experiment, a large part of the sewage smell and the color was disappeared. Wastewater after exposure to DBD plasma becomes transparent and odorless. This results suggested that DBD plasma has important contribute to increasing of dissolve oxygen in wastewater and a part of ozone was used to oxidize organic matter in

Figure 6 shows the reducing of organic compounds in wastewater during experiment. COD of wastewater decreased 40% after 120 minutes treated. Organic compounds is a major component to be treated in wastewater treatment. It also caused color and odor in wastewater due to the anaerobic decomposition of organic compounds. In other words, due to the shortage of oxygen in the water.

sewage. Because a large amount of ozone was generated by DBD plasma in gas phase, so oxidized by ozone become the most likely factor. The general chemical reacts follow [4,5]:



The decreasing of COD of surface water (Figure 7) was also recorded in this experiment. After 120 minutes exposure to DBD plasma, 33% organic compounds in surface water were decomposed. The result with surface water is approximately identical with wastewater. Organoleptic quality also improved by DBD plasma. Although ozone is a strong oxidizer, DBD plasma cannot oxidize all of organic compounds in water, there was a part of organic compounds still remain in water after treatment. The remaining organic matters in both wastewater and surface water may in the form of insoluble suspended solids or non-oxidized by ozone and oxygen radicals.

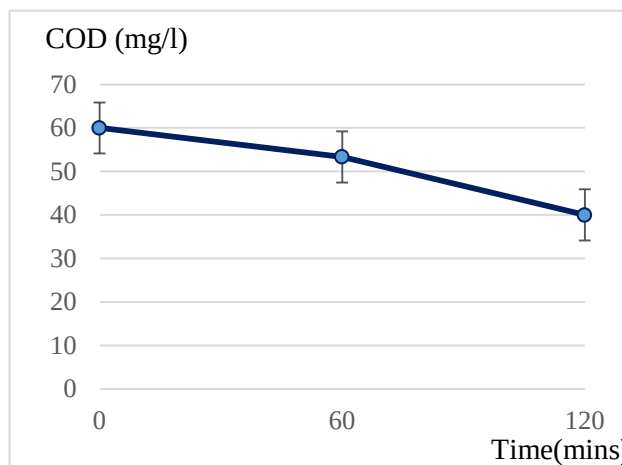


Figure 7. COD of surface water during treated.

These results suggest that plasma treatment is also working as a microbiological method to reduce organic compounds though it has lower efficient than microbiological method. So, if we want to use plasma as a comprehensive system, the addition microbiological is suggested.

4. Conclusion

In this experiment, the atmospheric DBD plasma has potential to apply in water treatment as a comprehensive system without addition of physical or chemical methods. After treated by DBD plasma, both waste water and surface water quality were improved. TSS of both types of water has significantly reduced and also help improve visual water quality. The number of organic compounds in wastewater and surface water have decreased after plasma treated. Chemical oxygen demand of wastewater and surface water reduced 40% and 33% after 120 minutes treating, respectively. Atmospheric DBD also plasma caused acidify in all types of water includes DI water, surface water and wastewater. Strongly acid with pH ≈ 2 was detected with all types of water. This acid condition is stable for 26 hours.

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