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Date Submitted: 2020-08-29

Keywords: oxidation, TiO₂ catalyst, DC plasma jet, non-thermal plasma, contaminated water

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Freshwater is only 2.5% of the total water on the Earth and rest is contaminated or brackish. Various physical and chemical techniques are being used to purify the contaminated water. This study deals with catalytic plasma treatment of contaminated water collected from different sites of Faisalabad-Pakistan. A non-thermal DC plasma jet technique was used to treat the water samples in the presence of TiO₂ catalyst. The plasma-assisted catalytic treatment introduced some oxidative species (O₃, H₂O₂, HO₂·, OH·) in the water. These species reacted with pollutants and cause the degradation of harmful contaminants, especially dyes. The degradation of dye sample during plasma treatment was more pronounced as compared to other samples. pH, conductivity and TDS of dye containing sample decreased after catalytic plasma treatment. The degradation of organic pollutants increased due to presence of several oxidants, such as TiO₂, ferrous ions and hydrogen peroxide. FT-IR analysis revealed the degradation of some functional groups during treatment process and confirmed the effectiveness of the process. The residue of the treated samples was consisted of amines, amides and N-H functional groups. XRD analysis showed the presence of Alite, Ferrite, aluminite, Si, S and some heavy metals in the residue. The effect of plasma treatment on activity of gram-negative *Escherichia coli* (*E. coli*) bacteria in water was also checked. The bacterial activity was reduced by almost 50% after 2 min of plasma treatment.

Record Type: Published Article

Submitted To: LAPSE (Living Archive for Process Systems Engineering)

Citation (overall record, always the latest version):

LAPSE:2020.0942

Citation (this specific file, latest version):

LAPSE:2020.0942-1

Citation (this specific file, this version):

LAPSE:2020.0942-1v1

DOI of Published Version: <https://doi.org/10.3390/pr8060667>

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Article

Catalytic and Non-Catalytic Treatment of Industrial Wastewater under the Exposure of Non-Thermal Plasma Jet

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Received: 24 March 2020; Accepted: 28 May 2020; Published: 4 June 2020



Abstract: Freshwater is only 2.5% of the total water on the Earth and rest is contaminated or brackish. Various physical and chemical techniques are being used to purify the contaminated water. This study deals with catalytic plasma treatment of contaminated water collected from different sites of Faisalabad-Pakistan. A non-thermal DC plasma jet technique was used to treat the water samples in the presence of TiO₂ catalyst. The plasma-assisted catalytic treatment introduced some oxidative species (O₃, H₂O₂, HO₂[−], OH[−]) in the water. These species reacted with pollutants and cause the degradation of harmful contaminants, especially dyes. The degradation of dye sample during plasma treatment was more pronounced as compared to other samples. pH, conductivity and TDS of dye containing sample decreased after catalytic plasma treatment. The degradation of organic pollutants increased due to presence of several oxidants, such as TiO₂, ferrous ions and hydrogen peroxide. FT-IR analysis revealed the degradation of some functional groups during treatment process and confirmed the effectiveness of the process. The residue of the treated samples was consisted of amines, amides and N-H functional groups. XRD analysis showed the presence of Alite, Ferrite, aluminate, Si, S and some heavy metals in the residue. The effect of plasma treatment on activity of gram-negative *Escherichia coli* (*E. coli*) bacteria in water was also checked. The bacterial activity was reduced by almost 50% after 2 min of plasma treatment.

Keywords: contaminated water; non-thermal plasma; DC plasma jet; TiO₂ catalyst; oxidation

1. Introduction

The depleting fresh water sources is a global issue. For the existence of living organisms, the water is the most vital component. The use of polluted water is causing numerous diseases. About 3.4 million people, mostly children, die every year from waterborne diseases [1–3]. Population of the underdeveloped countries is rising exponentially and so does the demand of clean water. Most parts of Punjab and Sindh in Pakistan have polluted and brackish ground water. Faisalabad is the second largest city in eastern province of Punjab and third most populated city of Pakistan. Faisalabad has a semi-arid four-season climate with very low to high temperatures and nearly 320 days of annual sunshine. Faisalabad has grown into a multi-industrial metropolis and distribution center due to its central location in the region. This city contributes over 20% of GDP of Punjab with annual GDP of USD 20.5 billion. Textile industry and agriculture remain its hallmark. However, this city lacks basic data related to air and water quality. Apparently, no planned environmental monitoring is being undertaken by the government in this city.

Iron, chemicals, steel, leather, electroplating and textile industries are the major sources of water pollution in the city. The other notable sources are pastures, feedlots, croplands, petroleum drilling, mining and landfills. The anthropogenic sources of water pollution include industrial, sanitary and storm sewers. The typical pollutants are different kinds of pesticides, hydrocarbons, alcohols, sulfates, nitrates, phosphates, oxalates, chlorides, fluorides, heavy metals, unhealthy microbes, etc. [4]. These pollutants may be of any type, like organic, inorganic or biological. The removal of such strong and lethal pollutants is difficult by using the ordinary methods, for example, chlorination, adsorption, ultra-sonication, coagulation, etc. [5]. Therefore, to address the issue, many techniques like oxidation using ozone, high-energy electron irradiation, carbon absorption, advanced oxidation processes (AOPs), ionizing radiations, non-thermal plasma and sonolysis are preferred to remove infectious pollutants from polluted water [6].

AOPs are substantial techniques that are preferred over other techniques [7,8]. These techniques neither yield harmful sedimentation nor alter pollutants from one phase to another [7]. Recently, plasma technology has also been tested for cleaning of polluted water [8]. More than 99% of our universe is made of plasma. Based on electron temperature and density, plasmas are classified into thermal and non-thermal segments [9,10]. The non-thermal plasmas (NTPs) are being used for processing of materials, removal of contaminants, ozone generation, synthesis of nanomaterials, medical treatments, etc. [11]. Plasma produces oxidizing species, radicals, charged species and UV radiations that themselves are supposed to be AOPs. Oxidizing species, produced by NTPs, are O_3 , H_2O_2 , $\bullet HO_2$ and $\bullet OH$. The radical " $\bullet OH$ " is a strong oxidizing agent that rapidly reacts with pollutants in water. The plasma produced oxidizing species do not contribute harmful side-products, which are unhealthy for human being. Unlike the chlorination and other traditional methods, no additional chemical ingredients are required during plasma treatment process [12].

The reactive neutral species are generally capable of disintegrating microorganism cell walls, coverings and sheaths depending on their own oxidizing impact. The reactive oxygen-based species (O , O_2 , O_3 , OH) and nitrogen-based species (NO , NO_2) decompose the compounds that cannot be oxidized by regular oxidant [11,12]. Several authors discussed the use of plasmas for disinfecting the pathogens [12–16]. Plasma emits UV radiations, which interact with bacteria cell wall. An argon–air mixture plasma contains reactive oxygen species, which may have strong oxidizing impact on cell membrane. Additionally, electrostatic effect due to charging of membrane weakens the tensile strength of cell.

In the presence of a suitable catalyst, NTP can be more effective in degrading the contaminants, especially the dyes. Some of the reported catalysts are silica gel, alumina, TiO_2 photocatalyst, Fe^{2+} , Fe_3O_4 and activated carbon [13]. In this study, contaminated water is treated with an atmospheric pressure DC plasma jet in the presence of a TiO_2 catalyst. TiO_2 is used as photocatalyst for the water treatment. TiO_2 converts surfactants, aliphatics, pesticides, polymers, aromatics, dyes and herbicides into water, carbon dioxide and mineral acids without giving any solid by-products [14]. TiO_2 is regarded as an environment friendly, stable and relatively less expensive. It is mostly used as a photocatalyst, which is used for environmental cleanup, water and air purification, bactericide, optical and antireflective coatings, sensors and water splitting. The aim of this study is to obtain contaminants' free water through an atmospheric pressure DC plasma jet processing in the presence of a metal oxide catalyst.

2. Materials and Methods

2.1. Water Sampling

A non-thermal DC plasma jet of argon gas in open atmosphere was used to treat the contaminated water collected different sites of Faisalabad district in Pakistan. The sources and type of water samples are given in Table 1. Three sets of water samples were prepared, including untreated samples (X_1 , X_2 , X_3 , X_4 , X_5 , X_6 and X_7), samples treated with plasma (Y_1 , Y_2 , Y_3 , Y_4 , Y_5 , Y_6 , Y_7) in the absence of a

catalyst and samples treated with plasma in combination with TiO_2 catalyst ($Z_1, Z_2, Z_3, Z_4, Z_5, Z_6, Z_7$). The flowchart of the process, adopted for plasma-assisted catalytic and non-catalytic treatment of water samples, is shown in Figure 1.

Table 1. Labeling of water samples collected from different sites in Faisalabad.

Water Sample	Source
X_1, X_2 and X_3	Tap water of different areas of Faisalabad
X_4	Dye sample of textile industry in Faisalabad
X_5	Industrial wastewater of Faisalabad
X_6	Sample of Chenab river in Faisalabad
X_7	Wastewater treatment plant

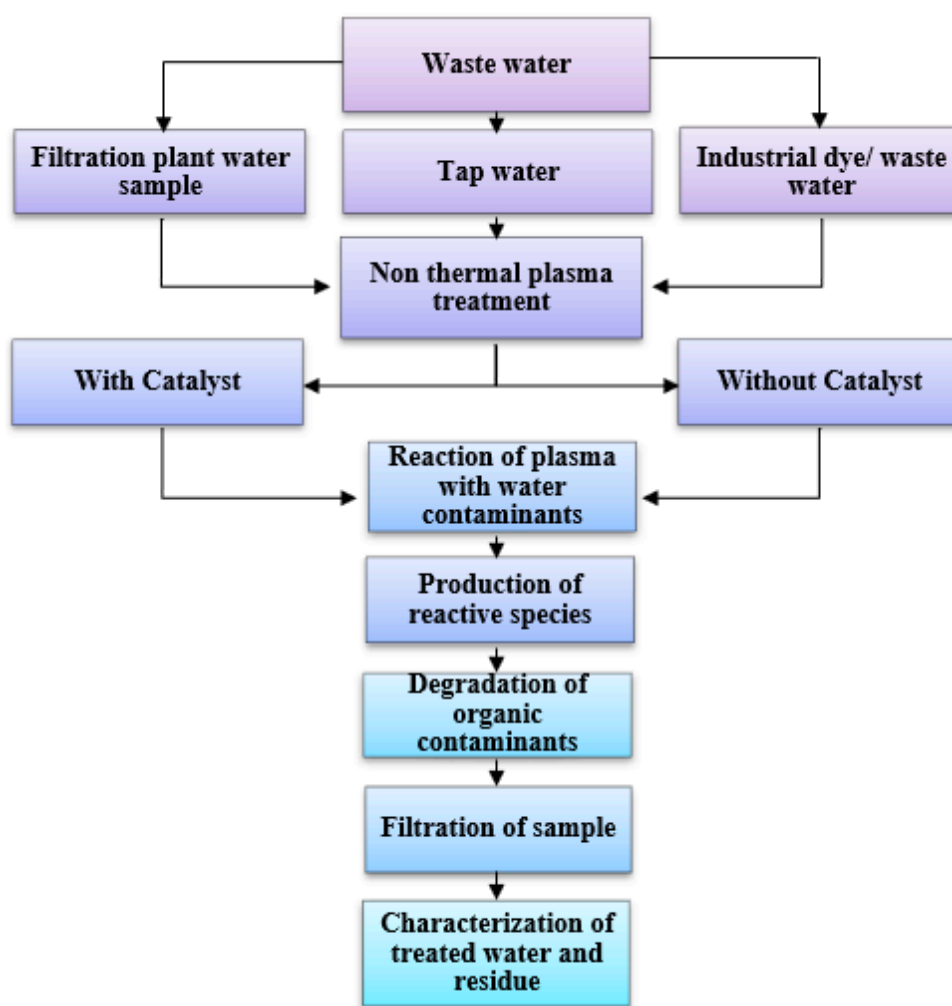


Figure 1. Flowchart of the plasma-assisted treatment of water samples with TiO_2 .

2.2. Plasma Treatment Setup

Schematic of an atmospheric pressure DC plasma treatment system is shown in Figure 2. The setup is consisted of a high-voltage DC supply, variable resistance box, Tungsten anode, copper nozzle of 2 mm orifice diameter, sample holder and gas supply valves. A total of 50 mL of a water sample was taken in a beaker and placed on the sample holder. The Tungsten anode was dipped in water sample. The copper nozzle, which also worked as a cathode, was fixed at 10 mm above the water level. The inter-electrode distance was set at 20 mm. A safety resistance of 100 k Ω was also added in the

circuit to avoid breakdown in case of direct contact between electrodes. Once the circuit was complete, the argon gas was passed through plasma nozzle at a fixed flowrate of 5 LPM. A fixed voltage of 6 kV was applied across the electrodes to produce plasma jet of argon–air mixture. The plasma jet interacted with contaminated water sample and initiated some chemical reactions.

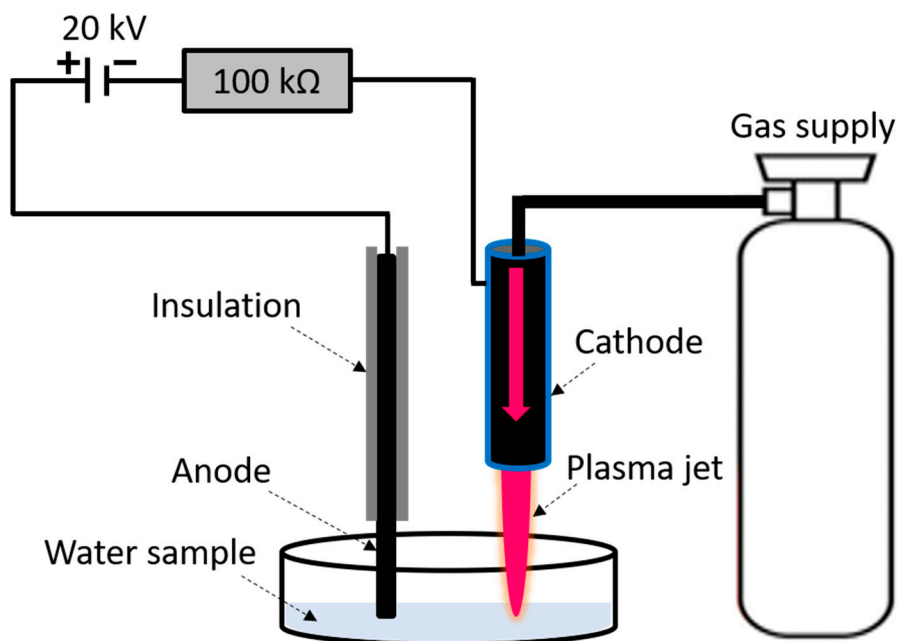


Figure 2. Atmospheric pressure DC plasma treatment system.

2.3. Plasma Chemistry

Since a plasma jet was generated by discharging argon–air mixture, the possible plasma chemistry is explained in Figure 3. The plasma jet may contain several species, including neutrals, ionized particles, excited particles and electrons. Oxygen (O_2), nitrogen (N_2), excited argon particle (Ar^*), argon ions (Ar^+), neutral argon (Ar), CO_2 , NO , N_2O and O_3 were expected in the discharge. Some other species may also be present in the plasma plume, depending on the local environment. The degradation of contaminants was anticipated due to chemical interactions of plasma species with water molecules and contaminants. The reactive species for these interactions are assumed as H_2O^+ , H^+ , O_3 , OH^- or HO^- . The oxidation potential of these species is provided in Table 2.

The water treatment process was carried out at room temperature. Each sample was exposed individually to plasma jet for 10 min without using TiO_2 catalyst. Then a similar procedure was repeated by introducing TiO_2 catalyst in the reaction. Only 0.5 g of catalyst was added in the water and exposed to plasma for 10 min. Filtration of the plasma-treated water was performed to remove the catalyst and solid residue. The filtered water was analyzed to check the removal of pollutants after catalytic and noncatalytic treatment under plasma exposure. Several analyses were conducted on water samples to examine the suitability of plasma treatment for removal of pollutants from industrial effluents. These analyses include testing of pH, TDS, turbidity, conductivity, alkalinity, color, etc. No solid particles were detected in the water samples before plasma treatment. However, a white solid residue emerged in the water during plasma treatment. The solid residue was separated from the water through centrifugation and dried in an oven for 6 h at 80 °C. The dried residue was characterized using X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FT-IR) techniques.

2.4. Plasma Inactivation of Bacteria

The industrial effluents may also contain gram-negative bacteria along with heavy metals, dyes and other pollutants. Therefore, the effect of plasma treatment on inactivation of gram-negative

bacteria in the water samples was also investigated. The *Escherichia coli* (*E. Coli*) bacteria was cultured and subjected to the argon plasma jet under similar conditions as set for treatment of water samples. The bacteria culture was exposed to plasma for 3 min under ambient conditions. The effect of plasma treatment on inactivation of bacteria was determined by counting the colony forming units (CFUs) in the sample before and after plasma exposure.

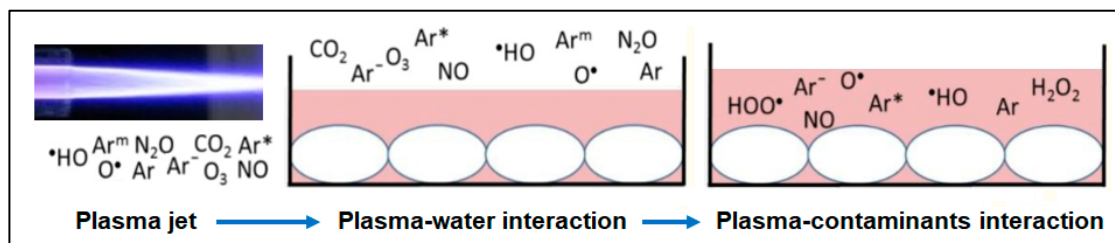


Figure 3. The expected radicals and species in argon–air mixture plasma jet.

Table 2. Oxidation potential of different chemical oxidizers.

Oxidant	Oxidation Potential (V)
Hydroxyl radical (OH)	2.80
Ozone (O ₃)	2.07
Hydrogen peroxide (H ₂ O ₂)	1.77
Permanganate ion	1.67
Chlorine oxide	1.50
Chlorine	1.36
O•	2.42

3. Results and Discussion

3.1. Water Quality Parameters

Most of the samples exhibited a slight increase in pH value during plasma treatment, as shown in Table 3. An increase in pH of water is related to increase of OH radicals during plasma treatment. A change in pH of sample depends on concentration of OH radicals in the sample. In this experiment, pH of X₁, X₂, X₃, X₅, X₆ and X₇ samples increased after plasma treatment. However, pH of dye containing sample (X₄) decreased from 12.2 to 12 after plasma treatment in the absence of catalyst. In the presence of catalyst, pH of sample declined twofold after 10 min of plasma treatment. Similar results were reported by Sugiarto et al. [15]. A decrease in pH of X₄ is attributed to the alkaline nature of the sample [16]. As shown in Table 3, the electrical conductivity of some of the samples increased after plasma treatment, while other samples exhibited a decrease in electrical conductivity. An increase in conductivity is attributed to the formation of by-products in the sample during plasma treatment while decrease in conductivity was due to conversion of soluble inorganic salts to insoluble ones. This change in electrical conductivity also depends on the nature of intermediates formed during plasma processing of the water samples [17].

Both catalytic and noncatalytic plasma treatments did not show notable influence on total dissolved solid (TDS) except for dye sample (X₄). TDS value of X₄ decreased by 140 points after simple plasma treatment and 190 points after catalytic plasma treatment. Similarly, some samples showed slight increase in hardness on plasma treatment. The degradation efficiency of organic pollutants increased in the presence of several oxidants, such as TiO₂, ferrous ion and hydrogen peroxide [18].

The inorganic particles like sulfates and phosphates were also present in the samples. A change in sulfate and phosphate contents of plasma-treated samples is attributed to the by-products obtained during plasma treatment. The presence of sulfate ions in solution also caused a decrease in percentage degradation because these ions could react with OH radicals in solution and result in their depletion.

According to Ghezzar et al. [19], degradation of inorganic compounds starts after 20 min of plasma treatment [20].

Hu et al. [21] reported photocatalytic degradation of two azo dyes called Procion Red MX-5B (MX-5B) and Cationic Blue X-GRL (CBX). They observed the effect of inorganic ions on the photocatalyst activity of TiO_2 and its role in degradation of dyes. Both dyes reacted differently with different pH ranges in the presence of a catalyst. The presence of inorganic ions (sulfates and phosphates) in the solution significantly influenced the degradation of dyes. Ghezzar et al. [19] degraded two textile wastewater samples having different pH values. They used gliding arc discharge technique to degrade the samples with and without using TiO_2 catalyst. The effect of catalyst amount and plasma treatment time on degradation of wastewater was investigated. The degradation activity of TiO_2 depends on pH, catalyst amount and treatment time. In the presented work, catalytic did not shown significant effect on removal of inorganic substances as the catalytic activity is pH dependent and almost all the samples were alkaline in nature. pH dependence may explain why the organic compounds are degraded in acid medium but not in basic solution [22].

Different water quality parameters, such as pH, TDS, hardness, conductivity, sulfates and phosphates for the tested samples are given in Table 3. Most of the samples did not show any noticeable change in quality parameters after plasma treatment. The dye containing samples (X_4 , Y_4 , Z_4) showed appreciable improvement in quality parameters. The acceptable ranges of standard water quality parameters are shown in Table 4.

Table 3. Summary of quality parameters of samples with and without plasma treatment.

Sample	pH		Conductivity		TDS		Hardness		Sulfates		Phosphates	
	Value	SD (\pm)	$\mu\text{S}/\text{cm}$	SD (\pm)	mg/L	SD (\pm)	mg/L	SD (\pm)	mg/L	SD (\pm)	mg/L	SD (\pm)
X_1	8.4	0.168	2020	40.4	1030	20.6	40	0.8	59	1.18	3.5	0.07
Y_1	8.7	0.174	2040	40.8	1040	20.8	56	1.12	48	0.96	3.3	0.066
Z_1	8.6	0.172	2000	40	1020	20.4	56	1.12	40	0.8	2.6	0.052
X_2	7.9	0.158	830	16.6	420	8.4	384	7.68	45	0.9	3.3	0.066
Y_2	8.2	0.164	820	16.4	420	8.4	408	8.16	51	1.02	2.6	0.052
Z_2	8.4	0.168	840	16.8	430	8.6	400	8	42	0.84	2.9	0.058
X_3	7.9	0.158	4660	93.2	2370	27.4	456	9.12	58	1.16	2.6	0.052
Y_3	8.3	0.166	4650	93	2370	27.4	504	8.08	60	1.2	2.8	0.056
Z_3	8.3	0.166	4670	93.4	2390	27.8	480	9.6	58	1.16	3.4	0.068
X_4	12.2	0.244	8040	98.8	4100	32	108	2.16	44	0.88	2.8	0.056
Y_4	12	0.24	7770	95.4	3960	39.2	97	1.94	54	1.08	3.3	0.066
Z_4	11.8	0.236	7470	84.4	3810	36.2	68	1.36	54	1.08	3.2	0.064
X_5	7.8	0.156	1220	24.4	620	12.4	416	8.32	42	0.84	3.4	0.068
Y_5	8.3	0.166	1220	24.4	620	12.4	416	8.32	58	1.16	3.6	0.072
Z_5	8.5	0.17	1230	24.6	630	12.6	440	8.8	46	0.92	3.3	0.066
X_6	7.9	0.158	440	8.8	230	4.6	184	3.68	48	0.96	3.5	0.07
Y_6	8.2	0.164	470	9.4	240	4.8	192	3.84	52	1.04	3.2	0.064
Z_6	8.3	0.166	460	9.2	240	4.8	200	4	44	0.88	3.5	0.07
X_7	7.8	0.156	5350	67	2740	34.8	872	12.44	46	0.92	2.9	0.058
Y_7	8.2	0.164	5420	88.4	2770	55.4	792	15.84	48	0.96	3.5	0.07
Z_7	8.1	0.162	5430	88.6	2770	55.4	944	0.8	40	0.8	3.6	0.072

Table 4. Acceptable ranges of standard water quality parameters.

Standard Water Quality Parameters	Range
pH	6.5–8.5
Conductivity	200–800 $\mu\text{S}/\text{cm}$
TDS	1000 mg/L
Hardness	<60 mg/L = soft water 60–120 mg/L = moderately hard 120–180 mg/L = hard >180 mg/L = very hard
Sulfates	250 mg/L
Phosphates	0.05–0.1 mg/L

The hardness testing of the reported samples produced random results. Hardness is basically referred to the amount of calcium and magnesium in water. It causes harmful impact on human health [23]. In this study, no predictable trend of hardness was observed. Some samples exhibited slight increase in hardness while others showed slightly decreasing trend. However, in the presence of the catalyst, most of the samples underwent a slight decrease in hardness. The possible reason for having least effect of plasma on hardness is the treatment of samples under constant plasma pressure, applied voltage and exposure time. Yang et al. [24] revealed that water hardness is mainly due to presence of CaCO_3 , Na_2CO_3 and CaCl_2 . To remove such water hardening particles, they adopted a pulsed spark discharge technique. The experiments were performed with different gas flowrates (200, 300 and 400 mL/min). Hardness was decreased with an increase in gas flowrate.

3.2. Identification of Heavy Metals

As shown in Figures 4–8, some heavy metals (Ni, Pb, Cd, Cu and Cr) were detected in the tested samples. The concentration of heavy metals in plasma-treated and untreated samples were examined by using atomic absorption spectrophotometer. This technique is used to identify the concentration of elements present in the sample. In dye containing sample, significant removal of metals was observed during plasma treatment. The notable removal shows the effectiveness of the treatment process, especially for dye containing water (Figure 4). The high degradation of dye in samples is attributed to its alkaline nature (pH 12) [25]. The removal of metals from the sample depends on the pH of the sample. Ke et al. [25] reported the highest removal of Cr (VI) from samples of high pH due to presence of more reducing species in the sample. As TiO_2 is more effective for organic compounds, some of the metals were removed from the water in the presence of catalyst while others were not.

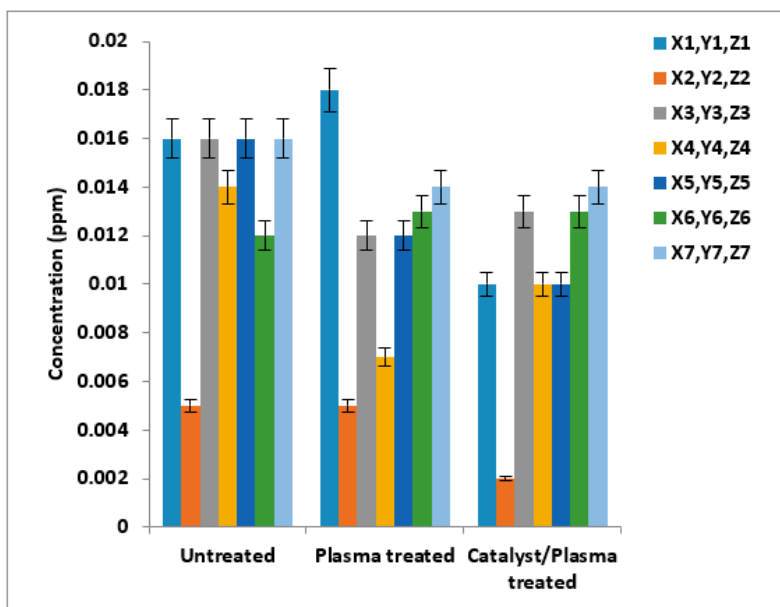


Figure 4. Cr concentration in untreated and plasma-treated water samples.

A comparison of heavy metals can be discussed based on concentration of metals. The concentration of some metals increased while others decreased after catalytic and noncatalytic plasma treatments. Due to the formation of by-products in the sample during plasma treatment, the increment levels of metals occurred through catalytic activity. As seen in Figure 5, concentration of Cu in all samples increased with plasma treatment except X_4 sample. As for Pb, it was found in most of the untreated water samples. Pb was removed from almost all water samples after plasma treatment. Upon plasma treatment, as shown in Figure 6, Pb was completely absent in dye containing water sample. Almost similar results were obtained for Ni, Cr and Cd metals in plasma-treated samples.

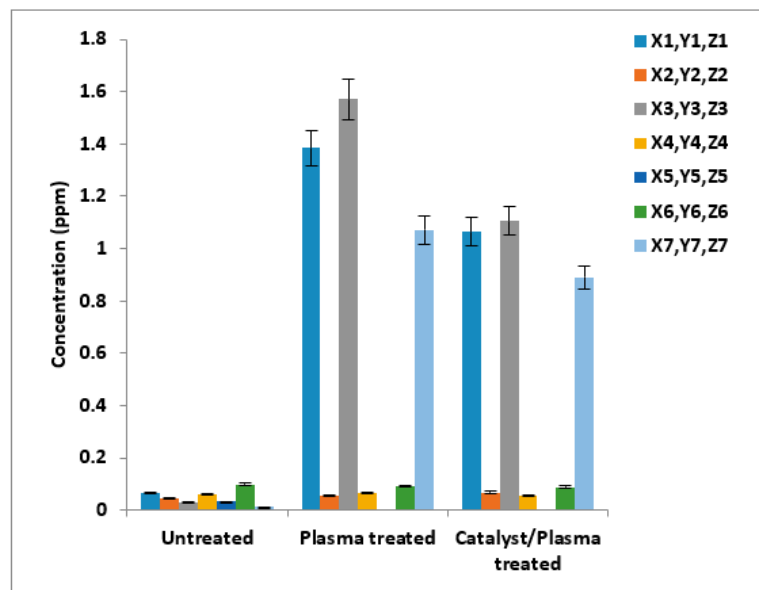


Figure 5. Cu concentration in untreated and plasma-treated water samples.

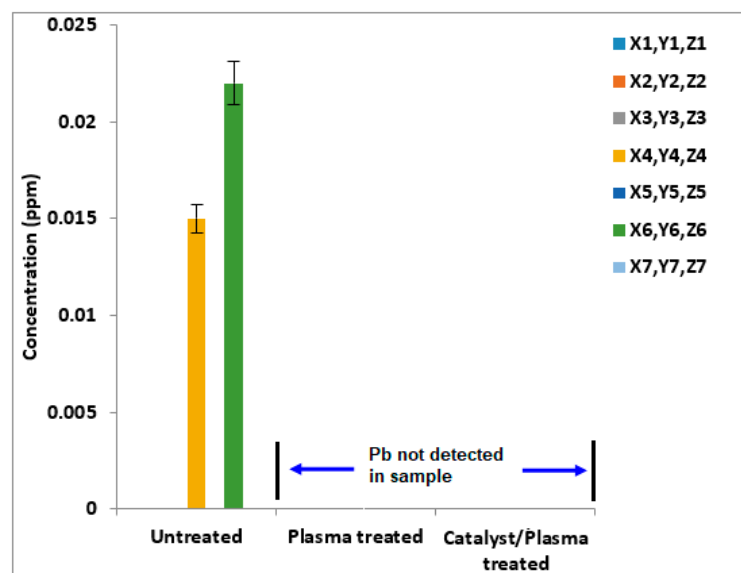


Figure 6. Pb concentration in untreated and plasma-treated water samples.

Icopini et al. [26] tested wastewater samples of different pH values for identification of Cr. It was observed that Cr containing solution will be either neutral or positively charged for lower pH values [26]. Cserfalvi et al. [27] used a glow discharge technique to figure out the presence of metals in the solution. The electron temperature in the glow discharge was measured about 5000 K. They used an advanced electrolyte–cathode discharge spectrometry technique for identification of metals, like Ni, Cu, Pb, Zn, Cd and Mn in water samples. Each metal had a specific peak intensity value and concentration curve, depending on pH and hydrogen ion concentration of the tested solution. In this work, the simple plasma treatment did not significantly promote the removal of heavy metals from the water samples. However, catalytic plasma treatment significantly suppressed Ni concentration. As shown in Figure 7, all untreated and plasma-treated samples measured Ni though, in the presence of a catalyst, it was almost absent from the sample treated with plasma. Cd was present in untreated tap water and the sample collected from wastewater treatment plant. The simple plasma and catalytic plasma treatments did not affect Cd in X₂ sample, while Cd was not detected in other plasma-treated samples (Figure 8).

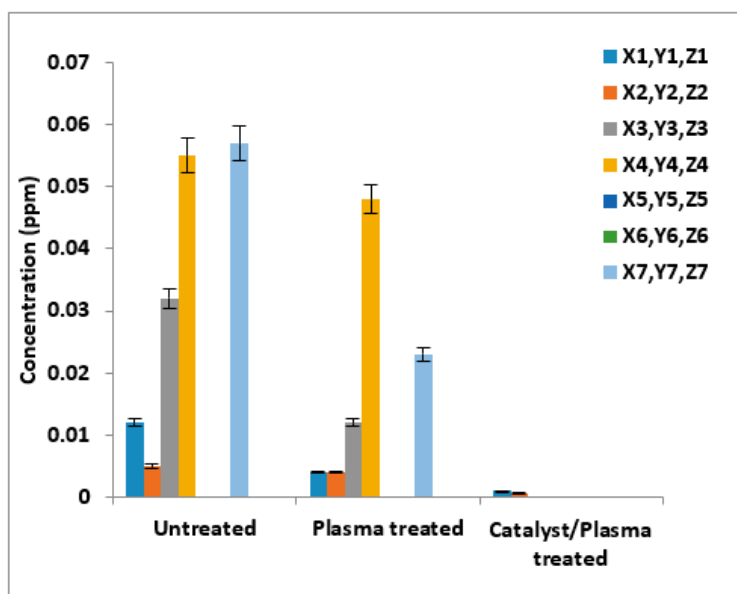


Figure 7. Ni concentration in untreated and plasma-treated water samples.

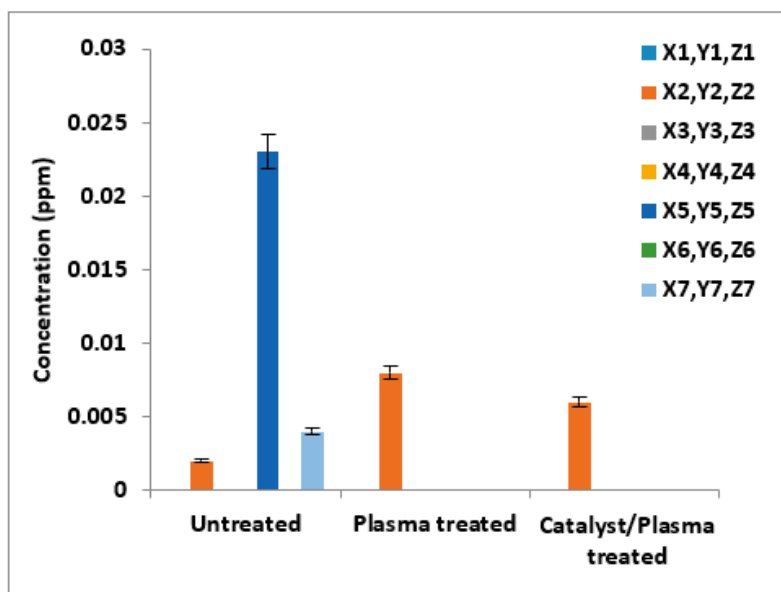


Figure 8. Cd concentration in untreated and plasma-treated water samples.

3.3. FT-IR and XRD Analysis of Residue

After sampling, the water samples were left undisturbed for 24 h. Some solid particles settled down at the bottom of container having industrial wastewater (X₅). The solid residue was separated from the wastewater through centrifugation. This water sample was given simple plasma and catalytic plasma treatment in separate runs. As shown in Figure 9, some solid residues again settled down at the bottom of beaker during plasma treatment, which were separated from the water through centrifugation. The solid residues of untreated (X₅), plasma-treated (Y₅) and catalytic plasma-treated (Z₅) samples were dried in an oven for 6 h. These residues were analyzed through FT-IR and XRD techniques, FT-IR patterns of the residue are shown in Figure 10. The degradation of some functional groups during treatment process confirmed the effectiveness of plasma treatment process. The residue contained hydroxyl, amine, amides, ester, ether, carboxylic acids and anhydrides. In the range of 3320–3520 cm⁻¹, aromatic amines, primary amines and amides with N-H stretching were

observed in the sample. The broad band at $\sim 3482\text{ cm}^{-1}$ was simply due to interaction of hydroxyl groups in water and the band near 1630 cm^{-1} comes from the scissoring of water molecules. C-O-C linkage in ether was observed in the range of $1070\text{--}1240\text{ cm}^{-1}$. In the range of $1140\text{--}1200\text{ cm}^{-1}$, sulfates (S=O) had SO_2 symmetric stretching, while the C-C=O group in ketones was present in the range of $510\text{--}560\text{ cm}^{-1}$. Similar results were reported by Tichonovas et al. [16] for plasma-treated industrial wastewater. They treated contaminated water with dielectric barrier discharge plasma under atmospheric conditions. The functional groups, found in their investigations, include amines, amides, nitrates and carboxylic acids. Parshetti et al. [28] used *Rhizobium radiobacter* pathogen for degradation of methyl violet and some other industrial dyes, such as red HE7B, yellow 4G, blue 2B, navy blue HE22, red M5B and red HE3B. Adsorption of methyl violet and removal of some organic contaminants were observed in the presence of poly (acrylamide-co-acrylic acid) hydrogels. Solpan et al. [29] used Poly(AAm-co-AAc) as an absorbent for dyes and other contaminants in the solution. FT-IR peaks of treated samples showed various functional groups, such as N-H stretching band of secondary amines, O-H band, C-H stretching, C=C stretching, C=O group and C-N stretching at 3416 cm^{-1} , $3100\text{--}3500\text{ cm}^{-1}$, 2900 cm^{-1} , 1581 cm^{-1} , 1736 cm^{-1} and $1159\text{--}1173\text{ cm}^{-1}$, respectively.



Figure 9. Photographic view of the solid residue produced during plasma treatment of industrial wastewater.

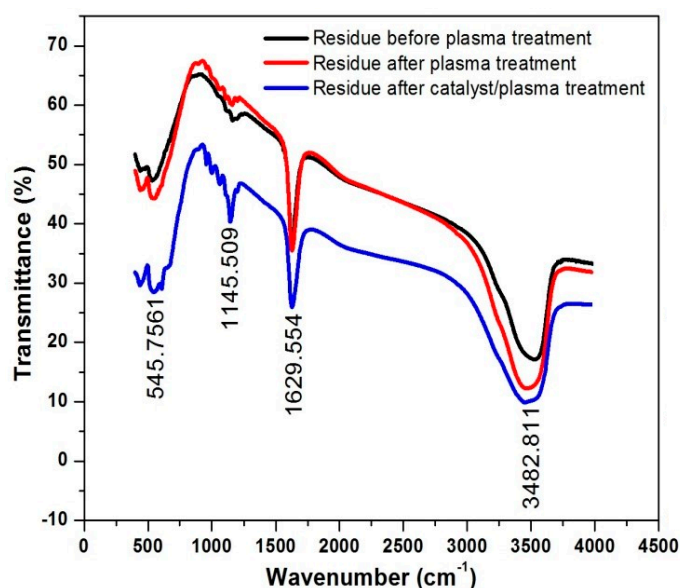


Figure 10. FT-IR patterns of the solid residue of untreated and plasma-treated industrial wastewater.

The plasma produced oxygen under plasma jet exposure and that was already present in water reacted with metals to form metal oxides. The residue of plasma treatment and catalytic plasma treatment was characterized by generating XRD patterns. The heavy metals in wastewater comes from both natural and man-made sources. The major natural sources of heavy metals are volcanic activities, soil erosion, urban runoffs and aerosols. The man-made sources are electroplating, metal finishing, textile dying, mining operations, leather industry, glass industry, metallurgical industry, automobile manufacturing, washing and direct industrial wastes. Faisalabad is a major industrial and distribution center and anchor of all these industries. The toxic metals from industry releases into wastewater through rinsing, spillage and dumping. The cleaning of bath tanks and chemical containers also produces substantial quantities of wet sludge of toxic metals. Sharma et al. [30] investigated the presence of heavy metals in industrial wastewater. They reported several heavy metals in the industrial wastewater collected from different parts of India. They used metallic nanoparticles for the removal of heavy metals. In this study, TiO_2 nanoparticles were used to remove the heavy metals under plasma exposure. XRD patterns of solid residue of plasma-treated water samples are shown in Figure 11. The atomic oxygen and oxygen radicals converted some metals into their oxides [30,31]. Both plasma-treated and catalyst/plasma-treated samples contained almost same metals and oxides. The only difference was the presence of TiO_2 , which was used as a catalyst in the second trial. XRD peaks of TiO_2 are identified as anatase and rutile phases.

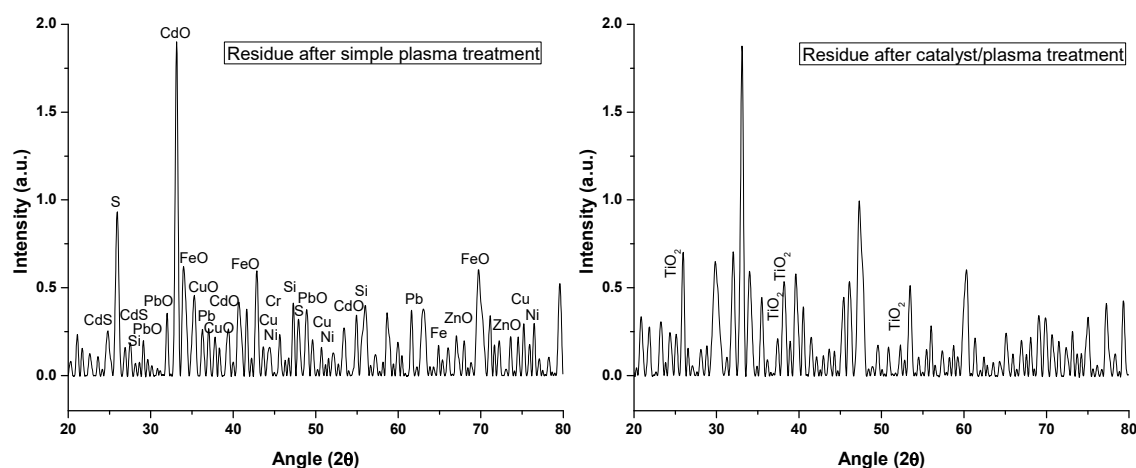


Figure 11. XRD patterns of the solid residue of plasma-treated and catalyst/plasma-treated industrial wastewater.

XRD peaks at 2θ of 54.34° and 36.06° show the presence of rutile phases, while peaks at 25.35° and 37.78° show the anatase phases of TiO_2 . The observed peaks and planes for TiO_2 matched well with the standard JCPDS no: 21-1272 and 21-1276. The percentage of anatase rutile phases were measured at about 68% and 32%, respectively. Ni was identified at 44.051° , 51.85° and 76.37° , Pb was identified at 36.27° and 62.12° , while PbO was identified at 2θ of 29.09° , 31.83° and 48.59° . Peaks at 2θ of 32.05° and 35.16° confirmed the presence of Cd, while peaks at 33° , 38.28° and 55.26° reflected the presence of CdO. The presence of Cu and CuO in the sample was confirmed from the peaks at 43.30° , 50.43° , 74.13° , 38.78° and 35.45° . Cr was identified only at 2θ of 44.39° ; however, in literature, some XRD peaks of Cr also appear at 81.75° and 115.26° . Since XRD patterns of the presented work were limited to 2θ of 80° , these peaks were not identified in these patterns. CdS was identified at 28.22° and 24.85° ; Si was identified at 28.46° , 47.38° and 55.88° ; CdO was identified at 33° , 38.28° and 55.26° ; Fe and FeO were identified at 65.03° , 42.07° , 60.99° and 36.35° ; and, finally, S at 26° and 47.75° .

3.4. Effect of Plasma Treatment on Bacteria Inactivation

In untreated and inadequately treated waters, various forms of bacteria can be present. Examining water for all types of bacteria is not feasible, but testing for coliform bacteria is a relatively simpler way of accessing the water quality. Coliforms are the naturally found bacteria in the environment. The presence of coliform bacteria in water is a sign of presence of several other dangerous bacteria. *E. Coli* is a gram-negative coliform and its presence in water causes short-term health problems by putting the health of elderly people, infants and those having weak immune systems at risk. Since most of the wastewaters contain gram-negative bacteria, the effect of plasma treatment on inactivation of *E. Coli* (gram-negative) was investigated. The bacteria culture was exposed to DC plasma jet for 2 min. The pre- and post-plasma treatment bacteria colony-forming units (CFUs) were counted using a digital counter. The binary converted photographs of untreated and plasma-treated bacterial cultures are shown in Figure 12. The change in CFU count of bacteria with plasma treatment time is shown in Figure 13.

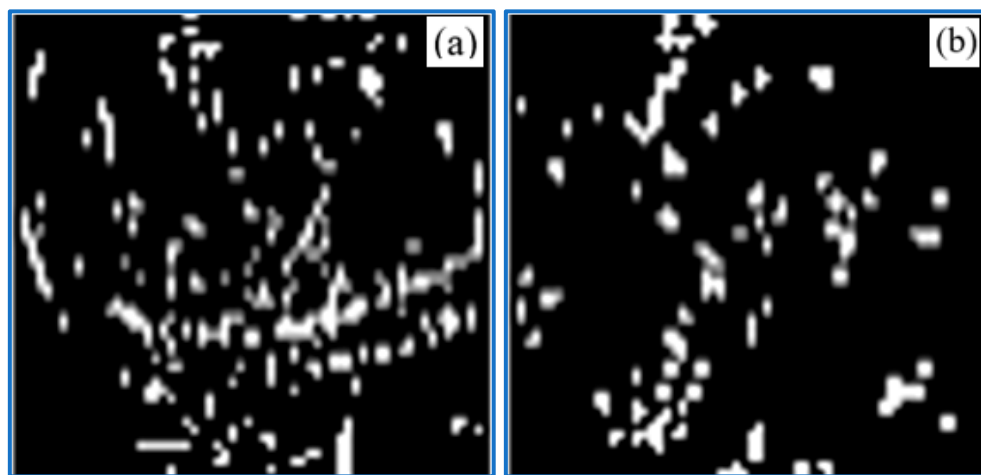


Figure 12. Scattering configuration of CFUs of *E. Coli* before (a) and after (b) plasma treatment. Only the plasma-exposed area is shown in the photograph.

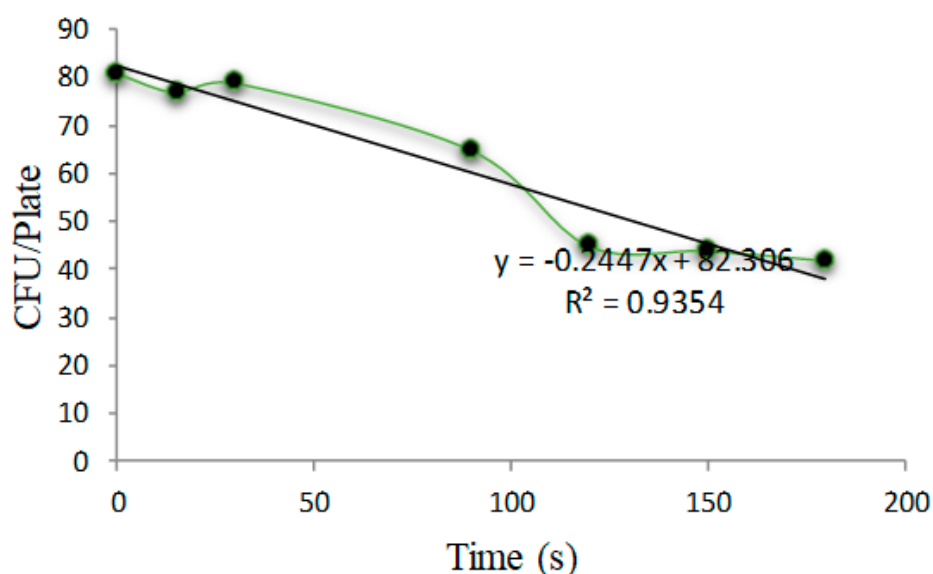


Figure 13. Change in CFU count of *E. Coli* with plasma treatment time.

CFU counts were reduced by 50% after plasma treatment time of 2 min. Hereinafter, plasma treatment did not show significant effect on bacterial culture. A similar bacteria inactivation trend was observed for catalytic plasma treatment. It reveals that TiO₂ nanoparticles are not very effective for antibacterial treatment of contaminated water. Raza et al. [31] used chromium oxide nanoparticles for killing micro-organisms, such as *E. coli* and *Pseudomonas aeruginosa*. Chromium chloride was used as precursor for synthesis of nanoparticles. Vo et al. [32] produced controlled size triangular nanoparticles of silver. They studied the effect of shape on antibacterial activity of these silver nanoparticles. However, the use of such materials for bacterial inactivation is itself an expensive process, which needs a lot of post processing as well. On the other hand, plasma treatment is a simple, nontoxic and single-step process for antibacterial treatments. Additionally, no post-treatment processing of the sample is need.

Several authors have confirmed the effectiveness of plasmas as pathogens disinfectant [12–16]. Several factors play a role in plasma inactivation of bacteria. Most atmospheric plasma jets produce UV radiations in the range of 200 to 300 nm. These radiations weaken the bacteria cell wall by transferring the energy of the cell membrane. Since a argon–air mixture was used as a precursor gas for production of plasma jet, the possibility of reactive oxygen species being present in plasma also ruptured the bacteria cell. The electrically-charged species in the plasma jet accumulated on the bacteria cell and ruptured the outer membrane by developing electrostatic forces. The forces put extra stress on the cell wall and weaken the tensile strength of cell membrane. The cell membrane bursts on sufficient accumulation of electrostatic charges. Naturally, the membrane of bacteria is cytoplasmic and semipermeable, which controls the type and flow of molecules into the bacterial cell. The binding of electrons to the cell membrane makes it more permeable. The control of membrane on flow of selective molecules losses and cell degradation increases with a decrease in permeability.

4. Conclusions

Industrial wastewater is a major issue for our environment, specifically when it contains synthetic dyes and other harmful pollutants. Many efforts have been made for the removal of pollutants from the industrial effluents. The plasma-based techniques are regarded as the most efficient and nontoxic among all the reported techniques. One such technique is non-thermal atmospheric pressure DC plasma jet. The catalytic and noncatalytic plasma treatments did not notably influence TDS of water samples except for the dye sample. TDS of dye containing sample decreased by 140 points after simple plasma treatment and 190 points after catalytic plasma treatment. Similarly, some samples exhibited slight increase in hardness on plasma treatment. The degradation efficiency of organic pollutants increased in the presence TiO₂, ferrous ion and hydrogen peroxide [18]. In dye containing sample, significant removal of metals was observed during plasma treatment. The notable removal shows the effectiveness of the treatment process, especially for dye containing water. The degradation of some functional groups during the treatment process confirmed the effectiveness of the plasma treatment process. CFU counts were reduced by 50% after a plasma treatment time of 2 min. Hereinafter, plasma treatment did not show significant effect on bacterial culture. A similar bacteria inactivation trend was observed for catalytic plasma treatment. It reveals that TiO₂ nanoparticles are not very effective for antibacterial treatment of contaminated water.

Author Contributions: S.S. and W.B. conceived and designed the experiments; S.S. and N.U.H.A. fabricated the plasma jet and performed the experiments; Y.K. analyzed the data; T.A.S. and A.A.A.-A. conducted antimicrobial tests; W.B. and S.S. wrote the paper; T.A.S. reviewed the draft; Y.K. secured the funding for project. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the King Saud University, Riyadh, Saudi Arabia under the grant number RG-1436-012. The APC was funded by Project No. RG-1436-012.

Acknowledgments: Authors are thankful to the Deanship of Scientific Research at King Saud University, Riyadh, Saudi Arabia, for funding this work under the Research Project No. RG-1436-012.

Conflicts of Interest: The authors declare no conflict of interest.

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