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Application of Non-Thermal Plasma to the Treatment of Effluent Discharged Into River Choumlou in Bafoussam, West Cameroon

Estella T. Njoyim*[A], Yves T. Djoko[a], Serge A. Djepang[b,C], Gervais Ndiffo[b], Bovarie Kingfack[a], Samuel Laminsi[b]

[A]*laboratory Of Noxious Chemistry And Environmental Engineering, Chemistry Department, University Of Dschang, P.O. Box 67, Dschang, Cameroon;*
[B]*laboratory Of Physical And Analytical Applied Chemistry, Chemistry Department, University Of Yaounde I, P.O. Box 812, Yaounde, Cameroon.*
[C]*nuclear Technology Section, Institut Of Geological And Mining Research, P.O. Box 4110, Yaounde, Cameroon.*

ABSTRACT
Most rivers in urban areas of developing countries are the destinations of effluents discharged from industries. This is the case of River Choumlou (in Bafoussam-West Region, Cameroon) which receives all discharges from "Brasseries du Cameroun", Bafoussam branch. The objective of this work was to determine the level of organic contaminants in water samples and to treat the polluted samples using the non-thermal gliding arc plasma. Non-thermal plasma consists of charged particles, radicals and excited molecules. The aim was to show the interest of such a process for cleaning up of surface waters (real effluent) and to cope with the protection of our environment. Due to the fact that pollution of streams and rivers from the discharge of sewage and industrial wastes poses a major problem to the environment, the researchers were particularly interested in investigating the oxidizing and acidifying properties of non-thermal plasma on polluted surface water. Samples were collected upstream and downstream from the brewery's effluent outlet. Samples taken at the point R_1 (downstream) were first analyzed by volumetric and instrumental methods in order to determine the organoleptic, physico-chemical and organic parameters. These samples were then exposed to the gliding discharge in humid air for a time period of between 3-30 minutes. After 30 minutes of exposure, a decrease in turbidity (24.09%), BOD_5 (44.93%) and COD (48.92%) were observed resulting in transparency apparition; with a decrease in pH (7.9 to 3) due to the formation of acidifying species in solution. These results reflect a considerable reduction in the pollution load of the water collected at R_1. This work shows that the effectiveness of the Gliding Arc in wastewater treatment is attributed to the oxidizing power of the hydroxyl radical and acidifying power of the nitrogen monoxide radical formed in the plasma. Despite the low rate of reduction of COD and BOD_5 in 30 min, it can be said that the plasma alone and post-discharge phenomenon (without catalyst or coupling) allows a good reduction of surface water by reducing effectively and appropriately organic matter.

Keywords: Environment, Surface water, Pollution, Gliding arc plasma, Degradation.

I. Introduction

Most industries discharge their effluents into nearby rivers thinking that they are doing dilution. In the same line, moving waste from one place to another does not solve the sanitation problem. Hence there is need to fight against pollution in all its forms, especially water pollution. By definition, Water pollution is the alteration of the hydrosphere in such a way as to create a hazard to the health, safety or welfare of any living specie [1]. However, uncontrolled discharge of these liquid wastes due to lack of treatment plants or non-operational stations for evacuation may lead to the pollution of surface water and groundwater which is a real threat to flora and fauna. This is the case of River Choumlou (in Bafoussam-West Region, Cameroon) which receives many discharges of wastes from "*Brasseries du Cameroun*", Bafoussam branch.

The pollution of streams and river Choumlou from large discharges of sewage and industrial wastes of the Bafoussam brewery plant is a serious and growing problem in Cameroon where waste treatment is almost practically non-existent. Often chemical substances contained in wastewater are hardly biodegradable and the lack or inadequacy of treatment systems leads to the accumulation in the surface water. The pollution of this source can lead to various health problems which directly affect human and aquatic lives. Thereafter, this river must be disposed off or safely treated even for reuse, which is often costly and problematic for most countries. However, it is said that using chemical substances for water treatment have the limitation

that the products needed for treatment are expensive and difficult to obtain. A number of physical, biochemical oxidation and chemical techniques had been reported for the treatment of all types of wastewaters with limited success. Biodegradation of wastewaters containing some dyes is not efficient enough due to the byproducts formed at the end and the presence of complex and stable aromatic structures of the numerous rings present in dye molecules, so that advanced oxidation processes (AOPs) have been investigated as an alternative [2]. One of the most recent developments of AOPs is concerned with using electrical discharges and the relevant chemical properties of the active species present in cold plasma.

In this work, cold plasma, also called gliding arc discharge is used to assess the level of pollution of surface water in Bafoussam and to find out the efficiency of treatment by employing the long processing time of treatment. The purpose of this study was not only to treat the water samples of the river but also to explain the origin of pollution in order to provide technical remediation. This study was initiated after the successful Plasma-chemical treatment of industrial wastewaters from the brewery "*Brasseries du Cameroun*", Bafoussam factory [3]. Advanced oxidation is chemical oxidation with the hydroxyl radical, which is a very reactive and short-lived oxidant [4]. The radical needs to be produced on a site, in the reactor, where it comes in contact with organic pollutants in the wastewater [5]. In this work, the hydroxyl radical is produced in a plasma system, specifically in a system using non-thermal plasma obtained by gliding arc discharge plasma.

A gliding arc is an electric discharge in a high-intensity electric field formed between two or more diverging electrodes [6, 7]. The discharge leads to the formation of positive and negative ions, photons, electrons and other chemically active species such as molecules and radicals. In gliding arc reactors, the gas flows between the electrodes at very high rates in order to maintain the quasi-thermal characteristics of the plasma. These plasmas are characterized by their acidic, oxidizing and complexing properties. The main chemical properties of a discharge in humid air are attributed to NO° and °OH radicals formed during the discharge, which are able to react with solutes at the plasma/liquid interface and to create its derivatives like H_2O_2 and peroxonitrites ions with high long life [3, 8, 9].

II. Materials and Methods

2.1. Presentation of the study area

River Choumlou is located in Bafoussam, latitude 5° 25' Nord, longitude 10° 25' Est, altitude 1310 m to 1470 m. Bafoussam town is the head quarter of the West region of Cameroon and is locate in the Mifi division and Bafoussan III sub-division. The map of this study area is giving by figure 1. River Choumlou is located 3000 m from the Bank of Central African States. More precisely, it is located about 1000 m downstream of the SABC-WEST (*Société Anonyme des Brasseries du Cameroun*) and SOC (*Société Oléagineuse du Cameroun*). It is the main effluent receiver of SABC-WEST and domestic waste from households in the area. In addition, it is subjected to excessive use by the surrounding populations for washing, livestock, agriculture and waste water drainage. The source pollution is primarily industrial, domestic and agricultural by origin.

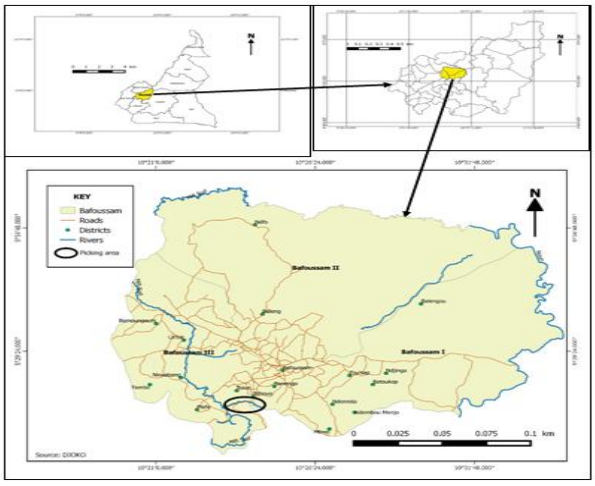

Figure 1 : Map of study area

2.2. Sampling of Choumlou river water and Storage of samples collected

Sampling points that caught our attention are three: The first point is located upstream about 5 m before the spill site (or rejection) of effluents from "*Brasseries du Cameroun*" (Bafoussam factory); the other two points are located downstream, that is, after the place of discharge of effluent from the said brewery. The second sampling point is located about 5 m from the point of effluent discharge of breweries; the third is located about 5 m from the second that is to say 10 m from the discharge point. Denoted by $R_{0,}$ is the point before the point of release, the release point, P, finally R_1 and $R_{2,}$ the second and third sampling point respectively. Only the sample collected at the point R_1 is the subject of the plasma processing, with the remainder used for characterization.

Samples were taken by means of a peristaltic pump provided with a fluid tube of 7.6 m in length of silicone (Masterflex Cole-Palmer Instrument, USA) and maintained at 12 volts using a battery.

Most of the time, samples were collected in PET bottles (Tangui bottle, juice bottle and can) of 1.5 L, 0.5 L and 5 L respectively. The huge advantage that we had was the proximity between the sampling site and the laboratory of the brewery with which a partnership was made so that samples were stored in their refrigerator after sampling for analysis. The samples were only transported from Bafoussam to Yaounde in the Laboratory of Physical and Analytical Applied Chemistry for the treatment phase.

2.3. Gliding arc apparatus

The gliding discharge (glidarc) was first proposed by Lesueur *et al.* [4, 6] and developed by Czernichowsky *et al.* [10, 11, 12] for the treatment of gases. The glidarc reactor used in batch conditions have been represented in simplified form by Serge Djepang *et al.* [13] as shown on Figure 2. Briefly, it consists of two diverging electrodes disposed in a gas at atmospheric pressure and connected to a suitable energy source, generally a high voltage leak transformer (5 - 10kV).

An arc forms at the narrowest gap between the electrodes [14]. A gas flow directed along the axis of the electrodes gently pushes the arc feet along the conductors, so that the arc length increases until breaking in a plasma plume and its temperature decreases, as does its energy, when the arc is short-circuited by a new one. The resulting plasma is actually quenched plasma, similar to non-thermal plasma, and operated at atmospheric pressure and at a (macroscopic) temperature which does not exceed 60°C. In our operating conditions, the fed gas was air saturated with water. Its flow rate was fixed at 800 $L{\cdot}h^{-1}$. The magnetically stirred batch reactor used for this study is thermostatted by water circulation, so that the temperature of the 500 mL sample solution never exceeds 310 K. The distance between the bottom of the electrodes and the top of the sample was 1.4 cm. A circulating water flow controls the temperature of the liquid target at 25°C [15] and limits evaporation. Air is provided by a compressor, it passes through a bubbling Duran flask that is filled with distilled water and becomes saturated. The choice of this gas is governed by economy and by the nature of the expected chemical properties of the mixture of O_2, N_2, and H_2O [16]. Emission spectroscopy measurements on gliding arc plasma in humid air revealed the simultaneous presence of $^{\bullet}OH$ and $^{\bullet}NO$ radicals in the discharge, with a much higher density for $^{\bullet}OH$ radicals than for $^{\bullet}NO$ [17]. The presence of $^{\bullet}OH$ was identified [18,19] in aqueous solutions exposed to immersed discharges, but not evidenced in solutions disposed under the discharge, probably due to the short half-life time of the radical in water or the limited temperature of the medium. The species formed in gliding arc discharge such as $^{\bullet}OH$ radicals (and its dimer H_2O_2) are responsible for strong oxidizing effects whereas acidifying properties are due to the $^{\bullet}NO$ radicals [16, 19]. When aqueous solutions are exposed to such plasma, chemical reactions occur at the liquid/gas interface and develop in the liquid target. The solute is thus subjected to the chemical properties of the impinging activated species provided they are water soluble (Reaction "(1)"- "(11)").

The diffusion process in the liquid is improved by conversion in the liquid phase due to the air flow and magnetic stirring.

$H_2O + e^- \rightarrow H^{\bullet} + OH^{\bullet} + e^-$ (1)

$O_2 + e^- \rightarrow {}^{\bullet}O\,(3P) + {}^{\bullet}O\,(1D) + e^-$ (2)

$N_2 + e^- \rightarrow {}^{\bullet}N\,(4S) + {}^{\bullet}N\,(2D) + e^-$ (3)

$^{\bullet}N\,(2D) + O_2 \rightarrow NO^{\bullet} + {}^{\bullet}O$ (4)

$H^{\bullet} + O_2 \rightarrow HO_2^{\bullet}$ (5)

$HO_2^{\bullet} + NO^{\bullet} \rightarrow NO_2 + HO^{\bullet}$ (6)

$NO_2^{\bullet} + HO^{\bullet} \rightarrow H^+ + NO_3$ (7)

$NO^{\bullet} + HO^{\bullet} \rightarrow HNO_2$ (8)

$HNO_2 \rightarrow H^+ + NO_2$ (9)

$NO^{\bullet} + {}^{\bullet}O\,(3P) \rightarrow NO_2$ (10)

$O_2 + {}^{\bullet}O\,(3P) \rightarrow O_3$ (11)

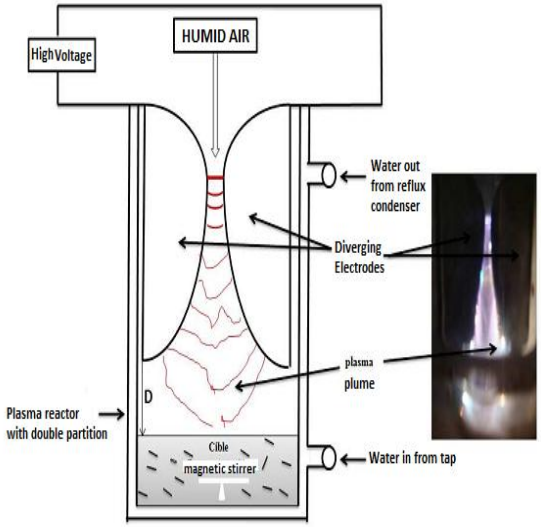

Figure 2. Scheme of the gliding arc batch reactor

Working parameters such as the nature and flow rate of the input gas, the electrodes material, and the organic solute play important roles in the degradation of organic pollutants.

2.4. Samples treatment: Procedure and Analytical Methods

In order to achieve these objectives, experiments were conducted through several stages: The first stage consisted of sampling. On each sample, a preliminary examination was used to assess odour, color and appearance. The next step was to measure the physicochemical parameters monitored by analyzing the parameters of the organic pollution. The third step was to treat the sample by non-thermal plasma gliding arc. Particular dosages enabled us in the fourth step to show the presence or the formation of trace elements in the water withdrawn and subjected to a treatment. For each sample, the measurement of each parameter was done three times and the average result was considered.

The treatments of the samples collected from river choumlou are investigated as a function of the exposure time t*(min) by keeping constant all the other working parameters. Wastewaters collected from the Choumlou river were exposed to the plasma for various treatment times (i.e., 3, 5, 10, 15, 20 and 30 min). Approximately 450 mL of the target sample to be treated is placed in the reactor and the flow rate of the plasma gas (humid air) was controlled by the flow meter connected to the gas compressor. Wastewater was magnetically stirred and disposed normally to the axis of the reactor at a distance of 40–45 mm (Figure 2). This prevented electrical contact of the liquid with the electrodes. The selected feeding gas which is water-saturated air was provided by a compressor. The gas was first passed through a bubble flask and then into the reactor with an air flow rate (Q) of 800 $L.h^{-1}$. After the discharge was switched off, approximately 350 mL of treated sample was removed from the reactor and analyzed for the desired parameters and the rest of the treated solution was kept in the dark for the final analysis in the brewery laboratory of Bafoussam. Each sample of the treated solution was analysed for standard control of colour, turbidity, absorbance, pH, total dissolved solids (TDS), suspended solids (SS), Chemical Oxygen Demand (COD), and biochemical oxygen demand (BOD). The effect of post-discharge phenomenon on target sample was also studied.

For analytical procedures, several techniques were used to determine the characteristics of wastewater samples before treatment and to follow the waste concentration with the exposure time *t** to the discharge.

Color was followed by absorbance A_{225} measurements at 225 nm using a UV/vis spectrophotometer (Aqualytic SpectroDirect). For a defined wavelength λ, a value of A (λ) is obtained; within a range of wavelength, a spectrum is obtained. Turbidity was determined by a portable turbidimeter mark Orbeco - Hellige (966 model Orbeco Analytical Systems, Inc., USA).

pH, TDS, and Conductivity were measured using a multi-parameter analyzer apparatus (Hanna HI9811 -5 cell with $1/10^{th}$ precision with digital display). SS content was determined by filtration on glass fibre filter.

COD measurement was carried out using a "*COD VARIO COMPACT PC*" devise aided by COD disposable tubes (Aqualitic). The BOD of the samples was determined using a Track BOD devise (BOD Instrument Track, Cat No. 26197 - 18th, Hach Company, USA) contained in a thermostatic cabinet at 20°C (BOD incubators, TS 606, WTW, France).The pH of wastewaters was adjusted from

6–8 with *NaOH* or H_2SO_4 solution and the BOD test was done on 5 days according to the BOD track procedure. Only samples collected at the point R_1 were submitted to the treatment. These samples were diluted to a half of the crude solution to facilitate the reading of parameters by measuring devices. For each sample only the mean values were considered. Each average was obtained from the results of 5 consecutives measurements performed on each parameter.

III. Results and discussion

3.1. Characterization of water samples of Choumlou river

Before any treatment of surface water, it is essential to characterize it in order to assess the impact it may have on the environment. To better assess this impact, it is necessary to begin the work of characterization upstream of the effluent outlet before progressing downstream of the effluent outlet. This is why our attention was focused on the water of a receiving environment (Choumlou river) after the successful study done by Njoyim *et al.* [3] on wastewater from the central collecting point of "*Brasseries du Cameroun"* in Bafoussam. This work [3] mentioned that this river is polluted by the activities of the surrounding populations, mainly by the "*Brasseries du Cameroun"*, Bafoussam factory.

The mean values of the wastewater samples collected from the river at the points R_0, P, R_1 and R_2 are presented in Table 1. All average values were obtained for each point from three consecutive measurements of each parameter, except for BOD analyses because these are very expensive and time consuming.

Table 1: Summary of Characteristic values of samples from river Choumlou

		Values					
		R_0	**P**	**R_1**	**R_2**	**Cameroonian Norms**	**WHO Norms**
parameters	pH	6,8	11,9	11,5	10,1	6,5-9	6,5-9
	Temperature (°C)	26,7	28,9	27,5	27,2	-	-
	Turbidity (NTU)	15,38	59	47,90	19,53	-	-
	Absorbance (225 nm)	0,2	3,4	2,7	2,65	-	-
	SS (mg/L)	16	500	80	42,6	50	-
	Conductivity(µS/cm)	47	2200	730	680	-	< 400
	TDS (mg/L)	25	1100	350	300	-	-
	COD (mg/L)	291	887	434	400	250	200
	BOD_5 (mg/L)	280	778	544	427	50	50
	Cl^- (mg/L)	32	60	60	60	≤ 250	≤ 250
	NO_2^- (mg/L)	0,135	0,062	0,184	0,061	-	-
	NO_3^- (mg/L)	0,2	0,8	0,2	0,2	-	-
	PO_4^{3-} (mg/L)	1,8	11	10,9	2,1	-	-

(-): not specified Limit: cannot be read by the device (>> 1000 mg/L)

It can be seen from this table that at upstream (R_0) of the discharge point of the effluent of "*Brasseries Cameroun S.A"*, the river water has an acidic pH (6.8). This implies that water upstream is acidic, corrosive and as a result, affects the metal solubility and hardness of the water. At the point of discharge (P), these waters have a very high pH (11.9). Downstream of the discharge point, the water in this river remains alkaline because pH = 11.5 and 10.1 at points R_1 and R_2 respectively. These higher values of pH could be ascribed to increased photosynthetic assimilation of dissolved inorganic carbon by planktons. High pH may also increase the toxicity of other substances. For example, the toxicity of ammonia is ten times more severe at a pH of 8 than it is at pH =7. It is directly toxic to aquatic life when it appears in alkaline conditions. This result shows that the pH of the river water is acidic at the upstream of the point of discharge of the brewery's effluent and remains alkaline downstream of this discharge point. This result is not in agreement with Cameroonian and WHO standards and as such makes us to conclude that the brewery plant in Bafoussam is largely responsible for this change in the pH of the water and therefore its pollution. At downstream (point R_1), this water also has very high values of COD (434mg/L), BOD_5 (439mg/L), Conductivity (730µs/cm) TDS (350mg/L) and SS (80mg/L) as compared to upstream point R_0 and Cameroonian and WHO standards. Correlational analysis showed significant positive correlation between those parameters. This reflects that the water from river Choumlou has a high concentration of biodegradable organic matter (the COD/BOD_5 quotient < 2, the effluent is therefore readily biodegradable) and is also very rich in dissolved substances and ions. As for ions, we noted the high values of chlorides. There is a low presence of phosphate ions and a very large presence of aluminum and iron ions since they are not detectable by the colorimeter. Turbidity at the

downstream point R_1 (turb = 38.75 NTU) is much higher than the upstream point R_0 (turb = 15.38 NTU). This result indicates that the water of river Choumlou has highly loaded with suspended solids.

This flow of pollution released into the environment without any treatment can cause adverse effects on human health and the environment. The industrial wastewaters of the Bafoussam brewery contain chemical substances that are causing the pollution of River Choumlou (receiving environment). It has been observed that these chemical subtances are mostly organic molecules of interest to humans, but which prove to be highly polluting once released into industrial wastewater. Human activities in the neighbourhood of the river include fish breeding and laundry and others. Ultimately, the river water from the study area does not meet the limits required by the standards in Cameroon during the period of the study. Given their high content in organic substances and the negative impact they have on the quality of river water, adequate treatment should be applied on wastewaters before discharge into the environment.

III.2. Characteristics of effluents treated by plasma glidarc

III.2.1. Organoleptic parameters: Evaluation of odor and appearance rating

Water samples from the river (R_1) destined for analyses and treatment were collected when the brewery was in full production of beer and Top Orange juice. This explains why water taken upstream (R_0) has a different smell from that taken downstream (R_1) of the effluent discharge point. Downstream, water has an almost unidentifiable smell. At point P, the odor is typically that of the bitterness of beer. At point R_1 (raw sample at 0 min), the bitter taste of beer tends to disappear. It is therefore difficult to identify the smell of the water from river Choumlou since this parameter depends on several factors such as the surrounding activities and the sampling point. The crude sample at 0 min treatment time showed a dark-brown coloration. This coloration may be due to sludge and other wastes dumped into the river. In this water, there is also the presence of solid particles such as stones and, tree fibers.

Figure 3 shows that the appearance of the solution changes during treatment. We start from a less transparent solution (Figure 3.a) to a more transparent solution (Figure 3.b). This difference in transparency resulting from disappearance of the dark-brown coloration indicates the destruction of pollutants. But it should be noted that transparency does not reflect the drinkable aspect of water but guarantees some protection for aquatic organisms.

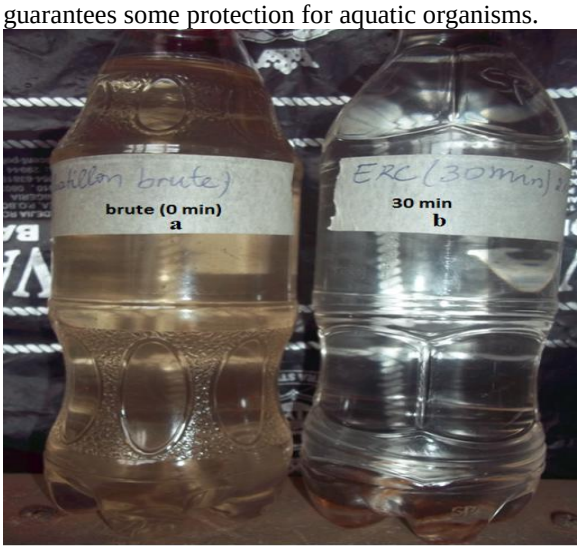

Figure 3: Water samples from river Choumlou (a): raw untreated sample (b): sample treated at 30 mins by the Gliding arc plasma

3.2.2. Physico-chemical parameters after plasma treatment

i) Acidity Control: pH lowering effects

In this work, we have studied the variation of pH as a function of the treatment time. From the first exposure minute of sample R_1, there is a rapid lowering of the pH value from 7.9 to 3.3 for exposure times included gradually between 3 and 10 minutes. Acidity increases and tends towards constant values of pH ranging between 3.3 to 3 (much lower than the standard value). It should be noted here that this is much lower than the standard values. This can be explained by the buffer effect due to the temporary presence of the couple *HONO/ONO*$^-$ whose pKa is around 3.3, and also by the presence of certain solutes that promote a buffer medium by neutralizing the carbonyl group molecules of waste waters (*RCOOH/RCOO*$^-$). These results are visualized on figure 4. This curve is similar to the half-portion of conventional titration curve of a strong acid with a strong base. A similar result was also obtained by Doubla *et al.* [19], Brisset *et al.* [20] and Mountapmbeme *et al.* [21].

This reduction in pH could be explained by the presence of the NO° radical in the discharge (in contact with air) which forms highly acidic species in solution, such as nitrous (HNO_2) and nitric (HNO_3) acids, which are incorporated throughout the solution according to the overall equations [20] below:

$$NO° + °OH \rightarrow HNO_2 \rightarrow H^+ + NO_2^- \quad (12)$$

$$NO_2^- + °OH \rightarrow NO_3^- + H^+ \quad (13)$$

$$H^+ + H_2O \rightarrow H_3O^+ \quad (14)$$

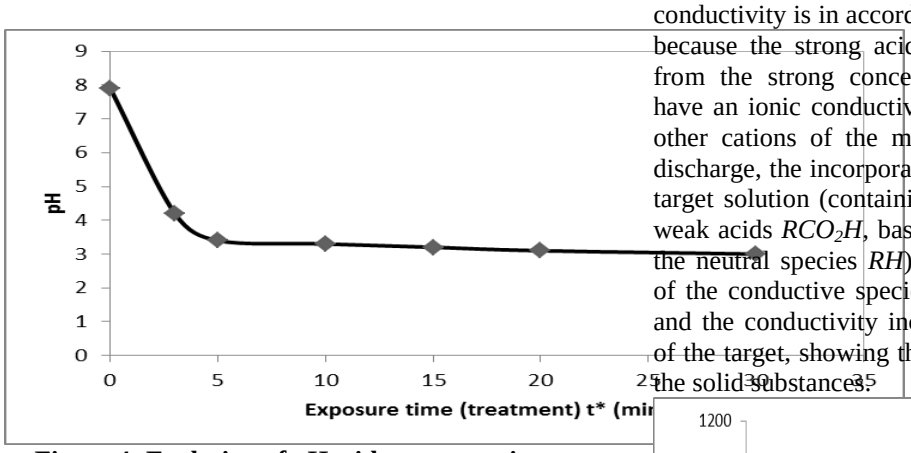

Figure 4: Evolution of pH with exposure time

This result confirms that the humid air plasma is a strong acid generator.

ii) Influence of exposure time on the conductivity and the Total Dissolved Solids (TDS)

These measurements illustrated on Fig 5 shows a curve having a great increase in TDS with exposure time. Just in 30 min of treatment, initial TDS of the river water moved from 330 to 530 mg/L, which corresponds to an increase of 60.61%. This increase in TDS indicates the presence and increase of new ionic species in solution coming from the electric discharge and the ionic species from the destruction of the pollutant compounds contained in the river water. As described by Njoyim *et al.* [3], this result confirms the oxidizing power of the species from the discharge into the solution being treated: Intermolecular chemical bonds are broken and chemical functions are oxidized; thus, soluble compounds are gradually charged and becoming highly polar and ionized. Solubilization of Total Solids Subtances (TSS) is also responsible for the increase in TDS. Doubla *et al.* [22] and Njoyim *et al.* [3] also obtained an increase of TDS during treatment of brewery effluents by non-thermal plasma.

Regarding the conductivity, there was a great similarity with the TDS because the dissolved chemicals induce conductivity since they affect the electrical properties of the solution. This observation is due to the fact that the measuring apparatus used had a correction factor of 0.5 relative to the conductivity and the total dissolved salts. According to French standards, conductivity between 666 and 1000 µS/cm is considered important. Conductivity grows and reaches a maximum value of 1080 µS/cm (approximately double the corresponding TDS) in the 30th minute, corresponding to an increase of 63.64%. This increase is also due to the oxidation of inorganic molecules into ions, thus increasing the concentration of dissolved salts. This increase in conductivity is in accordance with the pH reduction because the strong acidity of the medium results from the strong concentration of protons which have an ionic conductivity greater than that of the other cations of the medium. As a result of the discharge, the incorporation of the nitric acid in the target solution (containing organic species such as weak acids RCO_2H, bases R_1R_2NH and RCO^-_2, and the neutral species RH) increases the conductance of the conductive species. In conclusion, the TDS and the conductivity increases with exposure time of the target, showing that there is solubilization of the solid substances.

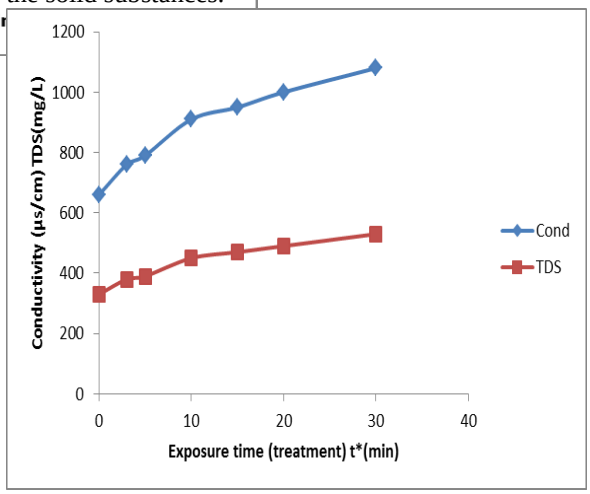

Figure 5: Evolution of TDS and conductivity with exposure time

ii) Evolution of the turbidity and the absorbance with the time of exposure

Figures 6.a, 6.b and Table 2 show the evolution of turbidity and absorbance with time of treatment. The results obtained for turbidity follow a trend almost similar to those of absorbance. Also, we observe that these two parameters decrease with increase in the treatment time. The results show that the turbidity decreases with increasing treatment time, which is due to the degradation of the suspended matter in the samples. These results also reflect that there is a decrease of intensity of the color of samples with the duration of the treatment and then appearance of transparency which is due to the degradation of coloring matter. As already mentioned by Doubla *et al.* [22] and Njoyim *et al.* [3] we had also observed in this case that for prolonged treatment durations (> 10min), there is a significant decrease in these two parameters. The more the solution was exposed, the more there was degradation of pollutant compounds and the more the discolouration was observed, hence the less the solution absorbs. Figure 3 shows the discoloration observed after 30 minutes of treatment by gliding discharge plasma.

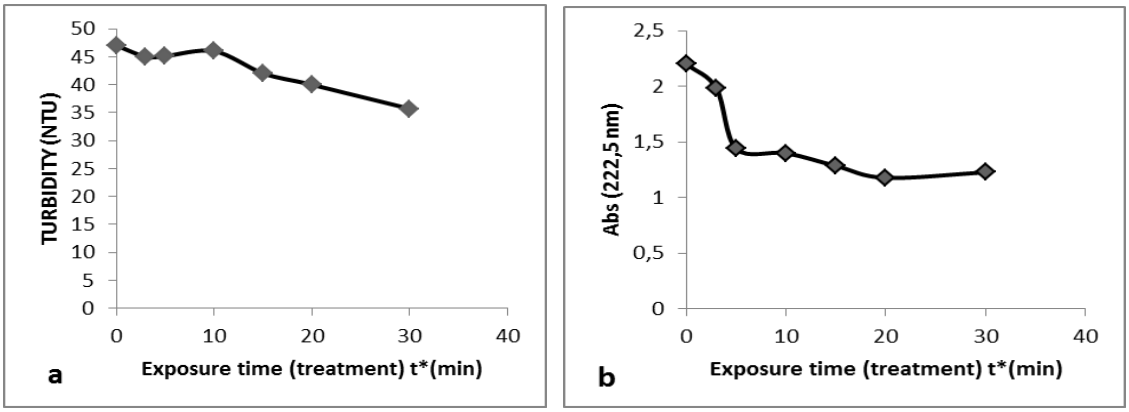

Figure 6: Evolution of (a) turbidity and (b) absorbance as function of treatment time

iii) Influence of treatment time on the evolution of Suspended Solid (SS)

Figure 7 shows the variation of suspended solids with the exposure time. Between the 3rd and 5th minutes of treatment, the amount of suspended material increases; which is evidence that organics were degraded into SS. Then the SS decreases globaly from the 10th min of treatment to achieve low values from the 20th to 30 minute of treatment. This may reflect the fact that the SS coming from the degradation of the organic material was dissolved. The rate of abatement was 55% in 30min. This solubilization of SS might be responsible for the increase in TDS. Njoyim *et al.* [3] obtained a similar result and explained the transformation by the following scheme:

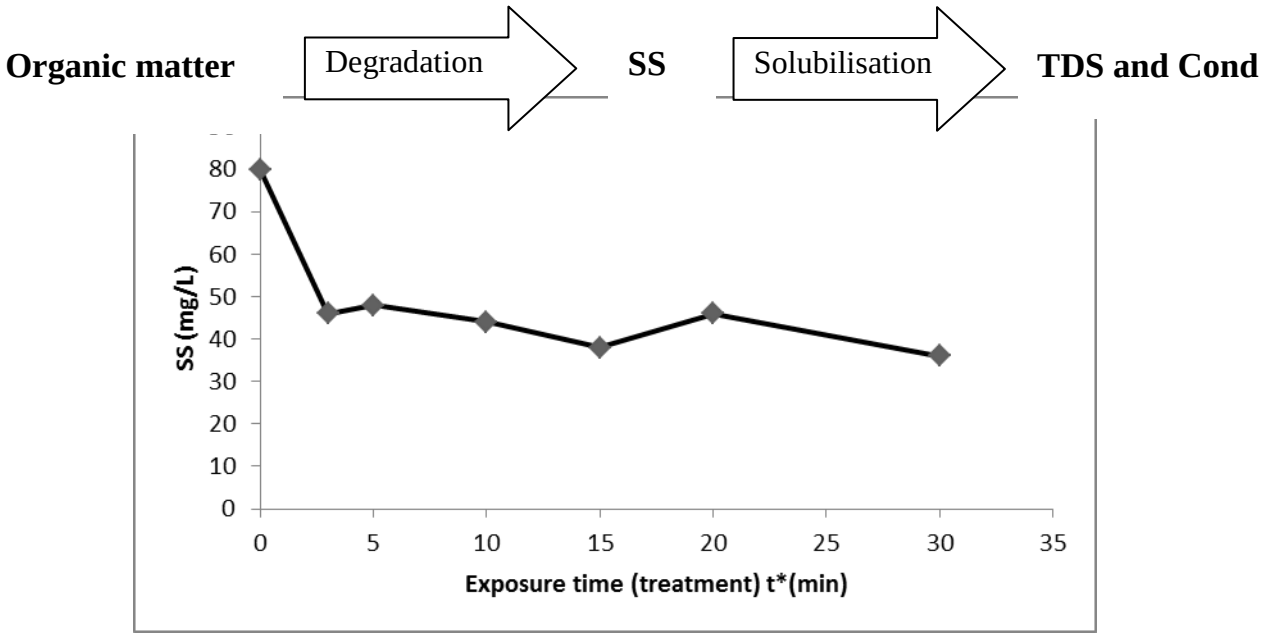

Figure 7: Evolution of Suspended Solids with treatment time.

3.2.3. Parameters related to organic pollution

3.2.3.1. Monitoring the evolution of Biochemical oxygen demand (BOD_5) and Chemical oxygen demand (COD) after the exposure time

To verify if the pollutants underwent complete mineralization, we followed the variation of the chemical oxygen demand (COD) and Biochemical Oxygen Demand (BOD_5) of the samples as a function of exposure time. In advanced oxidation processes, we often characterize the organic load of the effluent by measuring these two parameters. COD and BOD_5 values are illustrated on Figure 8.

The curve in this figure shows an overall reduction in COD with treatment time. This result confirms that exposure to the plasma generates oxidizing species which are capable of degrading the organic matter content in the wastewaters. The transient presence of nitrite ion in solution influences the growth of COD value for a given treatment, because this specie is oxidized to nitrate in the analytical process. The temporary increase of

COD could be explained by the emergence of new intermediate compounds (recalcitrant) resistant to oxidation by potassium dichromate but ultimately underwent degradation by strong oxidation with prolonged treatment time. It is important to note that COD decreases weakly at the beginning of exposure to the target. The reduction kinetics of chemical oxygen demand has a shape more or less regular depending on the exposure time. This result is explained by the fact that pollutants are not directly mineralized but transformed into intermediate products.

However, we can say that the organic matter was degraded until partial mineralization occurred. Starting from an initial abatement rate of 5.59 %, the overall reduction of COD was 48.92% only in 30 min of treatment. Therefore, we must achieve high processing time to observe a better reduction in COD. Non-thermal gliding arc plasma allows alone (without catalyst or combination) the degradation of organic matter. The final COD reached a value of 283mg/L, which is close to acceptable standards by Cameroon and WHO (250 mg/L).

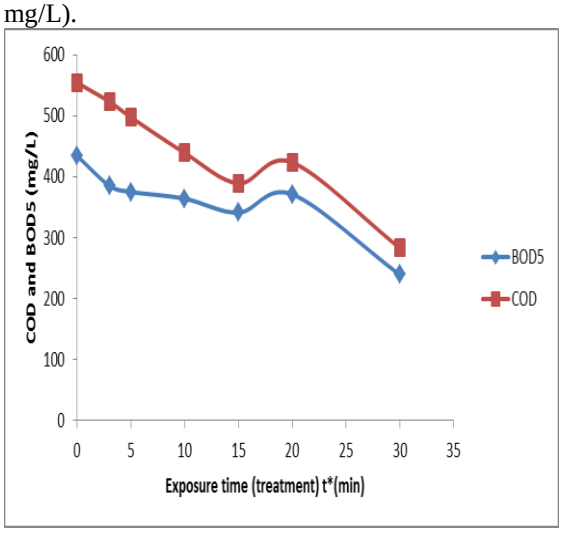

Figure 8: Evolution of COD and BOD_5 as a function of treatment time

BOD_5 decreases rapidly and gradually with treatment time. Just after 10 min of treatment, the abatement rate was 16.13%. Compared to the works of Doubla *et al.* [22], Njoyim *et al.* [23], and Brisset et al. [20], it was observed that the decrease of BOD_5 in this work is not much better. For example, Doubla *et al.* [22] obtained a value of BOD_5 reduced to half after 10 min of treatment. But in our case, after 10 min treatment BOD_5 is not halved. This large difference could be explained by the fact that the sample taken from the river at the point R_1 was not only a high pollution load but contained mostly very complex biodegradable organic pollutants. This is also why after 30 min of treatment the value of BOD_5 does not meet acceptable standards of Cameroon and WHO (<50 mg/L). BOD_5 moved from 434 to 239 mg/L in 30 minutes corresponding to a reduction of 44.93 %. The reduction in BOD obtained corresponds to a reduction of organic matter in relation with the appearance of oxidizing agents such as °OH inside the discharge and their derivatives in aqueous solutions [24, 25, 26], as previously described. The effectiveness of treatment is not reached for a maximum time of 30 min indicating that the exposure time on plasma has a positive influence on the quality of treatment. Thus, a high processing time must be achieved in order to observe a better reduction in COD and BOD_5. Njoyim *et al.* [3] also faced a similar problem.

3.2.4. Evolution of nitrates and nitrites with the exposure time

The results obtained from measurements of nitrates and nitrites are presented on Figure 9. It was observed that, the raw sample contained nitrate ions in small amounts (21.6 mg/L). From the first minute of exposure, the concentration of the nitrate ions increased more and more throughout the duration of exposure. This rapid increase in nitrates is evidence that, the method of plasma through the plasma gas (air) and water is a major source of generation of ionic species such as the nitrate ions. Brisset *et al.* [20], Doubla *et al*. [19] and Abba *et al.* [27] also mentioned the same observation. As for the nitrite ions, their presence is not negligible in the raw sample but their concentration varied very slightly during the exposure time. Their values were between 73 and 97 mg/L. This low concentration of nitrite ions is due to the fact that nitrous acid is thermodynamically unstable in acidic media. This is reflected by the conversion of the nitrite ions to the nitrates ions and NO° radical at pH = 5.98 [21]. This result implies that there is oxidation of nitrite to nitrate ions.

From the foregoing, we notice that increase in the concentration of the elements corresponds to increase in the acidifying properties of plasma. These nitrites and nitrates although being favorable for degradation of pollutants are causing eutrophication; therefore they do not favour the direct discharged of treated effluent into the aquatic environments. Therefore, these findings require a final 're-adjustment' of effluent that will aim not only to reduce the level of nitrites and nitrates but also to bring the pH to the neutral zone (6.5-9) before discharge. Reason being that very acidic or very alkaline water is dangerous to the natural environment.

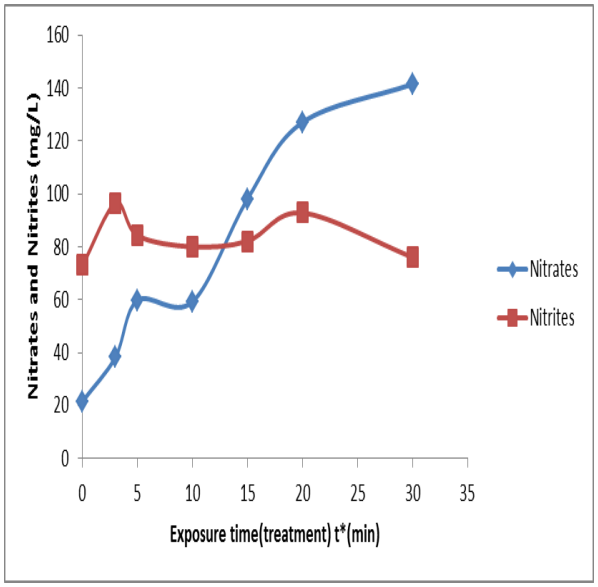

Figure 9: Variation of nitrates and nitrites with exposure time

The transient presence of nitrite ions alters COD measurements of wastewater treated by plasma since these ions are oxidized by Cr^{IV} as previously demonstrated. A similar result was also obtained by Doubla *et al.* [22] and Njoyim et al. [3]. Moreover, the formation of nitrites and nitrates was demonstrated by Elsayed [28]. The latter is accompanied by acidification of the medium as shown by the mechanism on Figure 10:

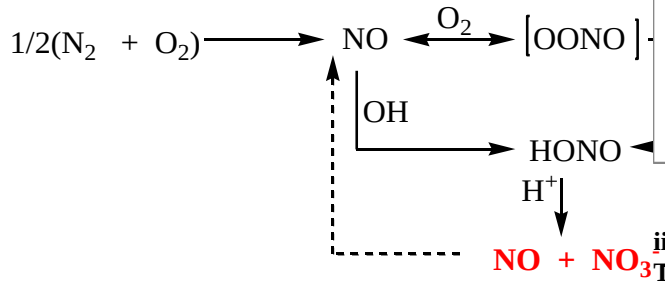

Figure 10: Scheme of formation of nitrate ions from nitrous acid HONO via acid peroxynitrous ONOOH adopted by Elsayed 1998

3.2.5: Effect of post-discharge phenomena in the river water, R_1

Post discharge, also called temporal post discharge is defined as a set of reactions that occur in solution after stopping the discharge. The aim of the following section is not to present the phenomenon of post-discharge in all its depth, but rather to present some characteristic traits not only to have a general idea about the phenomenon but also to be fully informed about its existence. For this reason, this phenomenon will be highlighted on the samples through parameters such as pH, conductivity and TDS. The phenomenon of post-discharge was assessed 48 hours after exposure. Many works such as those of Mountapmbeme *et al.* [21], Doubla *et al.* [22] and Brisset *et al.* [20] which have been broadly done on this phenomenon also mentioned its presence. Njoyim et al. [3] had also made a brief study on this phenomenon.

i) Effect of post-discharge on the change in pH

Figure 11 highlights a very important phenomenon in the chemistry of plasma: the phenomenon of acidity. Whatever the concentration of the polluting substances, the pH decreases after the exposure of solution to plasma and decreases gradually in the post-discharge. The phenomenon of post-discharge is weakly felt for short exposure times than for long exposure times. This is evidence that the exposure time to the plasma discharge has a very significant effect on the treatment phase in post-discharge. As a result, the more the solution is exposed to the plasma discharge, the more it is enriched with acidifying/oxidizing species.

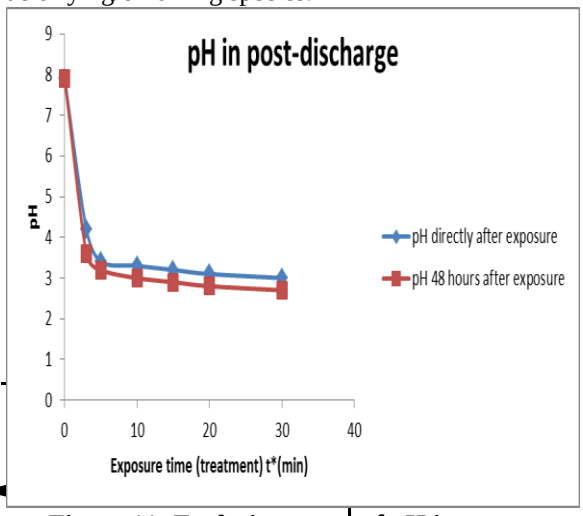

Figure 11: Evolution curve of pH in post-discharge

ii) Effect of post-discharge on the evolution of TDS and conductivity

Figure 12 also shows that, once the radicals from the discharge are in contact with the solution, ionic species responsible for the increase in conductivity and TDS are produced. The presence of these ions confirms the fact that, plasma is an ionizing medium. These radicals continue to act on the same solution after the treatment through secondary reactive species *(H_2O_2, NO_2^-, NO_3^-, etc.)*. This is why conductivity increases 48 hours after exposure to the discharge. This is the same for total dissolved solids (TDS), since these two parameters are closely related.

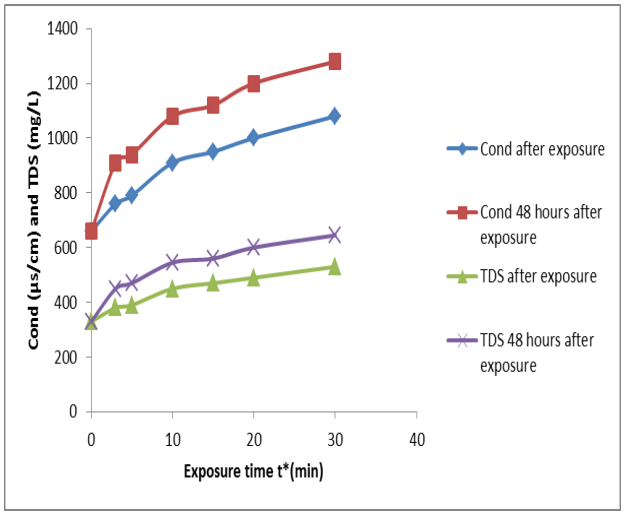

Figure III.12: evolution curve of TDS and Cond in post discharge

IV. Conclusion

Wastewater discharged by industries and by the surrounding populations are causing pollution to the aquatic environment. Faced with this problem, the search for solutions led us to highlight one of the applications of non-thermal plasma namely: depollution of surface water (the case of river Choumlou in Bafoussam, West region of Cameroon) which is the subject of this research work. The initiation of this work was directly related to the work done by Estella Njoyim *et al.* [3] and published in January 2016 who aimed to solve the problem of treatment of industrial wastewater from brewery. To better cope with the degradation of our environment, the objective was first to assess the level of pollution of river Choumlou and then show the use of the non-thermal plasma process for the treatment of real effluents as this river. The results of samples taken at points R_0 (upstream) and R_1 (downstream) shows that the river suffers heavy pollution whose origin is attributed to the activities of *SABC-WEST* (brewery). For example, we observed the values of COD (291mg/L), BOD_5 (280 mg/L) and pH (6.8) at the sampling point R_0. Respectively for the same parameters, we observed the values of 434 mg/L, 544 mg/L and 11.5 at the point R_1. These results are higher than the standards of Cameroon. Therefore this flow of pollution has repercussions on the receiving point (Choumlou river).

The various experimental results herein reported converged at verifying the two major plasma chemical effects of the gliding arc discharge in humid air on organic solutes, i.e., the acidifying and the oxidizing effects. Thus the first effect generally observed when a solution is exposed to the gliding arc plasma is the acidification of the medium and the increase in conductivity. The gliding discharge in humid air induces species (*NO*° and °*OH* radicals) that are effective in abating pollution in wastewaters at atmospheric pressure and ambient temperature through their oxidizing and acidifying properties. The results obtained show that, slow oxidation takes place in solution after the discharge is stopped. These results materialize the idea that species formed in the discharge diffuse through the solution and develop redox properties, allowing them to react in post-discharge. This phenomenon is probably due to the presence of secondary reactive species *(H_2O_2, NO_2^-, NO_3^-, etc.)* derived from radicals °*OH* and *NO*° (primary species) and which are known to have very high standard potentials. Our aim was to confirm the effectiveness of this method for the mineralization of organic compounds. We obtained after treatment of samples, an abatement rate of 48.92% for COD, 44.93% for BOD_5, and 24.09% for Turbidity after 30 min of exposure. The decrease in pH has permitted us to affirm that the gliding arc generates *in situ* species with acidifying properties. This reduction is more important than the duration of post-discharge which is large. The transient presence of peroxynitrous acid ONOOH is responsible for this acidification since it conditions the formation of nitrite and nitrates ions. The increase in SS and conductivity clearly explains the presence of ionic species that evolved with both the exposure time and time of post-discharge. As a result, it can be concluded that the exposure time is a very important factor for the degradation of pollutant molecules. This work also demonstrated that the phenomenon of post-discharge is a very important alternative for the depollution of wastewater polluted by organic compounds.

The parameters such as BOD, COD, turbidity, TSS and absorbance were evaluated from the sample treated 48 hours after exposure i.e. from the second day after exposure. This brings us to say that, almost all of the best results obtained are due to the post-discharge phenomenon, without forgetting in part the role played by the discharge itself.

We can conclude that, this method is effective and it is a sustainable alternative in the fight against environmental pollution caused by discharged wastewater since it generates in situ, without the addition of auxiliary reagents, highly reactive agents responsible for the cleanup. In the future, this process can be coupled with biological treatment to further lower the organic pollutant concentration more rapidly to an acceptable environmental level. On the basis of other studies, one can point out that a circulation process may be used instead of the presented batch device in order to significantly improve the efficiency of the plasma treatment in terms of kinetics.

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