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Plasma-chemical treatment of industrial wastewaters from brewery "*Brasseries du Cameroun*", Bafoussam factory

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Abstract
This work focuses on the study of the chemical reactivity of an advanced oxidation process (AOP), called the plasma technique, in order to prevent industrial effluent from pollution and better cope to several damage of environment. The oxidizing and acidifying properties of an electric discharge of the gliding arc plasma and its application to a target which is a real effluent (wastewater from *Brasseries du Cameroun* -Bafoussam plant) fascinated this study. Samples were collected from the central collecting point (CCP) of the effluent. The collected effluent samples were analyzed by volumetric and instrumental methods, and then exposed to the gliding discharge during specific time periods of 3-60 min to exhibit the desired decontamination effects. At the end of 60 min of exposure time to the discharge, 52.22% and 50.19% obtained respectively to abatement of turbidity and rate of fall in absorbance. This reduction can be explained by the fact that the coloured compounds were degraded and this degradation gave rise to the transparent appearance observed. After stopping the discharge process, the abatement percentage of BOD_5, COD and TOC, were obtained at the same time (60min) with values of 52.05%, 68.63% and 69.37% respectively. These results reflect the considerable reduction of the pollution load of the wastewaters collected from CCP of the brewery. These results showed that the effectiveness of the gliding arc plasma depends not only on the physico-chemical parameters of the target, but also on the exposure time and concluded that the non-thermal plasma process alone provides good reduction of organic pollutants in wastewater. Moreover, the phenomenon of post- discharge, even though not studied in details demonstrated that, after switching the discharge, the evolution of parameters such as pH, electrical conductivity and TDS increase.
Keywords: gliding arc plasma, Industrial wastewater, pollution, abatement, post-discharge.

I. INTRODUCTION

Water is one of the most important and abundant compound of the ecosystem. All living organisms on earth need water for their survival and growth. Due to increased human population, industrialization, use of fertilizers in agriculture and man-made activities, water is highly polluted with different harmful contaminants [1]. One major source of water pollution that has caused serious environmental and health problems are the pollutants coming from chemical and industrial processes [2]. Among water polluting industries, breweries occupy the greatest place because of their great consumption of water. As seen at the "*Brasseries du Cameroun, Bafoussam plant*", the beer brewing process often generates large amounts of wastewater effluent and solid wastes. Beer brewing involves three important steps (malting, mixing and fermentation) which can be reduce into two main steps, i.e., brewing and packaging of the finished product. The byproducts (e.g., spent grains from mashing, yeast surplus, etc)

generated from these steps are responsible for pollution when mixed with effluents [3]. In addition, some activities like cleaning of tanks, bottles, machines, and floors or activities coming from the industrial units produce high quantities of polluted water. In fact, wastewater from Bafoussam brewery plant may be discharged in several ways, mostly directly into a waterway like the Choumlou River chosen for this work. The pollution from these sources can lead to various health problems which directly affect human and aquatic lives. Thereafter, this water must be disposed off or safely treated even for reuse, which is often costly and problematic for most breweries. The disposal of untreated (or partially treated) brewery wastewater into water bodies can constitute potential or severe pollution problems to the water bodies since the effluents contain organic compounds that require oxygen for degradation [4]. For example, if water of high organic matter content flows into a river, the bacteria in the river will oxidize the organic matter consuming

oxygen from the water faster than the oxygen dissolves back in the river from the air [3]. So many brewers are today searching for ways to clean up wastewater coming from beer brewing process before disposal into the environment. Also another possible solution is to treat the brewery wastewater for eventual reuse.

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 [2]. Many physical, biological, and chemical processes are used in wastewater treatment. But some contaminants found in wastewater are recalcitrant to some degree, to commonly applied processes [5]. Among the available technologies, advanced oxidation processes (AOPs) are of special interest, as exemple of UV induced, photochemical effects combined with H_2O_2/O_3 [6]. Therefore chemical oxidation processes appear and are transformation processes that may augment current treatment schemes. Oxidation processes may destroy certain compounds and constituents through oxidation and reduction reactions [5]. Advanced oxidation is chemical oxidation with the hydroxyl radical, which is a very reactive and short-lived oxidant [7]. 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 discharge plasma.

In terms of new degradation techniques, electric discharge can be considered as a great source of reactive species that are able to degrade pollutant molecules. Gliding discharge [8-10] is one of the most promising and efficient representatives of such technology. This paper reports on, using humid air plasma also called non-thermal plasma provided by an electric gliding discharge in humid air, to lower the pollutant concentration in brewery wastewaters which comes directly from *"Brasserie du Cameroun, Bafoussam Factory"*. Subsequent post-discharge phenomena were observed and the effects of *ex-situ* chemical species on brewery wastewater were also investigated.

1.1. The plasma state: definitions and its generation

In physics and chemistry, plasma is an ionized gas containing free electrons, ions and neutral species (atoms and molecules) characterized by a collective behavior [11]. Plasma is often referred to as the *"4th state of matter"* since it has unique physical properties distinct from solids, liquids and gases. In particular, due to the presence of charge carriers, plasmas are electrically conductive and respond strongly to electromagnetic fields [11]. It can contain chemically reactive media as well as excited species and emits electromagnetic radiation in various

wavelength regions. In summary, plasma usually results from the increase of the energy of a gas provided by various sources, such as electric, magnetic, mechanical (shock waves and ultrasound), thermal or even optical (laser) sources [12].

The most common method of generating plasma for technological and technical applications is by applying an electric field to a neutral gas (figure 1). Alternatively, by the interaction of an electron beam with gaseous medium, plasmas can be generated. The type of plasma can be controlled by the electrical current flowing through the plasma or by the frequency of the applied voltage. The transition between different types of discharges at increasing current can be observed. Gliding arc discharge is an example of "cold" non-thermal plasma where electrical current remain low.
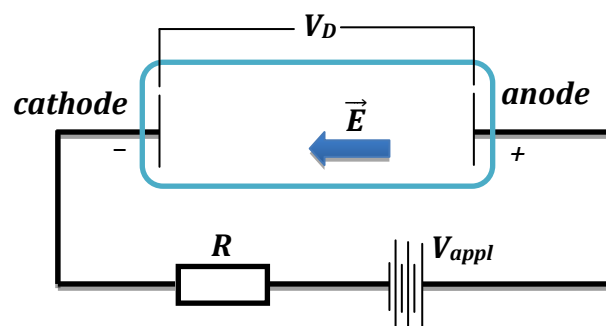

Figure 1: low pressure discharge tube [11]**.**

The term discharge was adapted when charged capacitors were discharged through the air gap between the electrodes. When the gap between electrodes became sufficiently thin, electrical breakdown occurred [11]. The space between the electrodes, so-called discharge gap can be several tens of centimeters while the diameter of the electrodes may be several centimeters. The tube is usually evacuated to 100-10000 Pa.

1.2. The gliding arc discharge (''glidarc'')

In this study the type of discharge used to create non-thermal plasma and to carry out this work is the Gliding Arc. Translational as well as cold plasmas are used for gas depollution and water depollution [11]. The electric discharge selected for this study was a gliding arc discharge. Doubla *et al.* [3] reported the use of humid air plasma created by an electric gliding arc discharge in humid air to lower organic pollutants in brewery wastewater. 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. These activated species are formed in advanced oxidation processes and are respectively responsible for acid and oxidizing effects in the

target solution. The gliding arc (or ''glidarc'') was first proposed by Lesueur *et al.* [13] and by Czernichowski [14] and was examined as a convenient source of quenched, non-thermal plasma in several laboratories, mainly for pollution abatement of gases [15,16]. In this work the non-thermal plasma was used for pollution abatement of wastewaters.

A gliding arc is an electric discharge in a high-intensity electric field formed between two or more diverging electrodes [13,16]. 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. A good description of this discharge is given in the experimental procedure.

1.3. Chemical properties of a gliding arc discharge

The chemical properties of a gliding arc discharge were already studied by Czernichowski *et al.* [16], Benstaali *et al.*, [12], Benstaali *et al.* [17],

Doubla *et al.* [18] and Geoffrey *et al.* [19]. Broadly, the acidifying and oxidizing properties of non-thermal plasma are attributed to the presence of NO° and $^{\circ}OH$ radicals formed during the discharge. The $^{\cdot}OH$ radical is a very powerful oxidizing agent $[E^0 (^{\cdot}OH/H_2O) =2.85\ V/NHE]$ and thus is responsible for oxidation reactions with organic targets, due to both its own properties and properties of its derivative and/or parent molecule H_2O_2 as shown in (Eq.(1)).

$$H_2O_2 \leftrightarrow 2\ ^{\bullet}OH. \tag{1}$$

Initially, NO° leads to the formation of nitrites in neutral media, but is further oxidized to nitrate ions as stable species. Additionally, the high standard oxidation-reduction potentials of the HNO_2/NO (1.00 V) and NO_3^-/HNO_2 (1.04 V) systems reflect the oxidizing power of the nitrate ion [3]. In other words, the nitrate ions participate in the oxidizing characteristics of the humid air plasma. The nature of the activated species formed in the discharge depends on that of the feed gas as mentioned [20] in the case of discharges in humid air. The activated species are derived from N_2, O_2 and H_2O [3].
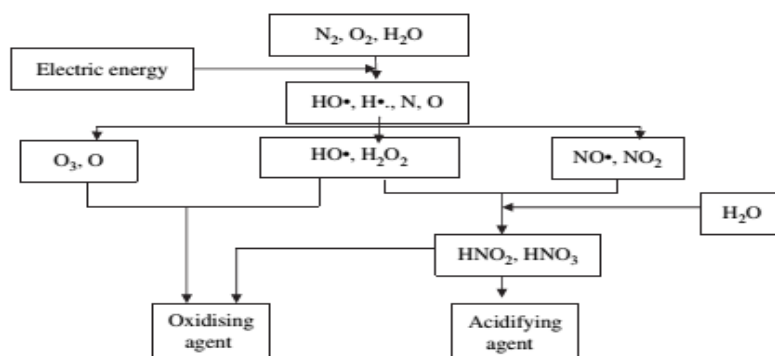

Figure 2: Main molecular species in humid air plasma

1.4. Pollution caused by Brewery: case of *"brasseries du Cameroun-Bafoussam plant"* in Cameroon

One of the main characteristics of brewery effluents is the high organic matter content and yeast used for fermentation, which are responsible for putrefaction. The brewery concerned in this study is located in Bafoussam, the head quarter of the West region of Cameroon. It is located 2000 meters from the Bank of Central African States. Used water, coming out from the brewery is usually polluted and is called industrial wastewater. This water is then poured out of the brewery and collected inside the central collecting point before being conducted to the Choumlou River This work is focused on the central collecting point.

II. Experimental methods

Brewery effluents having both chemical (with very high organic content) and microbial

contaminants are generally treated by biological methods using aerobic and anaerobic bacteria [21], but these methods require a lot of space and long treatment times. This has motivated us to outline some of the advantages of the gliding arc discharge that uses relatively short treatment times.

2.1. Gliding arc discharge device

The device employed for this study was developed from the gliding arc equipment previously described by [12, 13]. The glidarc reactor used in batch conditions is shown in Figure 3. It consists of a 23 cm long cylindrical vessel with an inner diameter of 10 cm. It is a non-thermal quenched plasma system operated at atmospheric pressure with humid air as the plasma gas. Briefly, it consists of two diverging electrodes raised to a high voltage fall (10 kV, 100 mA in open conditions) fitted with a gas feed nozzle attached along the axis of the reactor. An arc forms at the narrowest electrode gap and moves along the electrodes, being impelled by the gas flow

until it breaks into a plasma plume. A new arc then forms. When the plasma plume contacts with the solid target, the plasma active species react at the interface. For these operating conditions, the fed gas was air saturated with water. Its flow rate was fixed at 800 L.h^{-1}. The magnetically stirred batch reactor

used for this study was thermostatted by water circulation, so that the temperature of the 500 ml sample solution never exceeded 310 K. The distance between the bottom of the electrodes and the top of the sample was 1.4 cm.
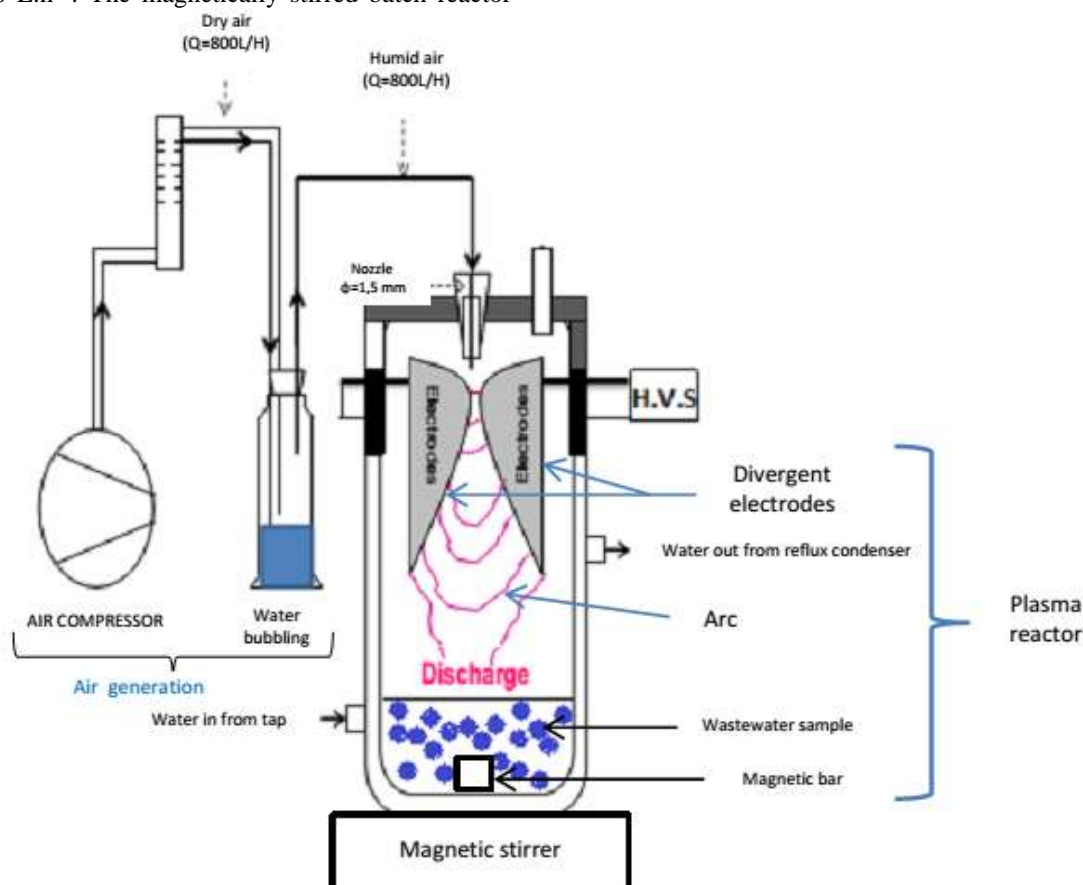
Figure 3: Experimental setup of the gliding arc discharge

2.2. Sampling and preservation of wastewaters from brewery of Bafoussam

The liquid samples were collected from central collecting point which is located directly out of the brewery. The samples were collected in august 2013, during the rainy season. These samples were collected by means of a peristaltic pump equipped with a 7.6 meters long silicon fluid tube (Masterflex Cole-Palmer Instrument, USA) and maintained at 12 volts using a battery. These samples were collected continuously during periods of production of drinks and an average sample was obtained every 1 h. After collection, the average sample was introduced into polyethylene bottles with a capacity of 1.5 liter and then transported to the physicochemical laboratory of *"Brasseries du Cameroun-Bafoussam plant"* for preliminary analysis. After this stage, the samples were now kept in a well portative refrigerator at low temperature (4°C) and transported from Bafoussam

to Yaoundé in the laboratory of Mineral Chemistry for the treatment phase.

2.3. Samples treatment

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, feeling of touch and appearance before storage. The next step was to measure the physicochemical parameters which were temperature, pH, turbidity, total dissolved solids, and electrical conductivity. These monitored by analyzing the parameters of organic pollution. The third step was to treat the sample by non-thermal plasma gliding arc.

In the procedure, 500 ml of brewery wastewater was magnetically stirred and disposed normally to the axis of the reactor at a distance of 40–45 mm (Figure 6). 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}. Wastewaters were exposed to the plasma for various treatment times (i.e., 3, 5, 10, 20, 30, 40, 50 and 60 min). 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 analyzed for standard control of colour, turbidity, absorbance, pH, total dissolved solids (TDS), suspended solids (SS), Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), according to the standard methods used in the Control Unit of the Plant. The effect of post-discharge phenomenon on target sample was also studied.

2.4. Analytical procedures used for the treated samples

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

Colour 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) was obtained; and within a range of wavelength, a spectrum was obtained. Turbidity was determined by a portable turbidimeter mark Orbeco - Hellige (966 model Orbeco Analytical Systems, Inc., USA).

pH, TDS and electrical conductivity was measured using a multi-parameter analyzer apparatus (Hanna HI9811 -5 cell with 1/10th precision 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$_2$SO$_4$* solution and the BOD test was done according to the BOD track procedure.

For each sample only the mean values were considered. Each average was obtained from the results of 5 consecutive measurements performed on each parameter.

III. Results and discussion

3.1. Characterization of water samples from the brewery of Bafoussam

The mean values of parameters of the wastewater samples collected from the central collecting point (CCP) of the brewery are presented in Table 1 below. These samples were diluted to a quarter of the crude solution to facilitate the reading of parameters by measuring devices.

Table I : Summary of Characteristic values of parameters of samples from brewery

Parameters	Values CCP crude	Cameroonians Norms	WHO Norms
pH	12.1	6.5-9	6.5-9
Temperature (°C)	29.7	-	-
Turbidity (NTU)	65	-	-
Absorbance (at 225 nm)	4.1	-	-
SS (mg/L)	587	50	-
Conductivity (µS/cm)	2205	-	< 400
TDS (mg/L)	1100	-	-
TOC (mg/L)	108.8	-	-
OM (mg/L)	187.57	-	-
COD (mg/L)	897	250	200
BOD$_5$ (mg/L)	782	50	50
NO$_2^-$ (mg/L)	0.064	-	-
NO$_3^-$ (mg/L)	0.9	-	-

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

It can be seen from this table that industrial wastewater collected from CCP of Bafoussam brewery is highly alkaline pH (12.1). These higher values of pH could be ascribed to basic compounds like soda which is used mainly for cleaning tanks.

This wastewater also has very high values of COD (897 mg/L), BOD$_5$ (782 mg/L), Conductivity (2205 µs/cm), TDS (1100 mg/L) and SS (587 mg/L) as compared to Cameroonian and WHO standards. This reflects that the wastewater from Bafoussam brewery

is very loaded with biodegradable organic matter since the COD/BOD5 quotient < 2; and is also very rich in dissolved substances and ions. This flow of pollution released into the environment without any treatment can cause adverse effects on human health and the environment.

3.2. Characteristics of effluents treated by plasma glidarc
3.2.1. Decoloration and turbidity

Figure 4 shows the evolution of the turbidity with treatment time t* (min) and figure 5 shows the evolution of colour intensity through absorbance with treatment time t* (min).
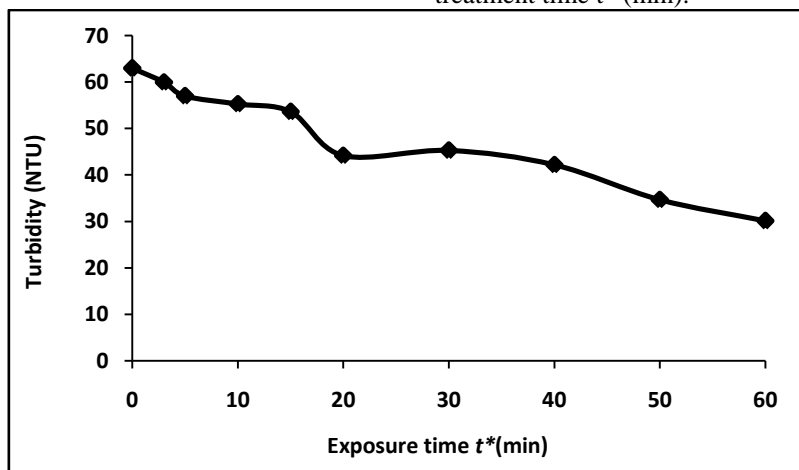
Figure 4: Evolution of turbidity with Exposure time
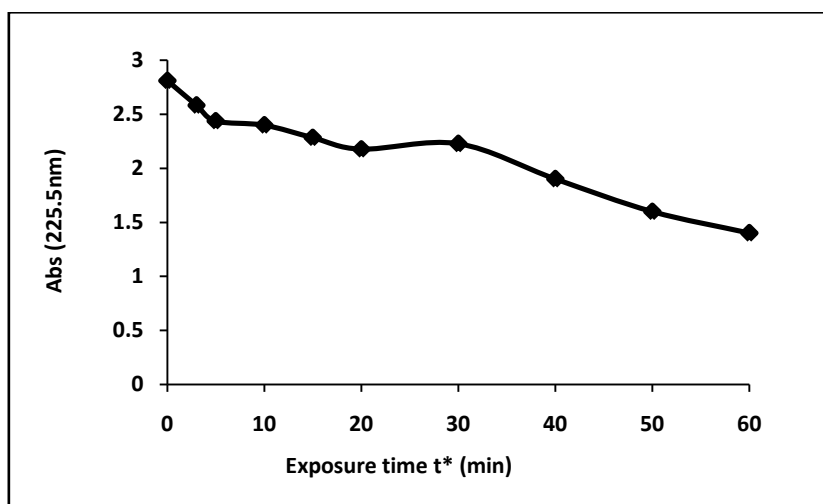
Figure 5: Evolution of absorbance with Exposure time

The results obtained for turbidity follow a trend almost similar to those of the absorbance. It was observe that these two parameters decrease with increase in the treatment time. The results show that the absorbance 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 colour of samples with the duration of the treatment. The appearance of transparency is due to the degradation of colouring matter. As already mentioned by Doubla *et al.* [22], it was observed in this case that for treatment times longer than 10 min, the colour intensity of the samples fell and reach the levels specified by international organizations. It was also noticed that for prolonged treatment durations (> 10min), there was 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 5 shows the discoloration observed after progressive treatment times.

Figures 8: Colors of treated samples at different times

3.2.2.   pH lowering effects

The pH evolution curve (figure 6) shows a rapid decrease in acidity during the first few minutes of exposure of sample and tends towards constant pH values between 3.3 and 3. It should be noted here that this is much lower than the standard values. This can be explained by the buffer effect arising from the temporary presence of the *HONO/ONO⁻* couple whose pKa is around 3.3, and also by the presence of solutes that can neutralize the carbonyl group present of wastewaters *(RCOOH/RCOO⁻).*
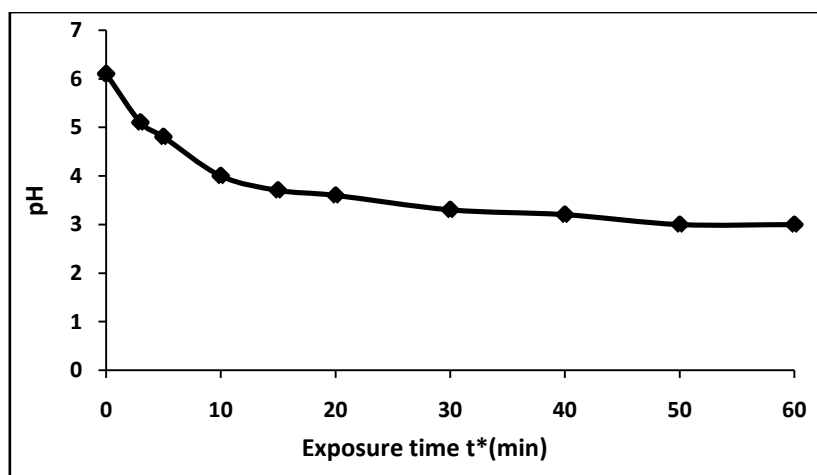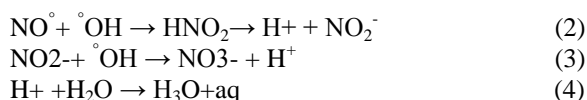

Figure 6: Evolution of pH as a function of exposure time

A similar result was also obtained by Doubla *et al.* [3], Brisset *et al.* [23] and Mountapmbeme *et al.* [24]. 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 *(HNO₂)* and nitric *(HNO₃)* acids, which are incorporated throughout the solution according to the overall equations [12] below:

$$NO^° + {}^°OH \rightarrow HNO_2 \rightarrow H+ + NO_2^- \qquad (2)$$
$$NO2- + {}^°OH \rightarrow NO3- + H^+ \qquad (3)$$
$$H+ + H_2O \rightarrow H_3O+aq \qquad (4)$$

This acidification is particularly important that the treatment time is increasingly high. This result confirms that the humid air plasma is a strong acid generator.

3.2.3.   Total dissolved solids and conductivity

The measurements illustrated in Figure 7 below shows a curve having a great increase in TDS and Conductivity with exposure time. Just in 30 min of treatment, initial TDS of the river water moved from 1000 to 2200 mg/L. The 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 wastewaters. Solubilization of TSS is also responsible for the increase in TDS. Doubla *et al.* [3] also obtained an increase of TDS during bio-decontamination of brewery effluents by non-thermal quenched plasma. Regarding the conductivity, there is a great similarity with the TDS. This is because the dissolved chemicals induce conductivity which affects the electrical properties of the solution. 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.
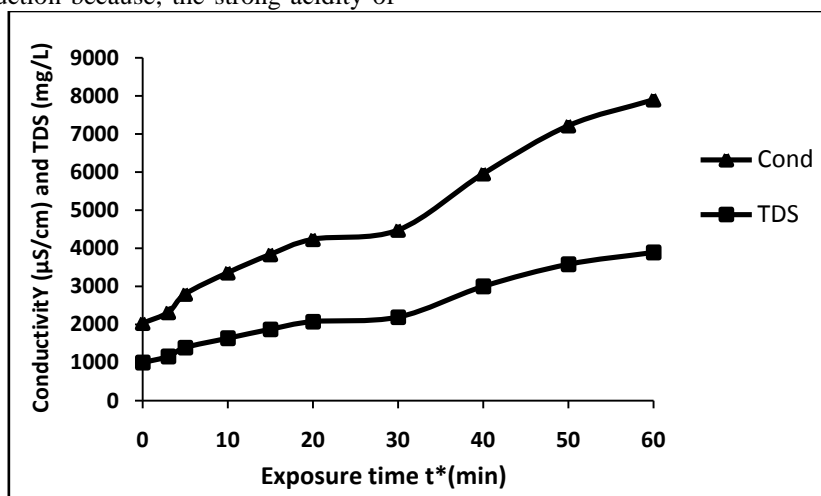

Figure 7: Evolution of TDS and conductivity with treatment time

3.2.4. Biochemical oxygen demand (BOD₅) and Chemical oxygen demand (COD)

In advanced oxidation processes, we often characterize the organic load of the effluent by measuring the COD (Chemical Oxygen Demand) and often by measuring the BOD_5 (Biochemical Oxygen

Demand in 5 days). To verify if the pollutants undergo 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. COD and BOD_5 values are illustrated in Figure 8.
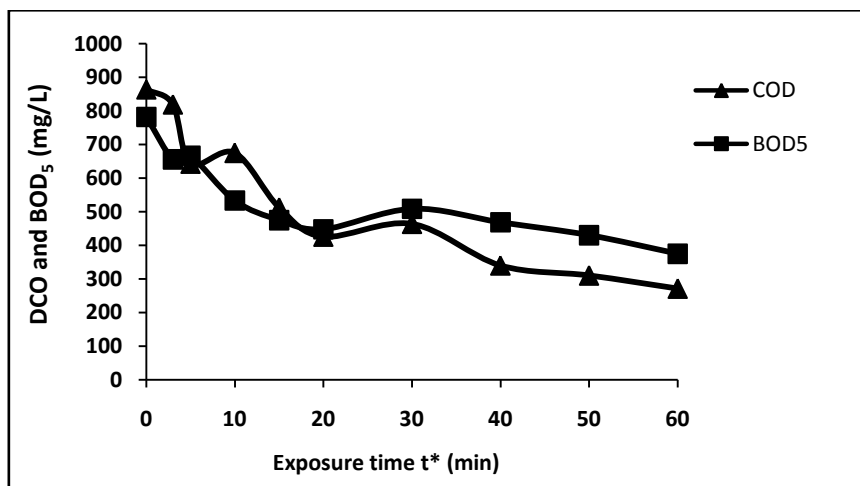

Figure 8: Evolution of COD and BOD₅ with treatment time

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. Starting from an initial abatement rate of 5.21 %, abatement rate of COD was 46.3% in

30 min but the overall reduction of COD was 68.63% only in 60 min of treatment.

BOD_5 decreases rapidly and gradually with time of treatment. After 10 min of treatment, the abatement rate became 31.80%. Compared to the works of Njoyim *et al.* [25], Doubla *et al.* [3] and Brisset *et al.* [23], it was observed that the decrease of BOD_5 in this work is not much better. For example, Doubla *et al.* [3] obtained a value of BOD_5 reduced into half after 10 min of treatment. But in this work, after 10 min of treatment, BOD_5 was not

halved. This large difference could be explained by the fact that the sample taken from the CCP of the brewery 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 (<50mg/L). BOD_5 moved from 782 to 375 mg/L in 60 min, corresponding to a reduction of 52.05 %. The reduction in BOD obtained corresponds to a reduction of organic matter in relation to the apparition of oxidizing agents such as $°OH$ and $NO°$ inside the discharge and their derivatives in aqueous solutions [12,26,27], as had been previously described. The effectiveness of treatment was not reached for a maximum time of 30 min indicating that the exposure time on plasma had a positive influence on the quality of treatment. Samples of the 4th treatment time had the best transparency than those of 1st, 2nd, and 3rd treatment time, with an abatement rate in COD of 40.74% after discolouration. This implies that discolouration can

provide a good aesthetic aspect of water but not its purification or total disinfection.

Therefore, we must achieve high processing time to observe a better reduction in COD and BOD_5. Non-thermal gliding arc plasma allows on its own (without catalyst or combination) the degradation of organic matter. The temporary increase of COD could be explained by the emergence of new intermediate compounds (recalcitrant) resistant to oxidation by potassium dichromate but ultimately undergo degradation by strong oxidation with prolonged treatment time. Pollutants are not directly mineralized but transformed into intermediate products. The final COD reaches a value of 271 mg/L, which is close to acceptable standards by Cameroon and WHO (250 mg/L).

3.2.5. Influence of treatment time on the evolution of Suspended Solids (SS)

Figure 9 shows the variation of suspended solids with the processing time.
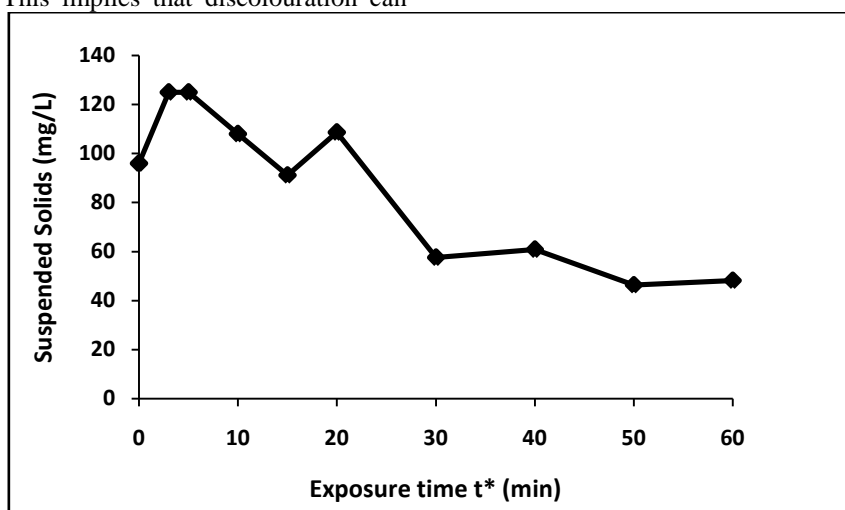

Figure 9: Evolution of Suspended Solids with the treatment time.

The curve in this figure shows an evolution almost in saw tooth. Between the 3rd and 5th min of treatment, the amount of suspended material increased, which is evidence that organics were degraded into SS. Then the SS decreases globally from the 10th min of treatment to achieve low values from the 30th to 60th min 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 49.80% in 60 min. This solubilization of SS might be responsible for the increase in TDS. The transformation scheme may be as follows:

Organic matter →(Degradation)→ SS →(Solubilisation)→ TDS and Cond
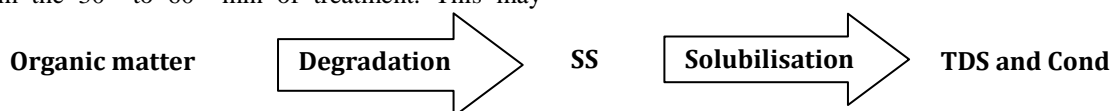
3.2.6. Evolution of nitrates and nitrites with the exposure time

The results recorded in Figure 10 are those of nitrates and nitrites. It was observed that, the raw sample contains nitrate ions in small amounts (3.6 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. This observation was also mentioned

by Brisset *et al.* [23], Doubla *et al.* [3] and Abba *et al.* [28]. As for the nitrite ions, their presence is not negligible in the raw sample but their concentration varies very slightly during the exposure time. Their values were between 100 and 160 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 [23]. This result implies in other words that, there is oxidation of nitrite to nitrate ions.
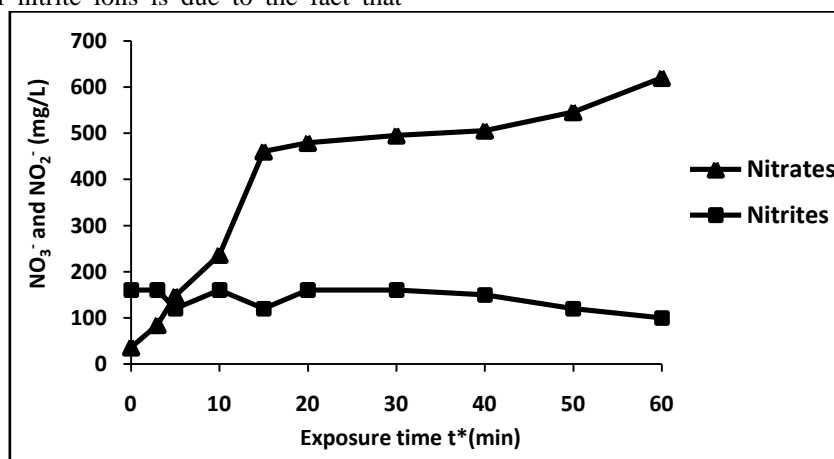

Figure 10: Variation of nitrates and nitrites with exposure time

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*. [3]. Moreover, the formation of nitrites and nitrates was demonstrated by Elsayed [29]. The latter is accompanied by acidification of the medium as shown by the mechanism in Figure 11:
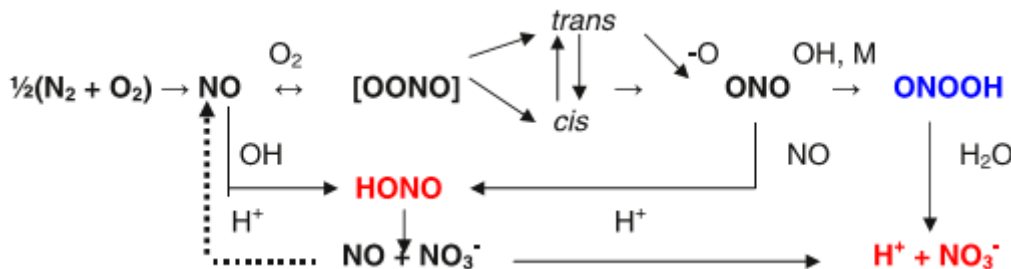

Figure 11: Scheme of formation of nitrate ions from nitrous acid HONO via acid peroxynitrous ONOOH adopted by Elsayed [29]

3.3. Effect of post-discharge phenomenon on samples

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 is 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.* [24], Doubla *et al.* [3] and Brisset *et al.* [23] which have been broadly done on this phenomenon also mentioned its presence. This

part, show the effect of post-discharge on the change in pH and on evolution of TDS and conductivity
Table II above highlights a very important phenomenon in the chemistry of plasma: the phenomenon of acidity. It should be noted that, whatever the concentration of the polluting substances, the pH decreases after the exposure of the solution to plasma and decreases gradually in the post-discharge process. 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.

Table II: Evolution of pH, TDS and conductivity in post-discharge as a function of exposure time

	Times (min)	0	3	5	10	15	20	30	40	50	60
pH	**Directly after exposure**	6.1	5.1	4.8	4	3.7	3.6	3.3	3.2	3.2	3
	48 hours after exposure	6.1	4.7	4.1	3.5	3.2	3.1	3	2.9	2.9	2.8
Cond (µS/cm)	**Directly after exposure**	2040	2320	2800	3360	3840	4240	4480	5960	7220	7900
	48 hours after exposure	2040	2670	3150	3715	4198	4590	4825	6350	7650	8510
TDS (mg/L)	**Directly after exposure**	1000	1160	1400	1640	1880	2080	2200	3000	3580	3890
	48 hours after exposure	1000	1345	1585	1858	2101	2295	2413	3177	3825	4255

The table 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. 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.

IV.   Conclusion

This research aims at testing the "glidarc" plasma system as a useful tool for the treatment of recalcitrant substances present in actual wastes, and explores working conditions close to industrial operations. This study was initiated after the successful plasma abatement and biodecontamination of Organic organic pollutants of brewery effluents by non-thermal quenched plasma at atmospheric pressure [3] and after the treatment of brewery wastewater for reuse [19]. 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 brewery 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 electrode potentials [3]. The main goal of this work was to confirm the effectiveness of this method for the mineralization of organic compounds. We obtained after treatment of samples, an abatement rate of 68.63% for COD, 52.05% for BOD_5 and 52.22% for Turbidity after 60 min of exposure. These results are consistent with the works of our predecessors. 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.

Parameters such as BOD, COD, turbidity, TSS and absorbance were evaluated from the samples treated 48 hours after exposure i.e. from the second day after exposure. Thus, it can be said 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 brewery wastewater since it generates in situ, without the addition of auxiliary reagents, highly reactive agents responsible for the cleanup. For the future this process can then be coupled with biological treatment or with UASB (Up-flow Anaerobic Sludge Blancked) of brewery-Bafoussam to further lower the organic pollutant concentration more easily and 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. In future, techniques that can eliminate nitrites should be searched for, since they increase the COD, so that treated wastewater can be reused. The coupling of non-plasma process with biological processes and membrane processes should also be investigated.

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