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## APPLIED CHEMISTRY

**Coupling Gliding Discharge Treatment and Catalysis by Oyster Shell Powder for Pollution Abatement of Surface Waters**

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Adsorption on oyster shell powder (OS) was combined with gliding electric discharge to abate pollution of surface waters sampled in brooks passing through large Cameroonian cities and collecting industrial and domestic wastes. OS powder incorporated into the aqueous samples after exposure to the discharge improved pollutant abatement as compared to the plasma treatment alone. The process kinetics involved pseudo zero-order reactions for treatments longer than 5 min. Total organic carbon linearly decreases with increasing exposure time to the discharge ( $k \approx 0.13 \text{ mgC L}^{-1} \text{ min}^{-1}$  for a  $1 \text{ g L}^{-1}$  standard OS charge). The rate constant linearly increases with the incorporated OS mass, which increases the sample pH. The coupled process is more efficient than a single plasma treatment of the polluted liquid in terms of operation cost, waste abatement ratio, and reaction rate. A chemical model involving known plasma generated species and matching acid–base effects is proposed.

**1. Introduction**

Most countries including countries under development are now concerned with acute problems of water, which result from the increase in their growing population and their developing industry; increasing volumes of drinkable and industrial water are required. Another aspect of the question lies in the quality of water, which must be also improved to limit public health risks: for example, industrial or even domestic waste waters should not be used in agriculture for watering crops. To face this problem, most countries under development have decided to take special regulations, limit the volume of harmful waste waters thrown away by plants, and develop new techniques for pollution abatement at the same time.

Usual purification techniques are obviously available, but their fitting in industrial plants is ordinarily expensive, as are the running costs. Besides, countries under development are not always equipped with suitably adapted networks of sewage systems for collecting liquid wastes and with plants for their purifying treatment. The country authorities then look after new efficient and cheap techniques suitable for the treatment of large volumes of water.

The advanced oxidation processes are among the most popular and seductive techniques, and the electric techniques are actually those that release the smallest quantity of wastes. An increasing number of papers are devoted to processes mixing an electric discharge, most often pulsed DBD or streamer,<sup>1–6</sup> or gliding discharge<sup>7,8</sup> and using a catalyst ( $\text{TiO}_2$ <sup>1,2,4–9</sup> or others<sup>9–13</sup>). The influence of the metal electrodes has also been considered.<sup>10,11</sup>

This study is devoted to the use of gliding electrical discharges at the laboratory scale to lower the pollutant concentration of liquid samples taken from brooks that pass through major Cameroonian cities and collect domestic and industrial wastes.

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This technique is connected with incorporation of powdered oyster shells (OS) to the samples, that is, useless solid wastes that are claimed to adsorb pollutants. Finely powdered OS is directly used after washing and drying and later incorporated to the liquid sample. Exposure to the electric discharge takes place before incorporating OS. Such a treatment leads to the abatement of organic pollutants with higher efficiency than the plasma treatment alone, which accounts for a positive synergism.

**2. Elements of Plasma-Induced Chemistry**

**2.1. Reactive Species.** The feed gas that fills the reactor is water saturated air: thus, the “parent” molecules are  $\text{O}_2$ ,  $\text{N}_2$ , and  $\text{H}_2\text{O}$ . The energy transfer by electron impact from the discharge to the ambient gas allows the breaking of water molecules into  $\text{H}$  and  $\text{OH}$  radicals, which can also result from the photochemical action of the UV photons on water molecules. Additionally to  $\text{H}$  and  $\text{OH}$ , the “primary species” are provided by the parent molecules  $\text{N}_2$  and  $\text{O}_2$ . Emission spectrometry showed the occurrence of  $\text{O}^+$  (enthalpy threshold: 13.6 eV  $\text{mol}^{-1}$ ) and  $\text{N}^+$  (enthalpy threshold: 14.5 eV  $\text{mol}^{-1}$ ) at the electrode shortest gap and  $\text{NO}$ , excited  $\text{N}_2^*$  (transition  $\text{C}^3\Pi_u - \text{B}^3\Pi_g$ ),  $\text{OH}$ , and  $\text{N}_2^+$  in the plasma plume.<sup>14,15</sup>

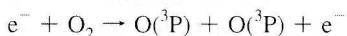
The primary species are able to react in the gas phase either with other primary species or with parent species and form “secondary species”, which are in position to react with the target molecules at the liquid surface. These “secondary species” are mainly  $\text{H}_2\text{O}_2$  provided by condensation of  $\text{OH}$ :



and  $\text{NO}$ , and its derivatives, such as  $\text{ONO}$ ,  $\text{HONO}$  (nitrous acid, which disproportionates into  $\text{NO}$  and  $\text{NO}_3^-$  in acidic medium), and  $\text{HOONO}$  (peroxynitrous acid), which results from the oxidizing action of  $\text{OH}$  on  $\text{ONO}$ , and slowly rearranges into dissociated nitric acid<sup>16,17</sup> in the solution (Figure 1).

The last species is  $\text{O}_3$ . The presence of ozone may also be considered<sup>18</sup> and results from the combination of  $\text{O}$  atoms with

molecular oxygen, in the presence of a third body, as precised by De Laat et al.<sup>19</sup> However, no O atoms in any excited state were spectrometrically identified in our discharges.<sup>15</sup>



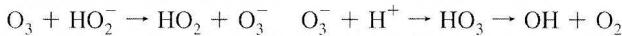
The work by Peyroux et al.<sup>20</sup> on corona discharges in dry and in humid air confirmed the industrial knowledge that water vapor does not favor ozone formation.<sup>21</sup> Additionally, O<sub>3</sub> combines<sup>19</sup> with O, OH, and mainly NO and NO<sub>2</sub> (in case of humid air discharges or stratospheric reactions), which lowers its concentration in the solution.



and



additionally to reactions involving anions, for example:

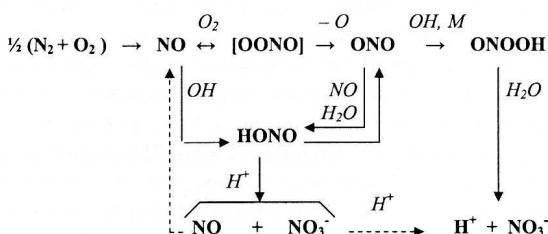


Because we are concerned with chemical reactions occurring in a condensed phase (i.e., water and occasionally at solid surface), O<sub>3</sub> is not considered in this work as a main species because of its limited solubility in water (around 0.17 g m<sup>-3</sup> at 25.5 °C and its limited stability (half-life time 20–30 min) in this liquid medium.<sup>21</sup>

**2.2. Acidity Changes.** The formation of nitric acid (and to a lesser extent, nitrous acid) in aqueous solutions exposed to the discharge accounts for an acidic effect, which is evidenced by color changes of acid–base indicators and pH fall by several units, down to pH ≈ 3 for pure water.<sup>22,23</sup> The pH change is very limited in case of large volumes of concentrated base or acid solutions.

The influence of protons on the oxidation reduction reactions concerning organic systems made necessary the preparation and the calibration of buffers,<sup>23</sup> which vary by less than one-half a pH unit for 1 h exposure to the discharge.

**2.3. Oxidizing Properties.** Most of the secondary species present the properties of strong oxidizers: OH and H<sub>2</sub>O<sub>2</sub> are among the known strongest oxidizing species [ $E^\circ(OH/H_2O) = 2.85 \text{ V/SHE}$ ;  $E^\circ(H_2O_2/H_2O) = 1.68 \text{ V/SHE}$ ] with potentials higher than ozone or oxygen [ $E^\circ(O_3/H_2O_{\text{liquid}}) = 1.51 \text{ V/SHE}$ ;



**Figure 1.** Scheme of the formation of nitric acid via transient nitrous and peroxy nitrous acids, adapted from Morrow<sup>16</sup> and reported by Elsayed.<sup>17</sup>

$E^\circ(O_2/H_2O_{\text{liquid}}) = 1.23 \text{ V/SHE}$ ], all the more because these latter values must be corrected for gas solubility in case of practical application.

The transient peroxy nitrous acid ONOOH ( $pK_a = 6.5$ ) and its matching base peroxy nitrite ONOO<sup>-</sup> are also strong oxidizers, with respective standard potentials  $E^\circ(ONOOH/NO_2) = 2.05 \text{ V/SHE}$  and  $E^\circ(ONOO^-/NO_2) = 2.44 \text{ V/SHE}$ ,<sup>24</sup> which make them able to degrade a large number of organic wastes and to inactivate microorganisms.<sup>25</sup>

### 3. Experimental Section

**3.1. Collecting the Liquid Samples.** The liquid samples were directly collected in several points of two brooks that flow through Yaoundé and Douala, the two main cities in Cameroon, and gather both domestic and industrial wastes. The samples were then stored in plastic containers at low temperature (4 °C) before analyses or treatments.

The organoleptic parameters of the samples, that is, appearance, feeling to touch, and odor, were immediately checked before storage and measurements of the physical-chemical parameters, which are temperature, pH, turbidity, total dissolved solids, and conductivity. The samples were stored in the cold before the measurements of parameters related to pollution (e.g., ions by chemical analysis, biological oxygen demand, BOD<sub>5</sub>, chemical oxygen demand, COD, and total organic carbon, TOC) were performed. One part of the samples was devoted to the plasma treatments and analyzed accordingly for pH, TOC (Walkley and Black's method<sup>26</sup>), BOD<sub>5</sub> (Hach BOD Track instruments), and COD (Hach COD reactor), and the other part to the purifying treatments.

The various origins of the liquid samples made mandatory a statistical analysis of the results, which was performed by means of analysis of variance program (minitab software).

**3.2. Collecting and Conditioning the Oyster Shells.** Oyster shells (OS) are waste products from aquaculture that present a major disposal problem in coastal regions such as southeast Korea. Also, it was reported in press that a Japanese fish farmer tossed OS into a pond and found out that it cleared the dirty water.

**Prior Art.** It was found out that pyrolysis of waste oyster shells under defined conditions (750 °C for 1 h under a nitrogen atmosphere) transforms this material into a sustainable reagent for efficient (up to 98%) removal of phosphates from wastewater. In comparison, raw oyster shells removed almost no phosphate from water, whereas oyster shells heated to 750 °C under an air atmosphere removed a moderate proportion (up to 68%) of phosphates from water. X-ray diffraction (XRD) analysis of pyrolyzed oyster shells showed peaks that were characteristic of calcium oxide, whereas analyses of raw oyster shells showed peaks that characterized calcium carbonate.<sup>27</sup>

As living organisms, oysters help filter and cleanse seawater. Now, scientists may be able to broaden that natural cleansing ability by using the bivalves' shells to obtain fresh water rid of pollutants. The University of Florida and Korean researchers have developed and successfully tested a new process to convert waste oyster shells into a compound that cleanses water off phosphorus, a common pollutant in urban, agricultural, and industrial runoff. The environmentally beneficial recycling technique appears to offer a way to use the millions of oyster shells produced annually as an unwanted byproduct of today's aquaculture operations, shells that have had few other uses until now. Because the ingredients (oyster shells) are free, a preliminary analysis suggests that the process is competitive costwise with traditional water-cleaning chemicals. Recycling

the oyster shells into the water treatment compound makes particular sense because intense aquaculture often spurs coastal growth.

Shamim et al.<sup>28</sup> investigated the effect of temperature on wastewater treatment using natural material (shell) and observed a significant enhancement of the removal of suspended solids and chemical oxygen demand. They equally added that the wastewater treatment system was simple, convenient, and low cost. Xiaojing and Zhilong<sup>29</sup> demonstrated that oyster shell shows great buffer capacity as an oyster shell biofilter had up to 97% ammonium-nitrogen removal efficiency from an influent concentration of  $60 \text{ mg L}^{-1}$  at a pH range of 5.3–5.7. They also observed that the effluent pH could be maintained at 6.5.

**Present Study.** For the present study, the collected shells were washed, sun dried, mechanically crushed in porcelain mortar, and sieved with a mesh of size 0.5 mm before use in plasma treatment. The shells were not pyrolyzed.

**3.3. Gliding Discharge.** The basic design of the reactor was proposed by Lesueur et al.<sup>30</sup> and by Czernichowski et al.<sup>31</sup> for the decontamination of gases. The reactor was developed several years later by the Electrochemistry Laboratory (Rouen University, France) and adapted to the treatment of liquids.

The equipment consists of a generator (an Aupem Sefli HV transformer: 9 kV; 100 mA in open conditions) operating at high voltage, which produces an arc between the electrodes at the electrode gap. This arc is pushed along the diverging electrodes by a gas flow provided by a compressor and directed along the axis of the electrodes. The arc moves along the electrodes to their tips where it bursts into a plasma plume when it is short-circuited by a new arc. The length of the arc (which is actually a thermal plasma) gradually increases, and its temperature falls until it breaks and becomes a quenched plasma close to ambient temperature at atmospheric pressure. Such a plasma has properties and composition that look like a thermal plasma (and in particular its ionization ratio is likely higher than for corona or DBD discharges, although the energy displayed in the discharge remains less than about 15 eV).

The plasma plume is in contact with the liquid target, so that the active species formed in the discharge are able to react at the liquid surface with target molecules.

The chemical batch reactor in which the treatment was carried out is fitted with a cooling device to limit evaporation and vapor stripping, and a magnetic stirrer and bar were used for stirring the sample and as a source of current. A sketch of the setup is presented in Figure 2.

About 400 mL of the target wastewater was placed on the axis of the reactor at a distance of about 40–45 mm, and the solution was stirred magnetically. The selected feed gas was water-saturated air: air provided by a compressor that passes through a bubbling flask before entering the reactor (gas flow rate:  $800 \text{ L h}^{-1}$ ). Samples of wastewater were exposed to the plasma for different treatment times  $t^*$  at controlled temperature and cooled by means of a reflux condenser. After treatment, the contents of the reactor were emptied into prewashed, dried, and labeled polyethylene containers for further analyses. These results were obtained as post discharge because the source of electrical discharge had to be interrupted prior to analyses.

**3.3.1. Selected Plasma Treatments.** Two kinds of treatments were considered: (i) exposure of the mere liquid sample to the discharge for  $t^*$  (min), “plasma only” (PO); and (ii) exposure of the liquid sample to the discharge for  $t^*$  followed by incorporation of a weighed mass  $m$  of OS, the “plasma with incorporation after” process (PA).

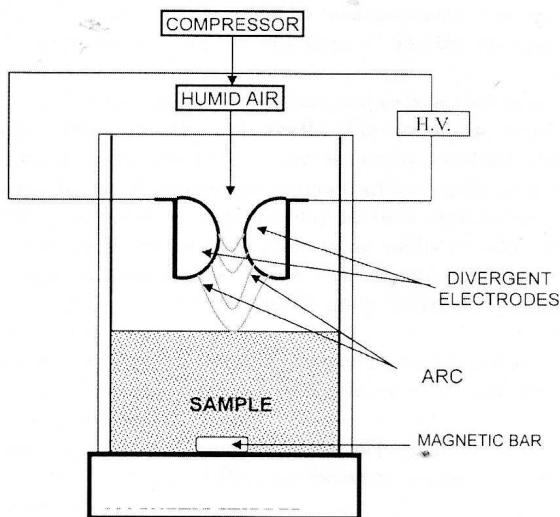


Figure 2. Scheme of the gliding arc batch reactor.

PO and PA treatments require the same energy expenses because the discharge is operated for the same time  $t^*$ : direct comparison of the efficiency of the compared processes can thus be achieved.

**3.3.2. Analytical Methods Used for the Treated Samples.** Several techniques were used to follow the waste concentration with the exposure time  $t^*$  to the discharge and with the added mass  $m$  of catalyst OS. Four techniques account for the target modification in PO conditions: pH-metry, total organic carbon (TOC), biochemical oxygen demand ( $\text{BOD}_5$ ), and chemical oxygen demand (COD) measurements.

The pH was measured with a Schott CH 837 pH meter according to the usual procedure.

The BOD was determined using a BOD Track Instrument distributed by Hach C°. It allowed one to determine the  $\text{O}_2$  concentration used by bacteria present in the sample volume.

COD measurements resulted from the oxidation of organic solutes by dichromate in sulfuric acid and the colorimetric measurement of the yellow color abatement. A portable Hach COD device was used for spectrophotometric measurements.

**3.4. Statistical Analysis.** Because of the large number of different samples considered, the use of statistical methods was found necessary. The results of the plasma treatments were discussed on the basis of one-way and individual 95% analysis of variance (ANOVA) statistical program, and this analysis allowed us to determine whether the files of results relevant to a couple of treatments were significantly different or not. The results reported in the tables are thus relevant to mean values.

## 4. Experimental Results

**4.1. Composition and Structure of the Shells.** The chemical analyses of the shells were performed with an inductively coupled plasma atomic emission spectroscopy device after dissolution in  $\text{HCl}$  or  $\text{HNO}_3$ . Calcium (Table 1) is the main component present as aragonite and mainly as calcite, that is, as carbonates, which were identified by X-ray diffraction and FTIR spectroscopy.

**4.2. Analyses on Collected Water Samples.** The results of physical, chemical, and instrumental analysis of water samples are gathered in Table 2. For additional information, the standard legal values accepted by Cameroon Authorities are also listed when available, as well as the global guidelines for effluents and the tolerance limits of the pollutants.

**Table 1. Results of Chemical Analysis of Natural Oyster Shells**

| oxide of elements              | % oxide in OS (HCl) | % oxide in OS (HNO <sub>3</sub> ) |
|--------------------------------|---------------------|-----------------------------------|
| Al <sub>2</sub> O <sub>3</sub> | 0.33                | 0.4                               |
| Fe <sub>2</sub> O <sub>3</sub> | 0.20                | 0.04                              |
| CuO                            | 0.37                | 0.19                              |
| PbO                            | nd                  | nd                                |
| ZnO                            | 0.58                | nd                                |
| MgO                            | nd                  | nd                                |
| CaO                            | <b>96.61</b>        | <b>83.02</b>                      |
| SiO <sub>2</sub>               | 0.60                | 0                                 |
| MoO <sub>3</sub>               | 0.37                | 0.07                              |
| B <sub>2</sub> O <sub>3</sub>  | 0.14                | 0.14                              |
| P <sub>2</sub> O <sub>5</sub>  | nd                  | nd                                |
| Na <sub>2</sub> O              | nd                  | nd                                |
| H <sub>2</sub> O               | nd                  | nd                                |
| total                          | 99.21               | 84.09                             |

Table 2 shows that some results are largely higher than the safety standards and that the sample sources thus have to be carefully purified. Also, the collected data are largely overdiversified, which justifies using statistical methods for obtaining a valuable view of the ability of the treatments.

**4.3. PO Treatments.** The mean pH values relevant to the numerous treated samples exposed to PO treatments (i.e., without incorporated shell powder) are gathered in Table 3. Acidity of the treated samples increases with the exposure time, as was already observed in studies specially devoted to the chemical properties of the discharges in air.<sup>22,23</sup> For a standard 30 min treatment, pH falls from 6.4 to 3.0.

Table 3 also reports results relevant to TOC, BOD<sub>5</sub>, and COD. The mean values of these three parameters decrease with increasing exposure time to the discharge, which confirms the efficacy of the discharge for pollutant abatement.

A one-way statistical ANOVA treatment was used to check whether a plasma treatment was significantly efficient or not by comparing two sets of data. In particular, a level of significance *P* quite low (*P* < 0.001) between nontreated (NT) and PO-treated samples illustrates the influence of the discharge on the considered targets.

Complementary multiple comparison tests at 95% confidence were also performed: they showed, for example, a wide separation between the mean values of nontreated samples and PO-treated liquid samples, while PA-treated samples overlap with NT samples. This observation explains the fact that when samples are treated with plasma only, the pH drops, but when oyster shells are incorporated, the pH rises again to almost the same magnitude as it was lowered. This phenomenon is expressed graphically in Figure 3.

**4.4. PA Treatments.** The considered plasma treatments, with shells incorporated into the sample after exposure to the discharge for time *t*\*, were performed for various *t*\* values but also with various concentrations, *m*, of added shells (for standard *t*\* = 5 min). Both sets of results were also statistically discussed.

**4.4.1. Experimental Results of the Treatment.** The pH abatement for samples exposed for *t*\* = 5 min to the discharge slightly increases with the incorporated mass of OS (Table 4).

Table 4 also reports the pH evolution with *t*\* of samples with known incorporated masses of oyster shells (*m* = 0.1 g L<sup>-1</sup>). For coupled treatments, the solution is acidified by the discharge before the shells are incorporated, and neutralization reaction takes place so that the pH gently increases to pH ≈ 8 (for *t*\* = 30 min), for the process PA.

Table 5 accounts for TOC results for PA treatments, that is, for the total degradation of organic matter from the aqueous sample, as a function of the exposure time to the discharge *t*\* and the mass *m* of incorporated oyster shells.

Table 6 gathers results of BOD measurements as a function of the exposure time to the discharge *t*\* and the incorporated mass of oyster shells.

Table 7 is devoted to COD data and depends on *m* and *t*\*.

**4.4.2. Incorporation of Shells.** The treatment results in incorporating the shell powder after having exposed the aqueous samples to the discharge: large modification of the properties of the system (OS + sample) may be thus expected because acid base reactions involving the basic shells powder dipped into an acidic solution take place. Neutralization is expected to occur readily and induces a significantly different behavior for pH evolution.

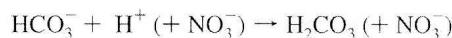
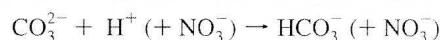
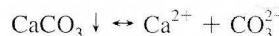
The experimental results are affected by the basic parameters *t*\* and *m*. They are gathered in Tables 4–7 to enlighten the relevant discussion.

One-way statistical analysis of the pH evolution shows that there is a significant difference between plasma-treated and untreated samples.

## 5. Discussion

**5.1. Chemical Interpretation of the pH Evolution (Tables 3 and 4).** The acid effect observed for PO treatment (Table 4) increases with the exposure time *t*\*, as usually observed for solutions of weak bases exposed to the discharge. The overall acid evolution results from adding HNO<sub>3</sub> to the solvent (see Figure 1 and section 2.2) and neutralizing the target impurities. The pH evolution with *t*\* is almost linear for 30 min.

The general behavior of pH versus *t*\* plot relevant to PA treatment is characterized by an overall acidity decrease with increasing *t*\*. This feature results from two successive reactions. The first one is described for PO treatment: the protons generated in the solution have neutralized the solutes in the absence of added oyster shells. The excess in protons from plasma treatment thus provides an acidic solution before incorporating the shells. The added shells are solid bases made of calcium carbonate, which tends to neutralize the acidic solution. Calcite slowly dissolves in acidic medium, so that the proton concentration decreases as the shells are dissolved, and pH increases due to the excess in base. The behavior of the relevant pH versus *t*\* plot is that of a strong base added to a solution of strong acid.



Adding various masses of powdered oyster shells to the sample solution submitted to a standard exposure time of 5 min confirms the observed pH evolution. pH slightly increases with *m*, which means that the neutralization ratio of the protons by carbonate is largely favored by incorporation of large quantities of shells.

**5.2. BOD<sub>5</sub> Measurements (Tables 3 and 6).** The biological demand of oxygen is a classical test performed in industry, in particular on waste effluents. The data reported in Table 3 for PO treatment (for *m* = 0) are plotted against *t*\* and reasonably arrange according to an exponential decay. The kinetic constant of a pseudo first-order kinetics is given by the slope of the transform  $\ln(\text{BOD}) = f(t^*)$ , that is,  $k_{\text{BOD}, \text{PO}} = 0.15 \text{ min}^{-1}$ .

Table 6 reports the BOD<sub>5</sub> data for PA treatments with varying *t*\* and *m* values.

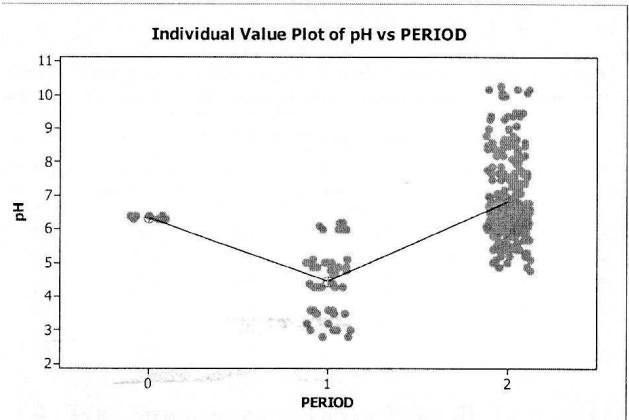
**Table 2. Chemical and Physico-chemical Analyses on Collected Water Samples<sup>a</sup>**

| parameters                                       | samples |       |              |       |       |              |       |       |     |      |     |
|--|---------|-------|--------------|-------|-------|--------------|-------|-------|-----|------|-----|
|  | 1       | 2     | 3            | 4     | 5     | 6            | 7     | 8     | L1  | L2   | T   |
| odor   | foul    | foul  | foul         | foul  | none  | none         | none  | none  |     |      |     |
| color  | gray    | dark  | gray         | clear | brown | clear        | clear | clear |     |      |     |
| pH   | 7.38    | 6.99  | <b>6.40</b>  | 6.14  | 7.08  | 6.59         | 7.44  | 8     | 6–9 | 6–9  | N/A |
| temperature (°C)                                 | 28.5    | 24.3  | 31.6         | 25    | 23.6  | 26.7         | 23.4  | 24.2  | 30  | <37  | 37  |
| turbidity (mg L <sup>-1</sup> SiO <sub>2</sub> ) | 4       | 0.56  | 77.04        | 2.72  | 0.6   | 56.52        | 6.3   | 10.5  |     |      |     |
| DS (mg L <sup>-1</sup> )                         | 12      | 85    | 6            | 197   | 17    | 650          | 200   | 150   |     |      |     |
| conductivity ( $\mu\text{Sc m}^{-1}$ )           | 25      | 173   | 12           | 397   | >1000 | >1000        | 410   | 310   |     |      |     |
| BOD <sub>5</sub> (mg L <sup>-1</sup> )           | 80      | 26    | <b>716</b>   | 54    | 10    | 350          | 79    | 150   | 80  | <30  | 100 |
| COD (mg L <sup>-1</sup> )                        | 38.4    | 9.6   | <b>960.1</b> | Nd    | 76.8  | 168          | 154   | 280   | 200 | test | N/A |
| TOC (mg L <sup>-1</sup> )                        | 7.1     | 8.7   | 35.1         | 12.2  | 7     | <b>54.22</b> |       |       |     |      |     |
| chloride (mg L <sup>-1</sup> )                   | 0.3     | 20.5  | nd           | 100.1 | 9.6   | 10.06        | nt    | nt    |     |      |     |
| sulfate (mg L <sup>-1</sup> )                    | 51.18   | 25.51 | 21.42        | nd    | nd    | 85.9         | nd    | 14.8  |     |      |     |
| phosphate (mg L <sup>-1</sup> )                  | 0.03    | 0.01  | 1.07         | 0.09  | 0.01  | 0.01         | 0.14  |       | 10  |      |     |
| nitrate-N (mg L <sup>-1</sup> )                  | 2.09    | 10.6  | 3.98         | 0.71  | 1.51  | 1.62         | nt    | nt    | 30  |      |     |
| ammonium-N (mg L <sup>-1</sup> )                 | 10.6    | 8.9   | 31.9         | 12.9  | 7     | 5            | nt    | nt    |     |      |     |

<sup>a</sup> L1: Normes Environnementales et Procédures d'inspection des installations industrielles et commerciales au Cameroun. L2: Global Effluent guidelines. T: Tolerance limit. Sampling points: 1, river in Cité de Palmier, Douala; 2, stream in Monté Essec, Bepanda, Douala; 3, stream from Idokotti industrial centre, Douala; 4, stream in Bassa industrial zone, Douala; 5, river Wouri behind La Pasta, Douala; 6, river Wouri in industrial zone Bonabéri, Douala; 7, municipal lake (inlet from Cité), Yaounde; 8, river Mfoundi opposite Voirie centrale, Yaounde.

**Table 3. Results of Samples Only Exposed to the Discharge (Plasma Only, PO) [ $m = 0 \text{ mg L}^{-1}$ ]**

| parameter                              | exposure time $t^*$ (min) |       |       |       |       |       |       |
|--|---------------------------|-------|-------|-------|-------|-------|-------|
|  | 0                         | 5     | 10    | 15    | 20    | 25    | 30    |
| pH                                     | 6.4                       | 6.1   | 5.0   | 4.8   | 4.3   | 3.5   | 3.0   |
| TOC (mg L <sup>-1</sup> )              | 54.2                      | 38.3  | 28.9  | 19.6  | 15.6  | 14.0  | 12.0  |
| BOD <sub>5</sub> (mg L <sup>-1</sup> ) | 716                       | 350   | 98    | 46    | 25    | 15    | 16    |
| COD (mg L <sup>-1</sup> )              | 960.1                     | 912.3 | 882.4 | 782.4 | 729.6 | 512.2 | 456.3 |

**Figure 3. Individual value plot of pH with type of treatment (nontreated, NT, "0"; PO, "1"; and PA, "2").**

The general behavior (Figure 4) of BOD versus  $t^*$  (at given  $t^*$ ) plots for PA plasma treatments is that of smoothly decreasing (with slopes close to  $-1.9 \text{ min}^{-1}$ ) in the time range ( $30 > t^*, \text{ min} \geq 10$ ) with relevant BOD values roughly in the tiny range ( $200 > \text{BOD, mg L}^{-1} > 10$ ). The experimental values may obviously involve artifacts, and a limited accuracy results is discussed below. These lines intercept the PO versus  $t^*$  plot round 10 min, so that there is no significant difference between PO and PA treatments for long exposures. However, short treatments ( $t^*, \text{ min} \leq 10$ ) evidence a drastic BOD abatement larger than 500 units between NT and 5 min-treated samples. Because the BOD versus  $t^*$  evolution is assumed to be continuous, an exponential was preferred to a linear decay at the very beginning of the treatment. In other words, the PA treatment is more effective than PO for  $t^* < 10$  min, because the corresponding BOD abatements are much more important.

The results reported in Table 6 evidence some dispersion so that it is rather difficult to expect precise values but only trends. The dispersion may be related to sampling, to a lack of homogeneity in OS composition, to the relative and inherent lack of stability of the discharge, and to the fact that BOD<sub>5</sub> measurements require several days to be performed: changes in BOD of treated samples ( $t^* \neq 0$ ) might then be attributed to known postdischarge phenomena, which remain conjectural in the present case. Some figures had to be discarded as artifacts, and we only considered the overall effects given by the tendency of the pseudolinear part of the plots BOD versus  $t^*$  for PA treatments longer than 10 min.

The BOD values are also affected (Table 6) by the incorporated mass of OS, but the experimental results are hardly reproducible, which prevents one from deriving valuable conclusions on the influence of  $m$  upon BOD. One can however point out that the plots ln BOD versus  $m$  tend to lines with negative slopes (e.g., plots for  $t^* = 10$  and  $t^* = 20$  min).

**5.3. COD Measurements (Tables 3 and 7).** The carbon organic demand is another popular parameter for water quality control. The experimental results are gathered in Table 7 with the corresponding exposure time  $t^*$  and incorporated OS mass  $m$ . For comparison purpose, Table 3 gathers the relevant PO values.

The COD values generally decrease with increasing exposure time, taking into account the uncertainties above-discussed. This feature confirms that exposure to the plasma generates oxidizing species, which are able to degrade organic solutes, in agreement with previously observed plasma treatments of waste effluents.

The main observed effect of increasing  $m$  on COD (for given  $t^*$ ) is a noticeable abatement by at least  $400 \text{ mg L}^{-1}$ , which is observed for limited OS concentrations ( $m < 1$ ). For the larger considered concentrations (i.e.,  $1 < m < 2.5$ ), all of the COD data are gathered in a limited range of values ( $19 < \text{COD} < 99$ ), so that the relevant COD versus  $m$  plots approximately correspond to a plateau.

The discussion on COD results needs no further development, because we consider that they are only indicative in the case of discharges in air. The transient presence of nitrite in the solution leads to an enhanced COD value for a given treatment, because this species is oxidized to nitrate in the analytical process. The result actually depends on the time elapsed between sampling and analysis of  $\text{NO}_2^{-31}$  and cannot be unreservedly trusted.

**Table 4.** Effect of Exposure Time ( $t^*$ ) and Mass of Natural Oyster Shell ( $m$ ) on the pH of Samples, with Respect to Type of Treatment

| type of treatment | exposure time $t^*$ (min); $m = 0.1 \text{ g L}^{-1}$ |     |     |     |     |     | parameter |     |     |     |     |     |     |     |
|-------------------|---|-----|-----|-----|-----|-----|-----------|-----|-----|-----|-----|-----|-----|-----|
|                   | 0   | 5   | 10  | 15  | 20  | 25  | 30        | 0   | 0.1 | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 |
| NT                |   |     |     | 6.4 |     |     |           |     |     |     |     |     |     |     |
| PO                | 6.4   | 6.1 | 5.0 | 4.8 | 4.3 | 3.6 | 3.0       |     |     |     |     |     |     | 6.4 |
| PA                | 6.4   | 6.4 | 6.8 | 7.2 | 7.9 | 8.3 | 8.1       | 6.4 | 6.3 | 7.1 | 7.3 | 7.5 | 7.9 | 8.6 |

**Table 5.** TOC (mg C L<sup>-1</sup>) of Samples with Respect to Type of Treatment, Mass ( $m$ , g L<sup>-1</sup>) of Natural Oyster Shell, and Exposure Time  $t^*$  (min)

| $t^*$ min | mass OS (g L <sup>-1</sup> ) |      |      |      |      |      |      |
|-----------|------------------------------|------|------|------|------|------|------|
|           | 0 (PO)                       | 0.1  | 0.5  | 1    | 1.5  | 2    | 2.5  |
| 0         |                              |      | 54.2 |      |      |      |      |
| 5         | 38.3                         | 14.8 | 16.3 | 16.1 | 21.5 | 19.9 | 20.0 |
| 10        | 28.9                         | 14.4 | 15.6 | 15.6 | 20.0 | 20.2 | 19.7 |
| 15        | 19.6                         | 14.1 | 14.4 | 14.7 | 18.4 | 19.9 | 20.0 |
| 20        | 15.6                         | 13.5 | 14.3 | 14.0 | 17.4 | 16.6 | 19.6 |
| 25        | 14.0                         | 13.3 | 13.9 | 14.0 | 15.7 | 16.1 | 17.9 |
| 30        | 12.0                         | 13.2 | 14.1 | 13.6 | 15.6 | 13.5 | 16.7 |

**Table 6.** Variation of BOD<sub>5</sub> (mg L<sup>-1</sup>) with Exposure Time  $t^*$  (min) and Mass  $m$  (g L<sup>-1</sup>) of Oyster Shell

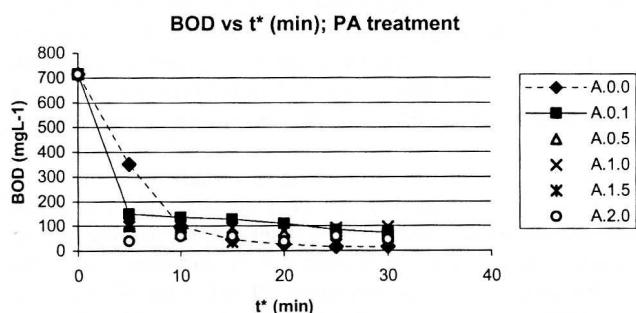
| $t^*$ (min) | mass $m$ of OS (g L <sup>-1</sup> ) |     |     |    |     |     |     |
|-------------|-------------------------------------|-----|-----|----|-----|-----|-----|
|             | 0 (PO)                              | 0.1 | 0.5 | 1  | 1.5 | 2.0 | 2.5 |
| 0           |                                     |     | 716 |    |     |     |     |
| 5           | 350                                 | 150 | 100 | 98 | 85  | 40  | 115 |
| 10          | 98                                  | 135 | 94  | 98 | 76  | 60  | 80  |
| 15          | 46                                  | 129 | 75  | 92 | 35  | 60  | 70  |
| 20          | 25                                  | 110 | 72  | 80 | 39  | 38  | 45  |
| 25          | 15                                  | 85  | 61  | 93 | 25  | 60  | 36  |
| 30          | 16                                  | 73  | 56  | 95 | 30  | 45  | 28  |

**Table 7.** Variation of COD (mg L<sup>-1</sup>) with Exposure Time  $t^*$  (min) and Mass  $m$  (mg L<sup>-1</sup>) of Incorporated Oyster Shell

| $t^*$ (min) | mass $m$ of incorporated shells (g L <sup>-1</sup> ) |     |     |    |     |     |     |
|-------------|--|-----|-----|----|-----|-----|-----|
|             | 0 (PO)   | 0.1 | 0.5 | 1  | 1.5 | 2.0 | 2.5 |
| 0           |  |     | 960 |    |     |     |     |
| 5           | 912  | 766 | 73  | 65 | 73  | 96  | 86  |
| 10          | 882  | 524 | 96  | 73 | 20  | 96  | 48  |
| 15          | 782  | 426 | 19  | 55 | 27  | 96  | 48  |
| 20          | 730  | 348 | 27  | 48 | 24  | 48  | 48  |
| 25          | 512  | 190 | 27  | 73 | 48  | 36  | 24  |
| 30          | 456  | 160 | 19  | 38 | 24  | 48  | 32  |

**5.4. TOC Measurements (Tables 3 and 5).** Total organic carbon measurement is probably the most reliable technique for controlling organic wastes abatement. The experimental data reported in Table 5 gather data affected by the exposure time  $t^*$  and the incorporated mass  $m$  of shells.

The general behavior of TOC is a decrease with increasing  $t^*$ , which corresponds to an abatement by 44 around 40 mg C

**Figure 4.** Biological oxygen demand evolution with exposure time to the discharge. The various plots are relevant to different  $m$  values.**Table 8.** Slopes  $\alpha_m$  and  $\beta_{t^*}$  of the Lines  $\text{TOC}(m, t^*) = \alpha_m \times t^* + \text{cst} = f(t^*)$  and  $\text{TOC}(m, t^*) = \beta_{t^*} \times m + \text{cst}' = f(m)$ 

| $m$           | 0.1   | 0.5   | 1.0   | 1.5   | 2.0   | 2.5   | 3.0 |
|---------------|-------|-------|-------|-------|-------|-------|-----|
| $\alpha_m$    | -0.07 | -0.12 | -0.13 | -0.21 | -0.24 | -0.26 | nd  |
| $t^*$         | 0     | 5     | 10    | 15    | 20    | 25    | 30  |
| $\beta_{t^*}$ | nd    | 2.7   | 3.1   | 3.2   | 3.2   | 3.4   | nd  |

L<sup>-1</sup> for 30 min exposure time for PO and PA processes. The plots TOC versus  $t^*$  (at given  $m$ ) for the PA process rapidly decrease by around 40 mg C L<sup>-1</sup> to a plateau less than 10 mg C L<sup>-1</sup> broad within the first 10 min of treatment, and they overlap. These plots also intercept PO versus  $t^*$  in the range 15 <  $t^*$ , min < 27, which means that the efficacy of the PO and PA processes does not significantly differ in this range of long exposure times. Statistical analysis also fails to underline differences between the PA treatments.

However, the plateau is reached in the PA process within 5–6 min of exposure, that is, much more rapidly for PA than for PO treatment, which requires 15 min. This feature has important consequences because it clearly shows that a short exposure time to the discharge, which lowers the energy consumption and thus the operating cost of the process, is largely in favor of the PA process as compared to the PO. Another main difference is related to the involved kinetic law: PO reasonably obeys a first-order kinetic law, while the logarithmic transform  $\ln(\text{TOC})$  versus  $t^*$  of TOC (at given  $m$ ) for PA OS treatments is not linear in the investigated time range 5 <  $t^*$  < 30. However, the TOC values linearly distribute with  $t^*$ , and this accounts for an overall zero-order kinetic law in the considered exposure range.

$$\frac{d(\text{TOC})}{dt^*} = -k(\text{TOC})^0 \text{ or } (\text{TOC}) = -kt^* + \text{cst}$$

The kinetic constant  $k$  is close to 0.12 mg C L<sup>-1</sup> min<sup>-1</sup> for the particular value  $m = 1 \text{ g L}^{-1}$  of added OS. We then have the linear relationship for given  $m$  values:

$$(\text{TOC})_m = \alpha_m \times t^* + \text{cst}$$

The other parameter that affects TOC is the mass  $m$  of incorporated shells.

The general trend is an increase in  $(\text{TOC})_{t^*}$  with  $m$  or, otherwise, a decrease in TOC abatement. This is probably due to the conditioning procedure of the shells that are not pyrolyzed and may fix algae or other small organic particles.

PO treatment is characterized by a single value (TOC = 54.2 for  $m = 0$  and  $t^* = 0$ ). The  $\text{TOC}_{t^*}$  values at discrete exposure times arrange along increasing lines as  $m$  increases:

$$(\text{TOC})_{t^*} = \beta_{t^*} \times m + \text{cst}'$$

The relevant slopes  $\alpha_m$  and  $\beta_{t^*}$  are gathered in Table 8 for given  $m$  and  $t^*$  values, respectively. The slope  $\alpha_m$  is the zero-order rate constant at a given  $m$  value. These results show that TOC abatement increases with increasing OS mass (for given  $t^*$ ), and this is consistent with the increasing catalytic surface.

**5.5. Synergism or Not Synergism?** The TOC results relevant to PO and PA clearly differ for short exposure times ( $t^* < 5-10$  min) with always PO > PA, while for longer treatments, the PO and PA effects are similar or even in favor of PO. With respect to the initial TOC value (54.2 mgc L<sup>-1</sup>), this means that the PO process abatement is less important than PA for the same exposure time. For example, the relevant TOC data for  $t^* = 5$  min exposure are: 54 (NT), 38 (PO) and 16 (PA, with  $m = 1$  g L<sup>-1</sup>), which means pollution abatements close to 30% and 70% for PO and PA, respectively. The discrepancy between these abatements is related to the mere addition of nonpyrolyzed OS in limited quantity because both solutions were exposed to the discharge for the same time, which thus implies the same running cost. Although no data are available on the TOC evolution of samples with incorporated OS only, we can reasonably guess that merely washed and powdered OS (at 1 g L<sup>-1</sup>) is unable to cause a TOC abatement by 40%: few percents might even be considered from an optimistic point of view. We are thus inclined to consider this feature as a serious argument in favor of a synergistic effect between OS and plasma treatment.

## 6. Conclusion

This study has shown that coupling nonthermal plasma treatment in humid air with cheap solid adsorbents and useless wastes, such as powdered oyster shells, largely improved the process for the removal of organic wastes in surface waters. The comparison between PA and PO treatments involving or not involving powdered shells was performed for the same exposure time, that is, for the same electrical expense, and was thus clearly in favor of the coupled process for short treatments (5–10 min). This feature and the low equipment cost are good arguments for further industrial application.

Modification of the usual key parameters accounting for water quality was definitely improved by the coupled treatment:

BOD<sub>5</sub> is stabilized by 86% within 5 min exposure to the discharge (Figure 4). This estimate involves the starting BOD value for NT (700) and the mean value for ( $m = 1$ ) PA-treated sample (100). BOD linearly decreases for increasing  $t^*$  in the range ( $5 < t^* < 30$ ) with a slope close to  $-1.9$  min<sup>-1</sup> and depends exponentially on  $m$ .

COD decreases as the exposure time  $t^*$  increases for given mass. It is also affected by the concentration in incorporated shell powder and tends to exponentially decrease as  $m$  increases for given  $t^*$ , at first approximation.

TOC abatement was close to 75% within 30 min PO treatment, while it required only 5–10 min in the presence of small quantities ( $m \leq 1$ ) of OS. For example, a 5 min PA treatment with  $m = 1$  g L<sup>-1</sup> allowed an abatement close to 70% of the initial TOC NT (54.2) and PA (16) values.

Few minutes of exposure to the discharge complemented pH evolution, which was raised close to neutrality. The TOC abatement follows a pseudo zero-order kinetic law with a constant close to 0.1 mgc L<sup>-1</sup> min<sup>-1</sup>, which linearly increases with the mass of incorporated shell powder in the exposure range 5–30 min.

The reported study was performed with a batch reactor. An estimate of its efficacy may be derived from the working parameters (e.g., 600 V and 0.16 A as main values in optimized operating conditions;  $t^* = 5$  min;  $m = 1$  g L<sup>-1</sup>; and a volume of liquid 400 mL). The PA treatment of 1 L of sample with  $m = 1$  g L<sup>-1</sup> OS requires an exposure time of  $2.5t^*$  or 750 s and an estimate energy of  $100*5*60*2.5 = 75$  kJ for an abatement close to 70%.

The reported study was performed with a batch reactor. Its device may easily be adapted to circulating systems, which should enable one to treat larger volumes of sample. The coupled process is efficient, cheap, and green because it uses limited quantities of oyster shells as solid bases to help fix and concentrate organic wastes of various origins.

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