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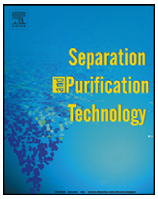

Gliding Arc Discharge (GAD) assisted catalytic degradation of bisphenol A in solution with ferrous ions

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ABSTRACT

The degradation of an endocrine disruptor (ED), the bisphenol A (BPA), was studied using Gliding Arc Discharge (GAD). This kind of discharge generates a non-thermal plasma at atmospheric pressure and quasi-ambient temperature. The resulting plasma is the source of several chemical reactions that lead to the hydroxyl radical formation. Hydroxyl radicals, $^\bullet OH$, are very powerful and non-selective oxidizing agents ($E^\circ_{^\bullet OH/H_2O}$ 2.8 V vs. normal hydrogen electrode) able to degrade compounds resistant to conventional treatment. GAD belongs to the group of advanced oxidation processes (AOPs).

Under different working gases such as air, argon, oxygen/argon mixture (20/80, v/v), a BPA aqueous solution (120 μM) was submitted to GAD. The evolution of BPA concentration was followed by high performance liquid chromatography (HPLC) method. The global oxidation of the organic matter was followed by chemical oxygen demand (COD) measurement. The mineralization was determined from the total organic carbon (TOC). The GAD treatment of the aqueous solution is accompanied by a massive production of hydrogen peroxide. The addition of Fe (II) to the reaction allows a better elimination of the organic matter through the production of additional $^\bullet OH$ radicals, issued from the decomposition of hydrogen peroxide according to Fenton reaction.

The optimized system – GAD with oxygen/argon (20/80) as working gas, in presence of Fe (II) – was very efficient for BPA treatment: the compound disappeared after 30 min, the abatement of the COD was total after 120 min and the TOC diminished by 70%.

1. Introduction

The glidarc procedure is based on the production of a non-thermal plasma generated by an electric arc [1]. Presented for the first time by Czernichowski and co-workers [2,3], it was used for industrial treatment of gases [4,5].

Further experiments showed that glidarc discharges could be adapted to solids, gases and liquids treatments [4,6–10].

This efficiency is due to the formation of reactive chemical species such as $^\bullet OH$, $^\bullet NO$, $HO_2{}^\bullet$, H_2O_2, O generated as follow:

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

$$O_2 + e^- \rightarrow O(^3P) + O(^1D) + e^- \quad (2)$$

$$N_2 + e^- \rightarrow N(^4S) + N(^2D) + e^- \quad (3)$$

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

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

$$HO_2{}^\bullet + HO_2{}^\bullet \rightarrow H_2O_2 + O_2 \quad (6)$$

$$HO_2{}^\bullet + NO^\bullet \rightarrow NO_2 + {}^\bullet OH \quad (7)$$

$${}^\bullet OH + {}^\bullet OH \rightarrow H_2O_2 \quad (8)$$

$$NO_2 + {}^\bullet HO \rightarrow H^+ + NO_3{}^- \quad (9)$$

$$NO^\bullet + {}^\bullet HO \rightarrow HNO_2 \quad (10)$$

$$HNO_2 + H_2O_2 \rightarrow HNO_3 + H_2O \quad (11)$$

An emission spectroscopy study carried out on glidarc humid air plasma [11] showed the simultaneous presence of $^\bullet OH$ and $^\bullet NO$ radicals respectively responsible for the oxidative power of this kind of plasma [8,12–14].

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Several works showed the potential of this technique for the elimination of pollutants from wastewaters:

(i) Degradation of various dyes, such as Orange II, yellow Supranol 4 GL, Red Nylosane F3 GL, NET, Orange I (azoic dye), green Malachite, Crystal Violet (triphenylmethane dye), Acid green 25 (anthraquinonic dye) [15–18].
(ii) Degradation of polymers rejected by industry [19].
(iii) Mineralization of the tributylphosphate, present in the nuclear industry rejects [7].
(iv) Degradation of phenol in solution [20].

The bisphenol A (BPA) is a monomer used in epoxy resins synthesis and in polycarbonates plastics production. Its plastic and optic properties, its thermal and electric resistance, made it widely used in industry. It is found in cans, medical equipment, plastic bottles, tapes and paints [21,22].

As several industrial compounds, the BPA is widely spread in the environment. It was detected at very high thresholds reaching 4.4×10^{-10} to $5.3 \times 10^{-8}\,\mathrm{mol\,L^{-1}}$ in surface waters [23] and 5.7×10^{-9} to $7.5 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$ in landfill leachates [24].

The bisphenol A was identified as endocrine disruptor (ED). It triggers biochemical problems in living beings because it is a substitute of natural estrogens [25–29]. It is implied in several endocrine disrupting effect such as fish feminization, low spermatogenesis, prostate and lung cancers [30,31].

Conventional wastewater treatments show some efficiency in BPA elimination, but the destruction is not total, and could produce secondary products far more dangerous than BPA itself [32].

In order to solve this problem, alternative treatments were developed: advanced oxidation processes (AOPs) known for their ability to oxidize and mineralize most of organic matter. These processes (heterogeneous photocatalysis on semiconductor surface; ozone photodecomposition; hydrogen peroxide photodecomposition; ozone/hydrogen peroxide association; Fe (II)/hydrogen peroxide association, etc.) rely on the production of highly reactive and non-selective hydroxyl radicals [33].

The efficiency of AOPs was tested on wastewaters contaminated by an endocrine disruptor compound such as BPA. The photocatalytic degradation of BPA was studied in TiO_2 aqueous suspension under irradiation. It led to the complete mineralization in 20 h [34]. The elimination of three EDs, the bisphenol A, the ethinyl estradiol and the estradiol was achieved by direct UV photolysis and UV/H_2O_2 process. The combined system is more efficient than UV alone for the three compounds [35].

Some authors mentioned the BPA treatment by Fenton procedure (Fe (II)/H_2O_2) association in which H_2O_2 is generated by electrochemistry with iron presence [36]. They showed that mineralization was complete for $[Fe^{2+}]/[BPA]$ ratio values between 3 and 4.

The photo-Fenton procedure (UV/Fe (II)/H_2O_2 association) is used also for BPA degradation; BPA conversion into CO_2 reached 90% in 36 h, whereas its disappearance was noticed after 9 min at optimal conditions [37].

The purpose of the present work is to evaluate the potential of using Gliding Arc Discharge (GAD) for the treatment of contaminated water by BPA. The study was done under different working gases (air, argon and oxygen/argon mixture), in absence and presence of Fe (II).

The GAD technique we are studying for BPA degradation has the following advantages:

(i) It does not need additional chemicals and can be seen as a clean technology, able to generate reactive species and to degrade resistant pollutants.
(ii) It generates $^{\bullet}OH$ radicals.
(iii) It leads to H_2O_2 formation and thus to additional $^{\bullet}OH$ radicals by Fe^{2+} addition.

2. Experimental

2.1. Materials and methods

Bisphenol A (Fig. 1), iron sulphate, potassium iodide, ammonium heptamolybdate, and sodium hydroxide were purchased from Aldrich. Silver sulphate, potassium dichromate and sulphuric acid came from Acros Organics society. The acetonitrile (HPLC gradient grade) was purchased from Fisher Scientific.

BPA solutions of 120 μM ($28\,\mathrm{mg\,L^{-1}}$) were prepared with acidified osmosis water at pH 3 with sulphuric acid. This acidification allows identical pH conditions for all gases at the beginning of the treatment.

The disappearance of BPA was followed by high performance liquid chromatography (HPLC). The apparatus used was made by Waters Associates 590 instrument, equipped with a C18-ABZ plus+ column (i.d. = 4.6 mm, length = 250 mm) and a UV detector (model 486). The mobile phase is a mixture of water/acetonitrile (50/50, v/v), the elution was done in isocratic mode ($1\,\mathrm{mL\,min^{-1}}$).

The COD was measured by the method based on the dichromate standard procedure [38].The total organic carbon (TOC) was determined by LABTOC analyzer calibrated from a potassium phthalate solution. The hydrogen peroxide quantities were determined by iodometry [39].

Nitrites formation during humid air plasma treatment was followed with a Shimadzu spectrophotometer UV-2101 PC.

2.2. Plasma-producing apparatus

The experimental apparatus of the glidarc plasma used is shown in Fig. 2. Compressed gas is led through a bubbling water flask to get water-saturated. The gas flow then passes between two semi-elliptic electrodes connected to a 220 V/10 kV high voltage Aupem Sefli transformer. It produces an alternative potential difference of 10 kV and a current intensity of 100–150 mA, thus it delivers a maximum power of 1.5 kW.

An electric arc forms between the two electrodes at minimal divergence. The arc is pushed away from the ignition point by the feeding gas flow and sweeps along the electrode gap to form a large plasma plume. The plasma plume is disposed close enough to the liquid target, so that it licks the liquid surface, and allows the chemical reactions to take place at the plasma–solution interface, thus generating highly reactive species.

A 300 mL solution is placed into the 2000 mL Pyrex reactor equipped with a cooling system to avoid evaporation. The treatment is done in closed system fixing the functioning parameters. The gas flow is fixed at $Q = 800$ L/h, the divergence between the electrodes $e = 3$ mm, the diameter of the nozzle $\Phi = 1$ mm and the distance between the electrodes and the target liquid surface $d = 2$ cm.

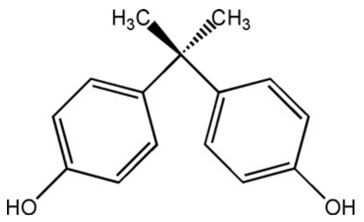


Fig. 1. Bisphenol A (2,2-bis(4-hydroxyphenyl)propane).

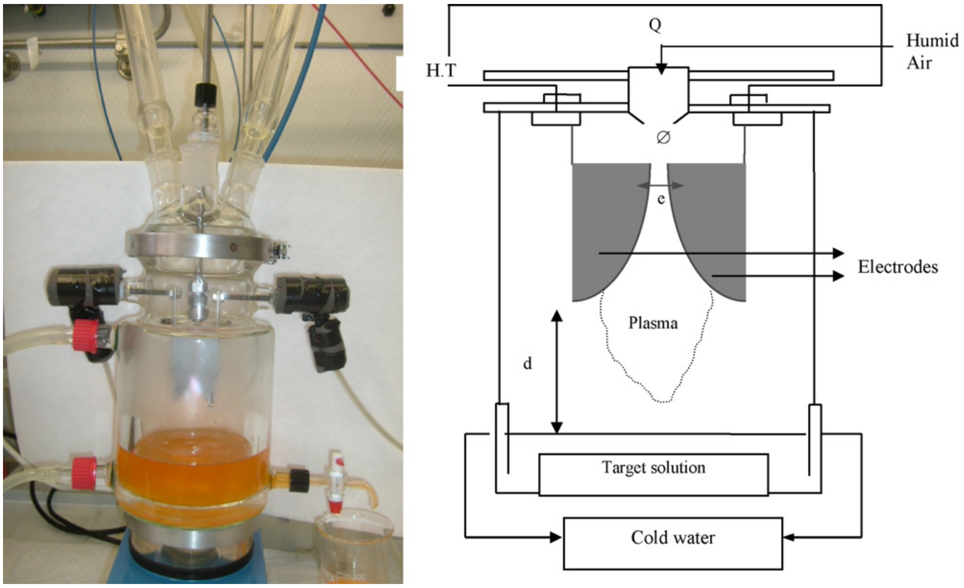


Fig. 2. Glidarc apparatus photo and drawing.

2.3. *Methodology*

A BPA aqueous solution with an initial concentration equal to 120 µM, was submitted to electric discharge under different plasma-producing gases: air, argon, and oxygen/argon mixture (20/80, v/v).

Acidified samples of the BPA solution were taken from the reactor at regular time intervals. The disappearance of BPA under treatment was followed by HPLC and the quantity of hydrogen peroxide formed was estimated by iodometry. The oxidation extend and the mineralization were respectively determined by the COD and the TOC measurements.

3. Results and discussion

3.1. *The evolution of the hydrogen peroxide concentration generated in solution by GAD*

3.1.1. *In an deionised water*

Fig. 3 shows the evolution of hydrogen peroxide generated during water treatment in absence of pollutant. This production of H_2O_2 results principally from the $^{\bullet}OH$ radicals combination generated by the discharge. The quantity of H_2O_2 produced is linked to the nature of the gas used. Indeed, the reactivity of each gas depends on its thermodynamical parameters such as ionisation U_i and excitation U_e tension values which are different from a gas to another [40].

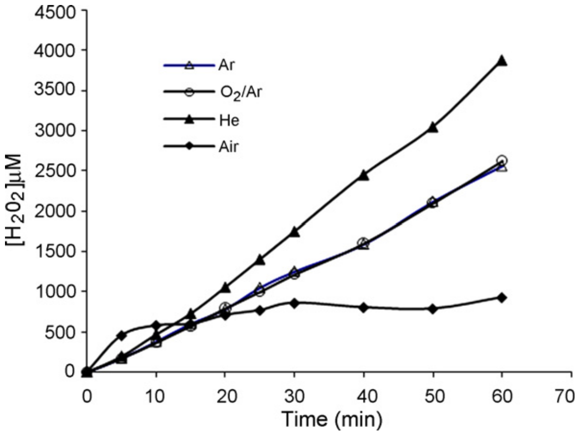


Fig. 3. Effect of working gases on the H_2O_2 formation in deionised water.

Fig. 3 shows that the use of helium allowed the production of 3880 µM H_2O_2. Pure argon and argon–oxygen mixture respectively gave 2620 and 2562 µM. However, air produced only 933 µM.

We notice in Fig. 3 that hydrogen peroxide formation is continuous and increasing for the first three gases. However, with air we rapidly obtain (15 min) a plateau for H_2O_2 concentration. This behaviour can be explained by the $^{\bullet}OH$ radicals and hydrogen peroxide consumption through nitrogen species oxidation (Eqs. (9)–(11)).

3.1.2. *In a 120 µM BPA solution*

The 120 µM BPA solution treatment with different gases (air, argon, oxygen/argon mixture) shows an identical H_2O_2 evolution to the one obtained with deionised water (Fig. 4a–c).

H_2O_2 formation is essentially due to $^{\bullet}OH$ radicals combination (Eq. (8)). However, there is another H_2O_2 formation pathway, which happens during organic compounds degradation [41].

Burlica and Yan's work showed that oxygen plasma generates high quantities of H_2O_2. But these quantities are tiny in the case of air plasma [9,10,19].

Burlica's work on organic dye elimination by glidarc discharges showed that the technique performance did not deeply vary with air, oxygen or nitrogen used as plasma-producing gases. However, argon gave bad results [9,10].

For economical reasons, we studied BPA degradation with air and argon–oxygen mixture (80/20, v/v) only. This gas combination allowed us to work in near air conditions while avoiding nitrites formation that could interfere with spectrophotometeric analysis and COD measurements.

3.2. *Study of BPA elimination by $GAD_{humid\ air}$*

3.2.1. *Study of BPA disappearance by HPLC*

The use of humid air as working gas (in absence of iron) allowed us to eliminate totally BPA in 30 min. Fig. 5 shows the disappearance of BPA and the increasing formation of H_2O_2 during the treatment

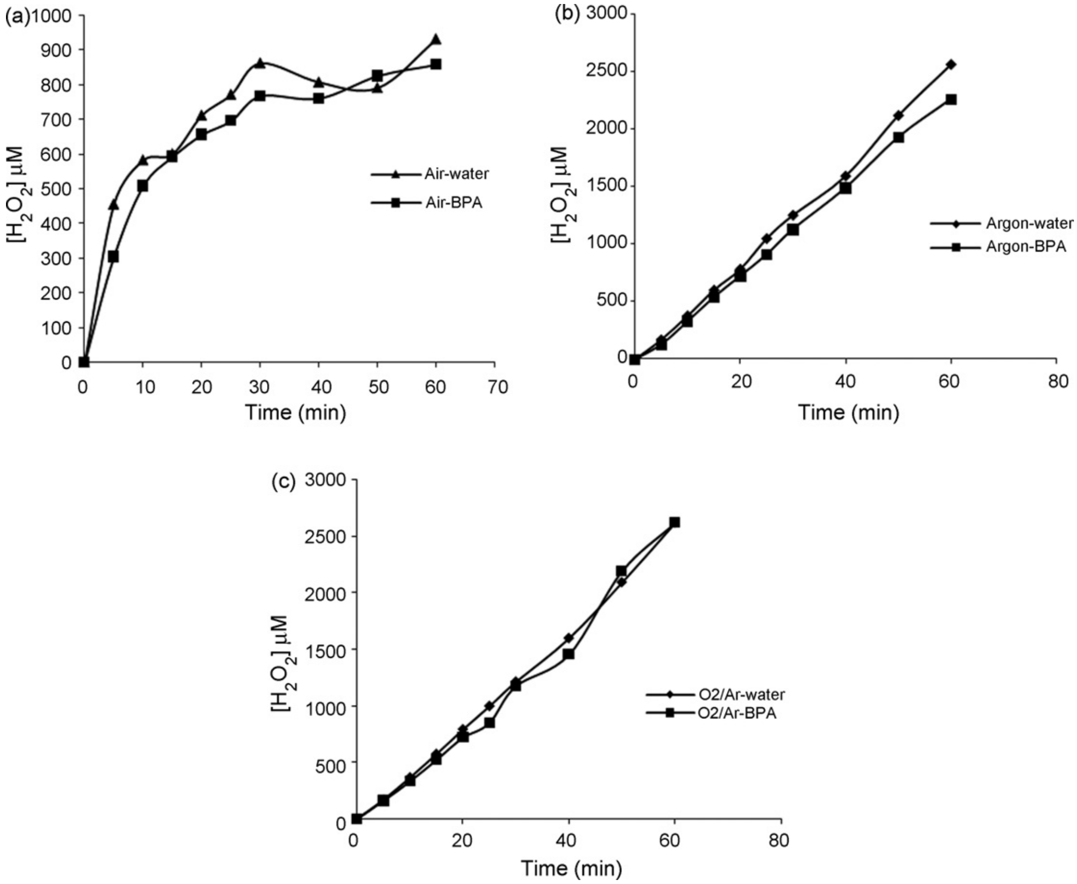


Fig. 4. H_2O_2 evolution in BPA solution and osmosis water with the different gases used. (a) Air treatment, (b) argon treatment and (c) oxygen–argon mixture treatment.

up to a plateau at 30 min explained by the reaction of hydrogen peroxide with nitrites generated by $GAD_{humid\ air}$.

UV/vis spectra (Fig. 6) show the presence of nitrites. Their imprints are in the wavelength domain of 320–400 nm. The absorption band at 275 nm corresponds to bisphenol A and to the products formed during the treatment.

We notice that absorbance corresponding to nitrites increases in function of treatment time up to 30 min and then decreases because of their oxidation into nitrates. This phenomenon was already observed during the treatment by humid air plasma of water only without BPA [14].

On the other hand, nitrites react with BPA to give nitro and dinitrobisphenol. These two compounds were detected by HPLC (Chromatogram 2) and identified by BPA solution (pH 3) injection under stirring during 1 h in presence of well defined nitrite quantities. This protocol was used by Masuda et al. during the study of oestrogen and mutagen activities of bisphenol A under nitrites treatment [42]. The compounds obtained were identified as 3-nitrobisphenol A and 3,3′-dinitrobisphenol A.

A similar work on phenol degradation by $GAD_{humid\ air}$ [20] gave some analogous results. The authors noticed the bad effect

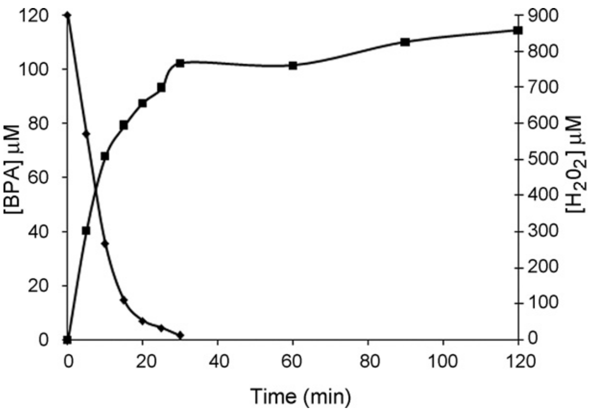


Fig. 5. Disappearance of BPA by $GAD_{humid\ air}$ treatment and H_2O_2 evolution.

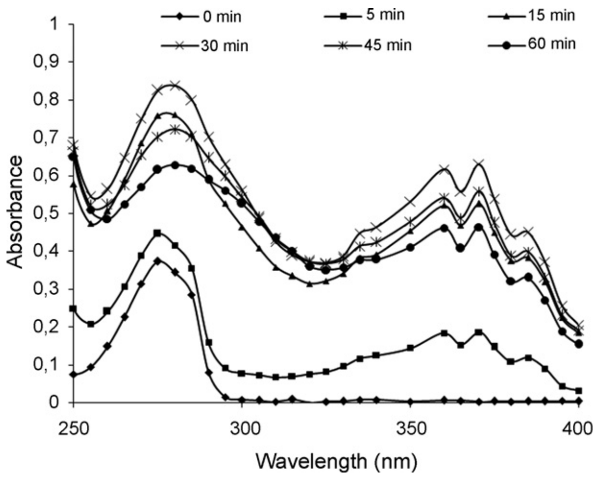
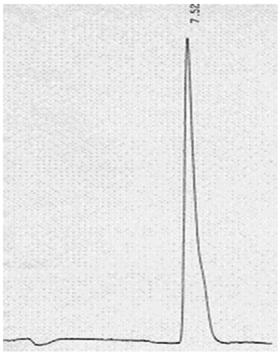


Fig. 6. Nitrites accumulation in BPA solution treated by $GAD_{humid\ air}$.



Chromatogram 1. HPLC of BPA alone.

of nitrites responsible of *p*-nitrosophenol ($C_6H_5NO_2$) and *p*-nitrophenol ($C_6H_5NO_3$) formation.

The formation of nitrous and nitric acids (Eqs. (10) and (11)) gives acid properties to humid air plasma. This was proved by the study of pH evolution during the treatment of natural BPA solutions. In these experiments the initial pH of 6.8 decreases to 1.4 and 3.9 respectively for 60 min of $GAD_{\text{humid air}}$ and $GAD_{\text{oxygen–argon}}$ treatment. In the case of oxygen/argon mixture, the decrease of pH is due to H_3O^+ formed from reactions (12) and (13).

$$H_2O + e \rightarrow H_2O^+ + 2e \qquad (12)$$

$$H_2O^+ \rightarrow {}^\bullet OH + H_3O^+ \qquad (13)$$

Reaction (12) could happen in gas or liquid phase and is rapidly followed by H_3O^+ and hydroxyl radicals formation [10]. However, we acidified all the treated solutions at pH 3 in order to operate in identical initial conditions of treatment.

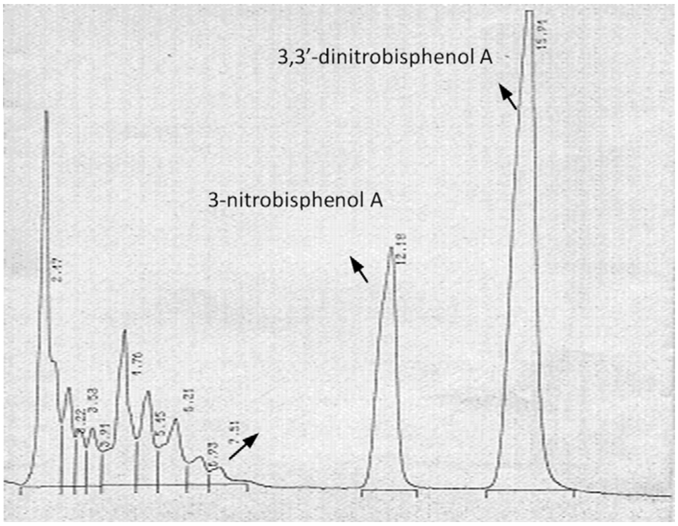
3.2.2. Degradation and mineralization of BPA by $GAD_{\text{humid air}}$

In order to establish the degree of BPA oxidation and mineralization, we followed the COD and TOC evolution in function of time. The complete oxidation reaction of BPA by oxygen is given by Eq. (14):

$$C_{15}H_{16}O_2 + 18O_2 \rightarrow 15CO_2 + 8H_2O \qquad (14)$$

The use of air gives a COD and TOC decrease of 47 and 70%, respectively. The residual COD obtained is important because of the nitrites reaction with the dichromate used in the COD determination according to reaction (15):

$$3NO_2^- + Cr_2O_7^{2-} + 8H^+ \rightarrow 3NO_3^- + 2Cr^{3+} + 4H_2O \qquad (15)$$



Chromatogram 2. Compounds obtained by $GAD_{\text{humid air}}$ treatment after 15 min.

3.3. Study of BPA elimination by $GAD_{\text{humid air/Fe (II)}}$

3.3.1. Study of BPA disappearance

In all cases, the electric discharge in humid air allows an accumulation of hydrogen peroxide in the solution. The hydrogen peroxide is used in several AOPs: H_2O_2 photodecomposition, O_3/H_2O_2 (peroxone) combination, Fenton system. Always, H_2O_2 decomposition leads to hydroxyl radicals formation. It is interesting to study the glidarc effect with H_2O_2 decomposition initiating ${}^\bullet OH$ formation. In this study, we chose a GAD/Fenton system combination.

The Fenton method is part of AOPs. The classic mechanism proposed by Fenton is based on the ${}^\bullet OH$ radicals formation [43,44], but it is not excluded that FeO^{2+} plays a role in the Fenton process [45]; the Fenton reaction is still discussed in literature [46]. The Fenton or Fenton-like processes are suitable for phenol degradation and non-biodegradable industrial products treatment in order to prepare them for secondary biological treatments [47,48].

Fenton system uses iron ions and hydrogen peroxide, whose reaction produces hydroxyl radicals (Eq. (10)), a powerful oxidizer efficient for organic pollutants degradation. If ${}^\bullet OH$ radical is the key factor, the initiation step would be:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + {}^\bullet OH \qquad (16)$$

Afterwards, the ${}^\bullet OH$ radicals could oxidize another Fe^{2+} in Fe^{3+} (termination step: Eq. (17)) or oxidize other species present in the solution (Eq. (18)) such as organic pollutants (RH):

$$Fe^{2+} + {}^\bullet OH \rightarrow Fe^{3+} + OH^- \qquad (17)$$

$$RH(\text{organics}) + {}^\bullet OH \rightarrow H_2O + R^\bullet \rightarrow \text{products} \qquad (18)$$

The hydroxyl radicals could react with H_2O_2 (propagation step) to give hydroperoxyl radicals (Eq. (19)) or react between them to form H_2O_2 (Eq. (8)):

$$H_2O_2 + {}^\bullet OH \rightarrow H_2O + OOH^\bullet \qquad (19)$$

$${}^\bullet OH + {}^\bullet OH \rightarrow H_2O_2 \qquad (8)$$

The iron (III) ions produced by Eq. (16) react with $HOO^\bullet$ to regenerate a part of ferrous ions (Eq. (20)).

$$Fe^{3+} + OOH^\bullet \rightarrow Fe^{2+} + H^+ + O_2 \qquad (20)$$

The BPA was treated in presence of ferrous ions at respective concentrations of 10^{-4} and 10^{-3} M.

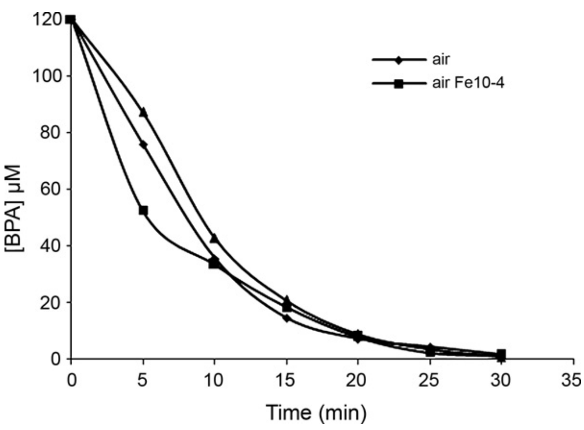


Fig. 7. BPA elimination by $GAD_{\text{humid air}}$ with or without iron addition.

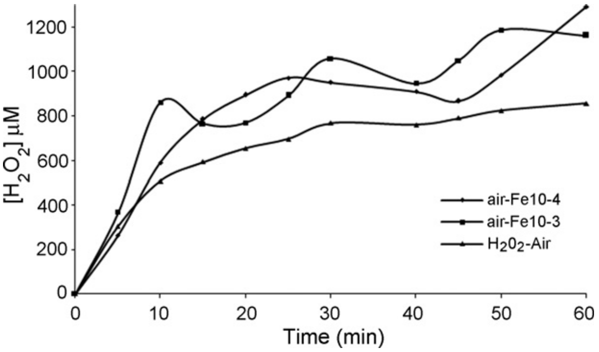


Fig. 8. H_2O_2 evolution during $GAD_{\text{humid air}}$ of BPA, with or without iron.

In the case of humid air, the disappearance of BPA with or without iron is practically identical as shown in Fig. 7. This indicates that the $GAD_{\text{humid air/Fenton}}$ treatment does not improve BPA elimination.

It is probable that catalytic activity of Fe^{2+} ions is negligible in a humid air plasma treatment because of their eventual oxidation by nitrites ions. The latter hinder them from reacting with hydrogen peroxide. This fact is verified in Fig. 8, where it is possible to see that the presence of Fe^{2+} does not reduce the quantity of accumulated hydrogen peroxide. On the contrary, the H_2O_2 accumulated is slightly superior in presence of Fe^{2+}.

3.3.2. *BPA degradation and mineralization*

The treatment produces a COD decrease by 33% and a TOC diminution by 74%. The mineralization is very important. However, the oxidation is relatively weak (Fig. 9). This could be explained by the presence of Fe^{2+} and $NO_2{}^-$ reductor ions. The latter compete with oxidizible organic substances towards dichromate, during COD determination.

In order to avoid interference problems (nitrites/BPA and nitrites/Fe^{2+}ions) and nitrogen products formation during air use, we retained argon/oxygen mixture for BPA treatment. This mixture is close to air by its oxygen content and allows us to avoid interferences caused by nitrites.

3.4. *Study of BPA elimination by $GAD_{\text{oxygen/argon}}$ and $GAD_{\text{oxygen/argon/Fenton}}$*

3.4.1. *Hydrogen peroxide evolution*

We compared H_2O_2 evolution in a BPA solution respectively treated by $GAD_{\text{oxygen/argon}}$ and $GAD_{\text{oxygen/argon/Fenton}}$.

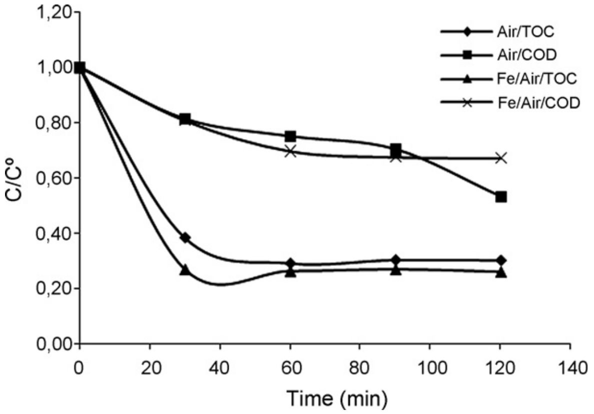


Fig. 9. COD and TOC evolution of BPA solution under GAD with and without iron (10^{-3} M).

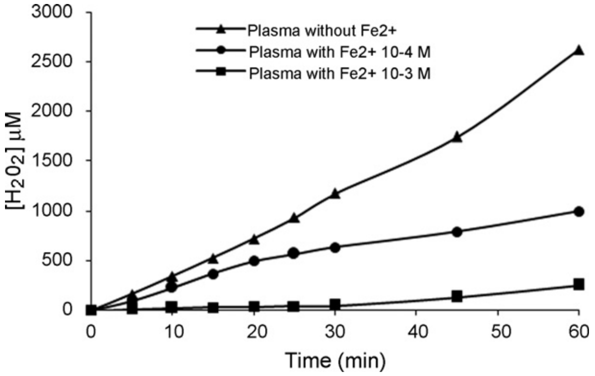


Fig. 10. H_2O_2 evolution during BPA treatment by $GAD_{\text{oxygen/argon}}$ with and without iron.

Fig. 10 shows H_2O_2 accumulation as a function of treatment time. For $GAD_{\text{oxygen/argon}}$ we obtained a continuous evolution until a concentration of 2620 μM after 1 h. In presence of Fe^{2+} at 10^{-4} M, the H_2O_2 accumulation diminished for more than half since it reached 1000 μM for the same treatment time. At 10^{-3} M of Fe^{2+}, H_2O_2 is not accumulated in a significative way. Its concentration is only appreciable after 30 min and, it reached no more than 250 μM after 1 h of treatment.

We noticed that the more the ferrous ions concentration increases, the less the hydrogen peroxide is accumulated. This behaviour is due to the H_2O_2 consumption by Fe^{2+} to form $^{\bullet}OH$ hydroxyl radicals (Eq. (16)).

3.4.2. *Study of BPA disappearance*

Fig. 11 shows BPA disappearance followed by HPLC with detection at 254 nm (Chromatogram 1).

The BPA concentration is reduced to half after 1 h treatment by $GAD_{\text{oxygen/argon}}$. In presence of iron, the same result is obtained in 15 min treatment and the total disappearance is reached after 30 min.

We notice that for both ferrous ions concentrations 10^{-3} and 10^{-4} M, the BPA disappearance rates are similar.

The BPA elimination efficiency and H_2O_2 evolution are well understood by comparison of treatments with and without iron (II) (10^{-3} M). Fig. 12 shows BPA treatment by $GAD_{\text{oxygen/argon/Fenton}}$ and $GAD_{\text{oxygen/argon}}$.

The treatment by $GAD_{\text{oxygen/argon}}$ triggers the BPA concentration diminution from 120 to 54, 5 μM (54.6%) in 60 min, whereas the hydrogen peroxide formation reaches 2623 μM (Fig. 12a).

The treatment of the same solution by $GAD_{\text{oxygen/argon/Fenton}}$ leads to the total disappearance of BPA in 30 min treatment and a

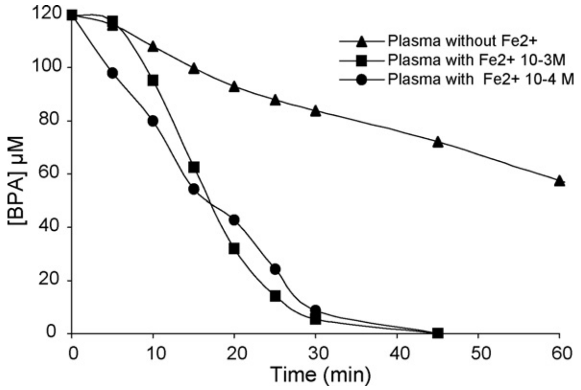


Fig. 11. BPA disappearance by $GAD_{\text{oxygen/argon}}$ with and without iron.

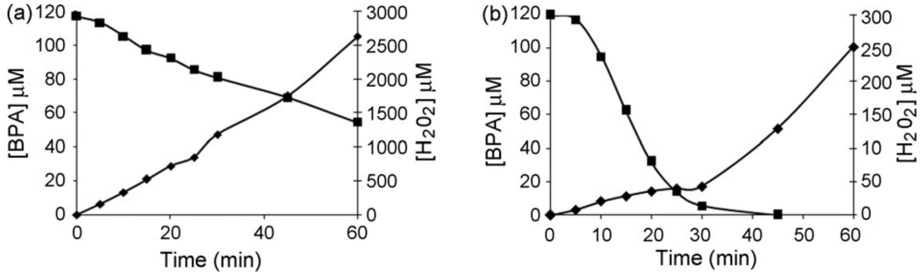


Fig. 12. BPA disappearance and H_2O_2 evolution. (a) $GAD_{oxygen/argon}$ and (b) $GAD_{oxygen/argon/Fenton}$.

production of only 252 µM of hydrogen peroxide after 1 h treatment (Fig. 12b).

We conclude from this comparative study that $GAD_{oxygen/argon/Fenton}$ is more efficient. Indeed during BPA elimination by $GAD_{oxygen/argon}$, we notice a higher H_2O_2 accumulation, identical to its evolution in deionised water treatment and a lower BPA diminution (Fig. 12a). However, in $GAD_{oxygen/argon/Fenton}$ treatment, the H_2O_2 concentration is quasi non-existing at the beginning of the treatment and remains 10 times weaker compared to $GAD_{oxygen/argon}$, thus confirming its reactivity with ferrous ions to form $^{\bullet}OH$ radicals. In this treatment, we notice a fast BPA diminution (Fig. 12b) up to a total disappearance (30 min). After this time, we notice an increase in H_2O_2 accumulation rate.

The treatment improvement by $GAD_{oxygen/argon/Fenton}$ is due to the catalytic effect of ferrous ions that generated additional $^{\bullet}OH$ radicals in comparison to those produced by GAD.

3.4.3. BPA degradation and mineralization

Fig. 13 shows COD and TOC evolution in function of treatment time by $GAD_{oxygen/argon}$ and $GAD_{oxygen/argon/Fenton}$.

An abatement of 38% for the COD and 34% for the TOC were obtained in 120 min of $GAD_{oxygen/argon}$ treatment, whereas $GAD_{oxygen/argon/Fenton}$ treatment gave better results reaching 100 and 70%, respectively.

The catalytic effect of ferrous ions in a solution treated by glidarc discharge generates reactive species besides additional $^{\bullet}OH$ due to H_2O_2 decomposition, thus accelerating bisphenol A and newly formed products degradation. As mentioned about phenol degradation in presence of iron [20], possible reactions between iron and bisphenol A and between iron and degradation by products catalyze the treatment. It could be as follows:

(i) Phenoxyl radical formation by Fe^{3+} action on bisphenol A.
(ii) Fe^{3+} reduction by hydroxybenzene and quinone-intermediate.
(iii) Photolysis of Fe^{3+}organic complexes—ligands (organic acids).

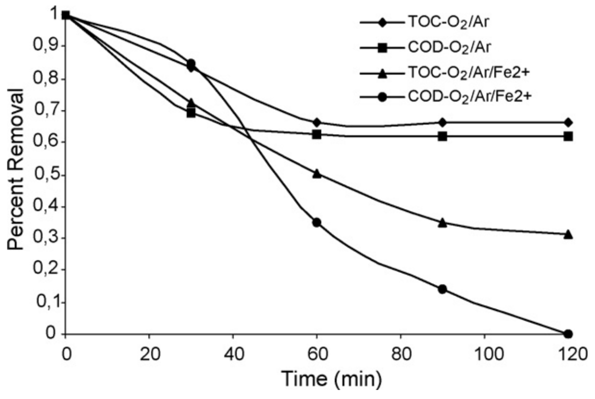


Fig. 13. TOC and COD evolution of BPA treated by $GAD_{oxygen/argon}$ with and without iron (10^{-3} M).

4. Energy consumption

One of the drawbacks of GAD treatment is the energetic consumption. In order to evaluate it, a counter was placed on the plasma-producing apparatus; the energy consumed was a linear function of time treatment and was estimated to 0.8 kW h for 120 min treatment.

5. Conclusion

The formation of reactive chemical species such as $^{\bullet}OH$, $^{\bullet}NO$, $HO_2^{\bullet}$, H_2O_2 from plasma at atmospheric pressure and ambient temperature gives to glidarc oxidizing properties as demonstrated in this study. Moreover, aromatic molecules with multiple —C=C— bonds are very sensitive to this kind of oxidation.

In the oxygen/argon plasma without iron, a high proportion of hydroxyl radicals recombine to give hydrogen peroxide, whereas in oxygen/argon plasma with iron, H_2O_2 formation generates additional $^{\bullet}OH$ radicals besides those obtained by the plasma, leading to an efficient and complete pollutant degradation.

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