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Synergistic Coupling Between Electrochemical and Ultrasound Treatments for Organic Pollutant Degradation as a Function of the Electrode Material (IrO_2 and BDD) and the Ultrasonic frequency (20 and 800 kHz)

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Solutions of the organic pollutant model, Crystal Violet (CV), were subjected to ultrasonic, electrochemical treatment and its combination. Ultrasound was tested at two frequencies (20 kHz or 800 kHz) and 80 W in deionized water. After 120 min, 20 kHz conducted to 6% CV degradation, while 50% elimination was observed at 800 kHz. No mineralization of the organic matter was detected in either case. Electrochemistry, using sulfate (0.35 mol L^{-1}) with IrO_2 or Boron Doped Diamond (BDD) electrodes at 20 mA cm^{-2}, was also evaluated. After 45 min the IrO_2 and the BDD electrodes conducted to 8% and 95% degradation of the initial substrate; while 15% and 43% mineralization, respectively, was removed after 120 min. The impact of anions was as follows: 3 mM bicarbonate enhanced 800 kHz ultrasonic yields, presence of chloride and sulfate benefit electro-oxidation with IrO_2 and BDD electrodes respectively. CV oxidation at an electrode surface can be synergistically improved by ultrasound action at 20 kHz and 800 kHz. In the best combination tested (BDD electrode and 800 kHz ultrasonic wave), CV was removed in 45 min, while 80% of the initial organic carbon was eliminate using BDD electrode and 800 kHz ultrasonic wave.

Keywords: Sonolysis; Electrolysis; Sonoelectrolysis; Crystal violet dye

1. INTRODUCTION

There is a growing risk of environmental hazards associated with dye effluents. Dyes can be harmful compounds, which can produce dangerous by-products through oxidation, hydrolysis, or other chemical reactions taking place in the waste phase [1]. Triarylmethane dyes containing polar chromophores, such as crystal violet (CV), are an important group of compounds that have traditionally been used in various chemical and industrial applications [2]. CV is normally present in a chromatic form, but it can be easily reduced to leuco (i.e., colorless) form. In a number of species, including human beings, it has been shown that intestinal microflora systems are capable of converting CV into the leuco form [3]. Other studies have also recently shown that CV is linked to an increased risk of cancer [4].

Traditional methods for dealing with dye wastewater consist of biological, chemical and physical methods [5-7]. The non-biodegradable nature of CV [8], its stability when exposed to light [9] and its known toxicity towards microorganisms [10] makes biological treatment ineffective for decolorization and degradation. Physical treatments are not the best option, since they only transfer dyes from water to another phase, thus causing secondary pollution. Consequently, regeneration of the adsorbent and/or post-treatment of solid-wastes, which are expensive operations, are needed [11].

Advanced oxidation processes (AOPs) are physico-chemical methods based on the generation and use of a powerful oxidant, the •OH radical, which is able to completely degrade a wide variety of organic pollutants [11, 12]. Dye effluents are characterised by the presence of inorganic ions which can scavenge •OH radicals in most AOPs. Electrochemical and sonochemical systems seem to be the most suitable AOPs to deal with organic pollutant degradation in water containing inorganic ions [13-15].

The sonochemical degradation of organic compounds in waters is based on the acoustic cavitation, in which •OH and HO_2• radicals are generated from the dissociation of water and oxygen (Eq. 1-4) [16, 17].

$$H_2O +))) \rightarrow \bullet H + \bullet OH \quad (1)$$
$$O_2 +))) \rightarrow 2\ \bullet O \quad (2)$$
$$H_2O + \bullet O \rightarrow 2\ \bullet OH \quad (3)$$
$$O_2 + \bullet H \rightarrow HO_2\bullet \quad (4)$$

Even if ultrasonic treatment is effective at the elimination of organic pollutants, the complete mineralization of organic compounds is hardly achieved [18, 19]. On the other hand, physical effects, such as an increase in mass transport and solid surface cleaning, etc., have also been reported during sonication. The impact of chemical and physical ultrasonic effects is strongly related to the ultrasonic frequency. Relatively low (below 100 kHz) and high (higher than 100 kHz) ultrasonic frequencies favour physical and chemical effects, respectively.

The electrochemical oxidation of pollutants can be carried out using active or non-active anodes. At active electrodes, a surface redox couple can act as a mediator in the oxidation of organic compounds. At non-active electrodes, weakly adsorbed hydroxyl radicals formed by water discharge are involved in the electrochemical oxidation of organic substrates [20]. Even if the degradation of organic substrates via electrochemical oxidation is proven, limitations in mass transfer and passivation of the electrode surface can reduce the efficiency of the technology [21].

The combination of ultrasound and electrochemical systems could be an interesting option to overcome the weaknesses of the individual technologies [22, 23]. Power ultrasound can enhance the mass transport of reactants to the electrode surface [24], increase the efficiency of electrochemical processes, and keep the electrode clean and activated [24, 25]. The ultrasonic frequency and the anode material could play an important role in this combination. Therefore, this work has been carried out to study the influence of the ultrasonic frequency (20 and 800 kHz) and the anode material (IrO_2 and BDD) on CV degradation under sonolysis, electrochemical and sonoelectrochemical processes. The influence of the usual inorganic ions in solution (Na_2SO_4, NaCl, $NaHCO_3$) on the efficiency of the individual systems was also evaluated.

2. MATERIAL AND METHODS

2.1. Reagents

The CV ($C_{25}N_3H_{30}Cl$, Basic Violet 3, CI 42555, also known as gentian violet or hexamethylpararosaniline chloride) was purchased from Aldrich and was used as received. Sodium chloride, sodium sulphate and sodium carbonate were all from Merck. Phosphoric acid and potassium hydrogen phthalate were obtained from Prolabo (VWR International). Potassium iodide and ammonium heptamolybdate were supplied by Sigma Aldrich and Carlo Erba, respectively. Deionized water was used throughout the preparation of the aqueous solutions.

2.2. Ultrasonic, electrochemical and sonoeletrochemical devices

All the experiments were carried out in a cylindrical glass vessel with a jacketed water cooler to maintain a constant temperature (19 ± 1 °C).

Ultrasonic experiments were carried out at two frequencies (20 and 800 kHz) and 80 W of electrical power input. The 20 kHz ultrasound was produced by a horn ultrasonic processor. The ultrasound was introduced directly into the sample solution through an immersible horn that emits the sound of vibration into the solution. The sound was produced via a titanium alloy rod (2.0 cm in diameter), which was dipped in the liquid at the top of the tank. For high frequencies (800 kHz), sonication was achieved through a flat piezoelectric disc (diameter 4.0 cm) mounted at the bottom of a reactor vessel holding the solution.

Electrochemical oxidation was carried out using a BDD or IrO_2 electrode as the anode with an area of 6.25 cm^2. The IrO_2 anode was prepared by the thermal decomposition of H_2IrCl_6 (99.9% ABCR) precursor at 500 °C in air. The BDD electrode was provided by Metakem^{TM}. Both anodes were supported on Ti. A titanium foil with the same area was used as the cathode and the inter-electrode gap was 1 cm. The current density was controlled at 20 mA cm^{-2} (~4.5 V). Prior the experiments the electrodes were activated by electrolysis of a sodium sulphate solution 0.05 M during 15 min under galvanostatic conditions (20 mA cm^{-2})

Sonoelectrochemical degradation was carried out by an ultrasound horn immersed in solution or a flat piezoelectric disc mounted at the bottom of the vessel at frequencies of 20 or 800 kHz respectively (as described above). The other conditions were the same as those in the ultrasound and electrochemical processes.

All experiments were carried out at natural pH (~5.5). During the electrochemical and sonoelectrochemical tests 350 mM (or 3 mM for some special cases) of the supporting electrolytes (sodium sulphate, sodium chloride or sodium bicarbonate) were used.

In each run, the volume of the CV solution tested for the ultrasound, electrochemical and sonoelectrochemical treatments was 250 mL (20 mg L^{-1} of CV or 10 mg L^{-1} of total organic carbon). Samples were withdrawn for analysis at different time intervals.

2.3. Analysis

Correspondence between the extent of CV removal as measured by spectrophotometry and HPLC techniques was evaluated. No significant differences in CV evolution were observed. Thus, due to economical and environmental reasons and the rapidness of measuring, quantitative analysis of CV was done by UV visible in a spectrophotometer (Shimadzu UV-1601) set a 590 nm. Total organic carbon (TOC) was assessed in a Shimadzu TOC-5050A analyzer with an auto-sampler and a solution of potassium phthalate as the calibration standard. The oxidants generated and accumulated in the system were evaluated during the degradation process utilizing the spectrophotometric method with KI (0.1 mol L^{-1}) and ammonium heptamolybdate salt as the catalyst (0.01 mol L^{-1}) [26].

3. RESULTS AND DISCUSSION

3.1. Sonochemical degradation of CV at 20 and 800 kHz

Frequency has been found to be an important parameter in sonochemical treatment of organic pollutants [27, 28]. Fig. 1 shows the effect of two different ultrasonic frequencies, 20 and 800 kHz, on the degradation of the cationic dye CV (20 mg L^{-1}). At 20 kHz, CV was poorly removed (after 120 minutes only 6% was eliminated), whereas at 800 kHz, 50% of the initial substrate was removed. In order to explain the difference between these results it is necessary to understand the effect of ultrasonic frequency on the sonolytic process. The larger number of oscillations at a high ultrasonic frequency favours chemical mechanisms involving •OH radicals, whereas a low frequency is more efficient for mechanical effects such as the generation of shock waves [29].

The CV structure has a positively charged nitrogen making it a hydrophilic substance. Its hydrophilic character makes the CV degrade in the bulk of the solution through reactions with •OH radicals. •OH radicals that do not encounter the target molecule recombine to produce hydrogen peroxide, which, due to its low oxidation power, is accumulated in the solution.

Thus, the strong differences in chemical effects, at high and low ultrasonic frequencies, can also be observed with H_2O_2 formation and accumulation. Contrary to what is observed at a low frequency (20 kHz), when the ultrasonic frequency is 800 kHz concomitant H_2O_2 production is evident.

Fig. 1 also shows that, with both of the tested frequencies, TOC elimination is practically insignificant. The high recalcitrance of CV by-products, even when a high ultrasonic frequency is used, indicates they have low volatility and high hydrophilic character. Because of low volatility, they cannot be incinerated into the cavitation bubbles; while the high hydrophilic characteristic means that these compounds remain in the bulk solution, far from the bubbles, and then most OH radicals, which have a very short lifetime, recombine to H_2O_2 before reaching them [30]. Thus, as reported previously for other pollutants [18, 19, 30] even if the ultrasound is able to eliminate the organic compound, a complete transformation of CV into CO_2, water and inorganic ions is not achieved.

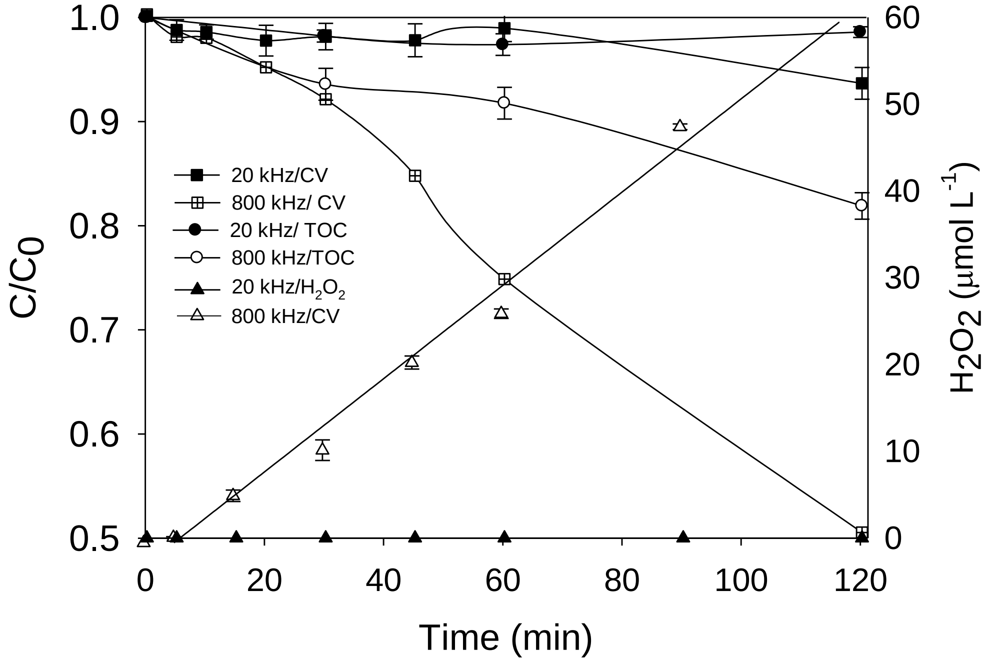

Figure 1. Crystal violet (20 mg L^{-1}) elimination, total organic carbon (10 mg L^{-1}) evolution and H_2O_2 accumulation during the sonochemical treatment of a 250 mL crystal violet solution saturated with oxygen at 80 W, 19 ± 1°C and a frequency of 20 kHz and 800 kHz.

3.2. Electrochemical degradation of CV at BDD and IrO_2 anodes

During the electrochemical process OH radicals are produced from the water discharge at the anode. However, the availability of hydroxyl radicals to oxidize organic pollutants during the process depends on the anode material. On DSA anodes, such as IrO_2 chemisorbed OH radicals are generated and then, they are not available to degrade pollutants. Instead, they transform the anode surface on IrO_3, which is then the main responsible of the transformation of chemicals in solution. On the contrary, on the BDD anode, the physisorbed OH radicals generated can easily interact with organic pollutants. Therefore, the hydroxyl radical is the main oxidative when BDD is employed. On the other hand, via OH radical reaction o by direct oxidation at the anode surface, other oxidative species, such as, hydrogen peroxide, peroxodisulphate, ozone, and chlorinated oxidizing compounds can also be formed. Fig. 2 shows the oxidants generated during the electrochemical process using sulphate ions as the supporting electrolyte. In the presence of BDD, the oxidants can be clearly seen. On the contrary, with IrO_2 no oxidants are observed, indicating that no hydrogen peroxide, peroxodisulphate, ozone or chlorinated oxidizing compounds are accumulated under these experimental conditions.

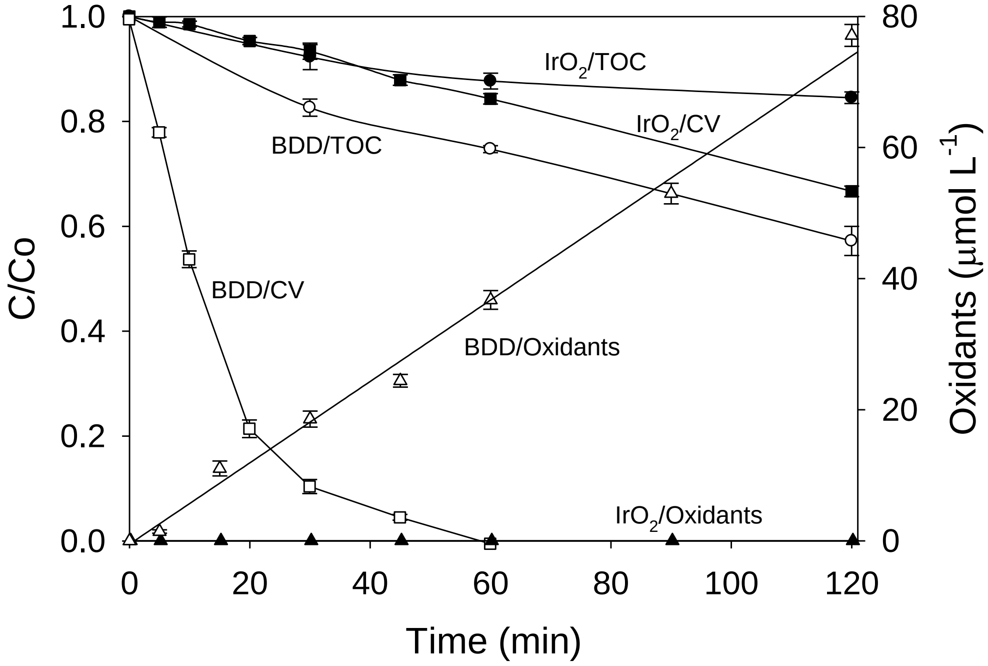

Figure 2. Crystal violet (20 mg L^{-1}) elimination, total organic carbon (10 mg L^{-1}) and oxidant accumulation using IrO_2 and BDD electrodes. The experiment was done for the electrochemical treatment of a 250 mL crystal violet solution saturated with oxygen at 20 mA cm^{-2} and 19 ± 1°C.

The results revealed that the BDD anode performed much better than the IrO_2 anode. When utilizing BDD, within a very short electrolysis period of 30 minutes, nearly 90% of the dye was eliminated. In contrast, when using IrO_2 only 6 and 33% was eliminated after 30 and 120 min, respectively. Additionally, the decrease of the TOC supports these results; 47 and 14% of TOC removal was accomplished after 120 min for the BDD and IrO_2 electrodes respectively.

As indicated, BDD anodes favor~~s~~ a more efficient degradation of organic compounds through the formation of BDD(•OH) active sites on the electrode surface. According to Kapalka et al. (2008) [31], the reactions can be summarized as indicated below:

$$BDD + H_2O \rightarrow BDD(\bullet OH) + H^+ + e \quad (5)$$

$$R + BDD(\bullet OH) \rightarrow\rightarrow\rightarrow CO_2 + BDD + H^+ + e \quad (6)$$

Although to a smaller extent, a certain contribution from the direct electrodegradation pathway and electrogenerated oxidants is also possible. Direct CV degradation [32], or indirect organic elimination via electrogenerated persulphate [33], has been previously reported.

On the other hand, at the IrO_2 anode the reaction mechanism occurs via the formation of elevated oxidation states [20] The first step is the formation of an adsorbed hydroxyl radical on the oxide (IrO_2) surface. The next step is the formation of an elevated oxidation state (IrO_3):

$$IrO_2(\bullet OH) \rightarrow IrO_3 + H^+ + e^- \quad (7)$$

Subsequently, IrO_3 can oxidize the organic, R, in solution;

$$IrO_3 + R \rightarrow IrO_2 + RO \quad (8)$$

From the above explanation, it can be seen that presence of inorganic ions, such as sulphate when BDD is employed, can contribute to the electrochemical oxidation of organic pollutants. Thus, the influence of the supporting electrolyte on electrochemical and sonochemical systems is an important parameter that should always be considered and will therefore be evaluated in the next section.

3.3. Effect of carbonate, chloride and sulphate ions on the sonochemical and electrochemical treatment of CV

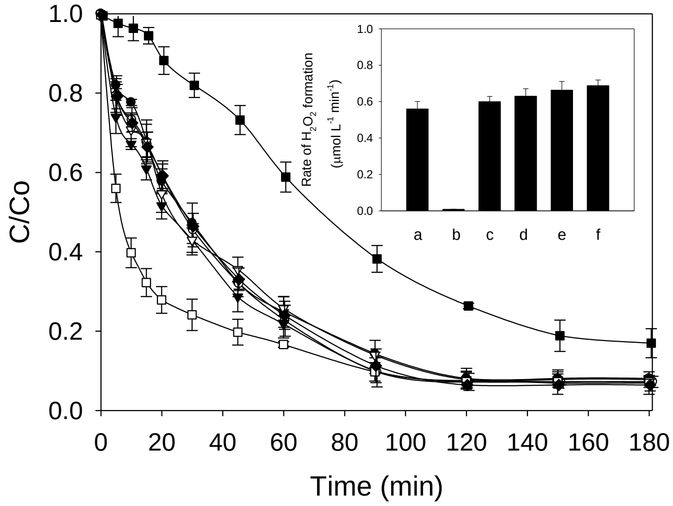

Figure 3. Effect of usual anions at 3 mmol L^{-1} (empty symbols) and 350 mmol L^{-1} (filled symbols) on sonochemical crystal violet degradation (1 mg L^{-1}) at 800 kHz, 80 W and 19±1 °C. Symbols are as follows: (♦) no salt, (●) SO_4^{2-}, (▼) Cl^- and (■) HCO_3^-. Inset shows rate of H_2O_2 formation after 180 min with different electrolytes. a) $NaHCO_3$ 3 mmol L^{-1}, b) $NaHCO_3$ 350 mmol L^{-1}, c) NaCl 3 mmol L^{-1}, d) NaCl 350 mmol L^{-1}, e) Na_2SO_4 3 mmol L^{-1}, f) Na_2SO_4 350 mmol L^{-1}.

It is well-known that during sonochemical [34, 35] or electrochemical [36, 37] water treatment, different oxidizing agents can form after the oxidation of anions that exist in the waste. These new oxidizing species may have an important role in the efficiency of the treatment. Fig. 3 shows the CV (1 mg L^{-1}) sono-degradation at 800 kHz in presence of some common inorganic ions (bicarbonate, chloride and sulphate).

The results showed no difference between when the chloride and sulphate anions were present and when the experiment was carried out in absence of anions. In fact, as can be seen in Fig. 3, 55% of CV was removed within the first 30 min and it was almost completely eliminated after 120 min upon ultrasonic action in presence of chloride, sulphate or in absence of anions. However, in the presence of the bicarbonate electrolyte, different behaviour was observed. An inhibition or enhancement effect in the CV degradation was evident at HCO_3^- concentrations of 350 and 3 mM, respectively. According to Eq. 9, when 3mM of bicarbonate are used, •OH radicals react with bicarbonate ions to produce the bicarbonate radical, which because of its low dissociation constant ($pK_a < 0$) is easily transformed in the carbonate radical (Eq. 10) [35]. Contrary •OH radicals, carbonate radicals are able to move to the bulk of the solution and then degrade hydrophilic pollutants [35]. At the high relative concentration of bicarbonate (350 mM), practically all of the •OH radicals sonochemically generated are scavenged by these ions to produce carbonate radicals (inset in Fig. 3). Because of the high concentration of the carbonate radical thus obtained, they recombine and the efficiency of CV elimination is lowered.

$$\bullet OH + HCO^-_3 \rightarrow HCO\bullet_3 + HO^- \qquad (9)$$

$$HCO\bullet_3 \rightarrow CO^-\bullet_3 + H^+ \qquad (10)$$

$$CO^-\bullet_3 + CV \rightarrow \text{Oxidised products} \qquad (11)$$

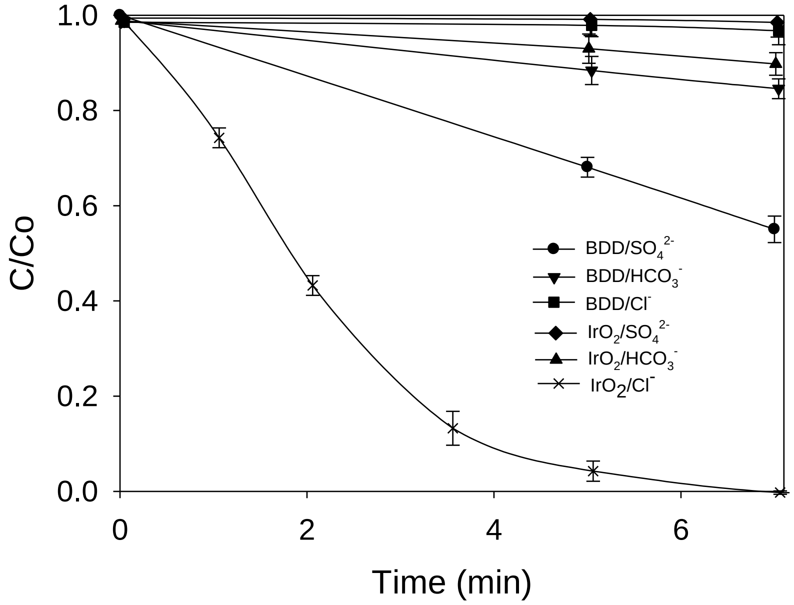

Figure 4. Effect of usual anions at 350 mmol L^{-1} on the electrochemical degradation of crystal violet. Crystal violet concentration: 2.45 µmol L^{-1}, Current density: 14.4 mA cm^{-2}, volume: 150 mL, temperature: 19±1 °C.

In the electrochemical systems, the effect of the anions was completely different. Degradation (Fig. 4) followed the order: IrO_2/Cl^- > BDD/SO_4^{2-} > BDD/HCO_3^- > IrO_2/HCO_3^- > IrO_2/SO_4^{2-} > BDD/Cl^-. The highest CV removal, practically 100% in only 7 minutes, was achieved when chloride was used with IrO_2. The BDD anode in the presence of sulphate (the second most effective system) removed almost half of the initial pollutant concentration in the same time. The differences in CV removal indicate that electrolyte-electrode interaction plays an important role in the efficiency of the process.

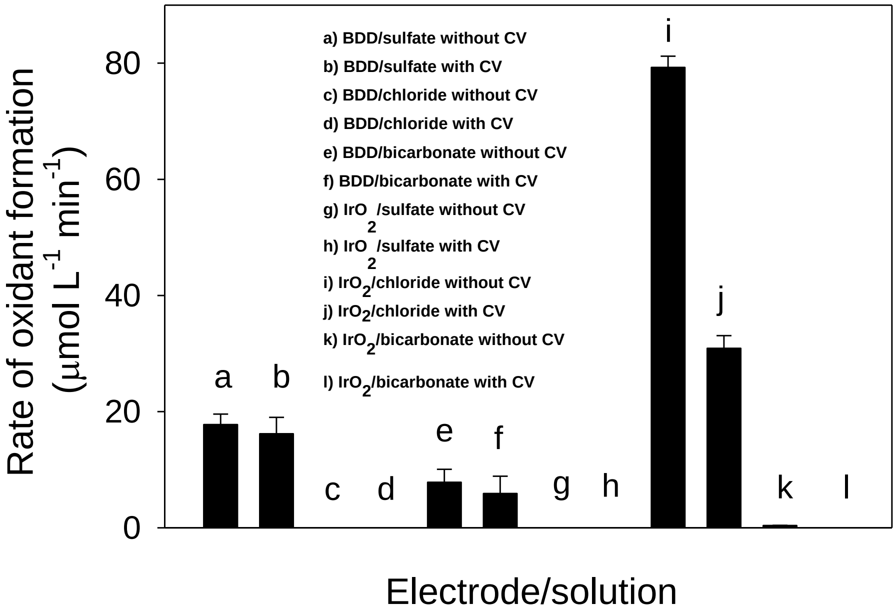

Figure 5. Rate of oxidant formation after 10 min, with IrO_2 and BDD electrodes and $NaHCO_3$, NaCl and Na_2SO_4 as electrolytes for electrochemical water treatment in the presence and absence of 1mg L^{-1} crystal violet.

Previous papers have shown that, depending on the electrolyte and electrode material, oxidative species that improve the degradation of pollutants can be generated. Therefore, iodommetry assays were also performed in order to measure the electrogenerated oxidant formation on IrO_2 and BDD anodes in the presence and in absence of the pollutant. The results presented in Fig. 5 are in total concordance with the observed CV elimination. This confirms that under the work conditions of this research, the generated oxidants contribute to the pollutant elimination. Consequently, when IrO_2 is used with chloride ions, the production of powerful oxidising agents, such as Cl_2, [38] and HClO [39], are mainly responsible for the high CV removal in an indirect oxidation mechanism.

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (12)$$

$$Cl_2 + 2OH^- \rightarrow H_2O + ClO^- + Cl^- \quad (13)$$

In the same way, when BDD anodes are used in the presence of sulphate ions, the persulphate [40, 41], hydrogen peroxide [42] and ozone [43] generated can increases the efficiency of the treatment. The lower extent of degradation of the BDD/HCO_3^- system suggests that, under our work conditions, persulphate is the species responsible for the improved CV elimination during the BDD/SO_4^{2-} electrochemical process. On the other hand, it has been reported that in presence of chloride, the potential window of BDD is narrow due to the active Cl_2 evolution just prior to the potential where OH radicals are generated [44]. This is responsible for the decreased efficiency of the BDD anodes in the presence of the chloride electrolyte.

Even though the IrO_2/Cl^- system presents the best performances for CV removal, several studies have reported the formation of dangerous chlorinated organic products when chlorine ions are employed as the supporting electrolyte. Therefore, from an efficiency and environmental point of view, the BDD/SO_4^{2-} system is the best choice to deal with water contaminated with CV dye.

3.4. Combinative sonochemical and electrochemical degradation of crystal violet at low and high frequencies

In order to improve the extent of degradation and mineralization of the pollutant, coupling between the electrochemical and ultrasonic (US) systems was evaluated. A new set of experiments, involving two ultrasonic frequencies (20 or 800 kHz) and two anodic electrodes (BDD or IrO_2), was carried out using sodium sulphate as the supporting electrolyte.

Fig. 6 shows the CV (Fig. 6A) and TOC (Fig. 6B) decay under low frequency ultrasound (20 kHz), anodic oxidation (with IrO_2 and BDD anodes) and by a combination of the two processes. The efficiency in both parameters was found to follow the order: US < IrO_2 < US/IrO_2 < BDD < US/BDD. As indicated earlier, 20 kHz ultrasound provides a low chemical effect. Therefore, a poor removal (0 % in 45 min) and mineralization (0 % in 120 min) take place when only US is applied. However, mechanical effects of low frequency ultrasound improve the efficiency of the treatment when it is coupled with electrochemistry.

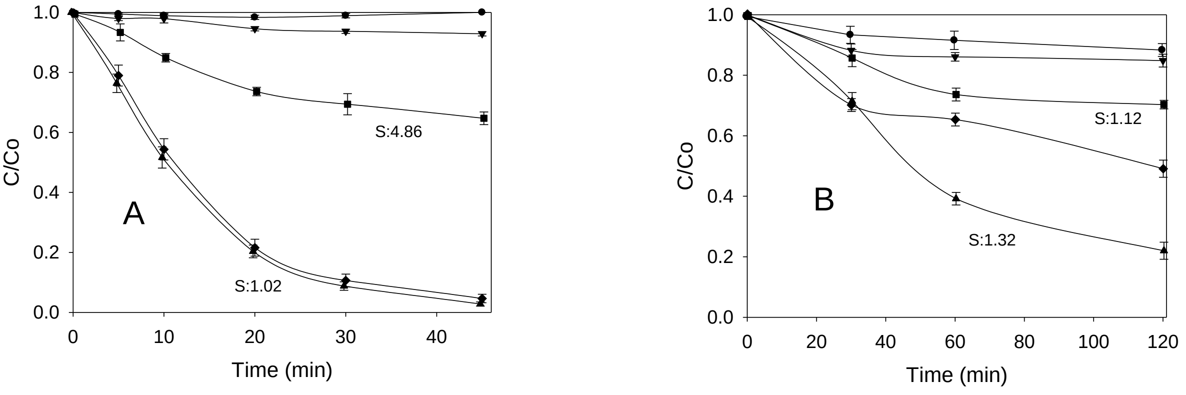

Figure 6. Substrate (A) and TOC (B) elimination of 20 mg L^{-1} CV solutions by electrochemical, sonochemical and sonoelectrochemical systems, with IrO_2 and BDD anodes and a frequency of 20 kHz at 80 W, 14.4 mA cm^{-2} and 19 ± 1^oC. The symbols represent: (●) 20 kHz; (▼) IrO_2; (■) 20 kHz-IrO_2; (♦) BDD; (▲) 20 kHz-BDD.

Figs. 7A and 7B show the same set of experiments, but this time using a high ultrasonic frequency (800 kHz). At difference of the mineralization extent, the CV removal followed a different degradation order: IrO_2 < US < US/IrO_2 < BDD < US/BDD. This time, ultrasound alone (13 % degradation in 45 minutes) is more effective than electrochemical treatment with IrO_2 anodes (7 % degradation in 45 minutes) for CV removal. The high chemical effect at 800 kHz is as a result of CV degradation via OH radicals, which are more oxidant than the oxygen transfer reactions provided by the IrO_2 electrodes (Eq. 8).

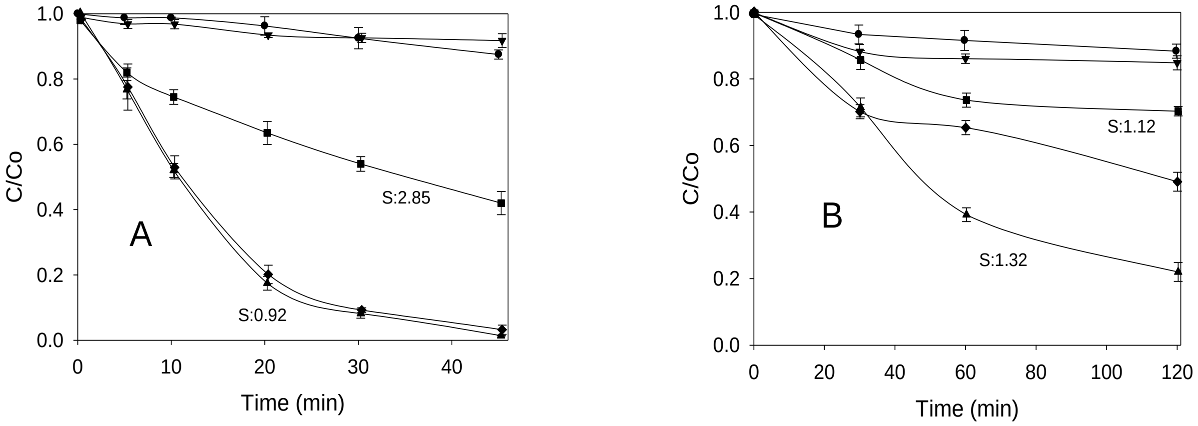

Figure 7. Substrate (A) and TOC (B) elimination of 20 mg L^{-1} CV solutions by electrochemical, sonochemical and sonoelectrochemical systems, with IrO_2 and BDD anodes and a frequency of 800 kHz at 80 W, 14.4 mA cm^{-2} and 19 ± 1°C. The symbols represent: (●) 800 kHz; (▼) IrO_2; (■) 800 kHz-IrO_2; (♦) BDD; (▲) 800 kHz-BDD.

Careful observation of Fig. 6 and 7 demonstrates interesting synergistic effects between the ultrasonic and electrochemical systems. Synergistic effects take place when the extent of degradation with the coupled system is higher than the corresponding degradation of each technology acting separately. This synergy (*S*) can be better discussed using the following equation [47]:

$$S = \frac{\text{E ultrasound+electrochemistry}}{\text{E ultrasound + E electrochemistry}} \qquad (14)$$

Where $E_{ultrasound+electrochemistry}$ represents the percentage of CV (or TOC) removed by the combined process, while $E_{ultrasound}$ and $E_{removed}$ represent the percentages of CV (or TOC) eliminated under ultrasonic and electrochemical processes alone, respectively. If *S* is equal to 1, the effect of combining the two methods is additive; if *S* is higher or lower than 1, the effect is synergistic or antagonistic, respectively.

Table 1 shows the *S* values for CV removal after 45 min of treatment. Results indicate that synergistic effects between these two techniques depend on the electrode and frequency used. For the initial substrate elimination, the US/BDD coupling clearly shows no evidence of a synergistic effect (*S* values of 1.02 and 0.92 for 20 and 800 kHz respectively). However, when the coupling is carried out with IrO_2 anodes, a very high synergistic effect is observed (*S* values of 4.86 and 2.85 for 20 and 800 kHz respectively). It has been reported that ultrasonic cavitation prevents passivation and leads to activation as a result of the continuous cleaning and abrading of the electrode surface [46]. Additionally, ultrasonic action improves mass transfer at the electrode surface [47]. These mechanical ultrasonic effects are more intense at low frequencies [29]. In it turn, anode passivation depends on the electrode and the conditions in which the experiment is conducted. In fact, it is known that, upon electrochemical oxidation, IrO_2 anodes are likely to suffer passivation due to the formation of a polymeric film on its surface [48]. The combination of these factors explains the higher synergy observed (4.86) for the US (20 kHz)/IrO_2 system in the removal of the initial pollutant.

Table 1. Synergy values found according Eq. 10 for the degradation of 20 mg L^{-1} of crystal violet by combined sonochemical and electrochemical systems operated at 14.4 mA cm^{-2} in sodium sulfate 0.35 M

Synergy of Crystal Violet removal after 45 min of treatment		
Electrode	Ultrasonic Frequency (kHz)	
	20	800
IrO_2	4.86	2.85
BDD	1.02	0.92
Synergy of total organic carbon removal after 2 h of treatment		
Electrode	Ultrasonic Frequency (kHz)	
	20	800
IrO_2	1.71	1.12
BDD	1.42	1.32

Table 1 also shows the *S* values for the extent of mineralization (TOC removal after 2 h of treatment) of the coupled systems. Contrary to the results observed for CV removal, when the BDD anode is used, a synergistic effect is observed on the TOC removal (*S* values of 1.42 and 1.32 for 20 and 800 kHz respectively). This suggests that the degradation of CV by-products is favoured by employing a combination of the two processes. The enhanced mass transfer provided by ultrasound helps the contact between the organic pollutants and the generated oxidative species, such as OH radicals, persulphate ions and hydrogen peroxide.

Analysis of Fig. 6 and 7, and Table 1, indicates that synergy between ultrasound and electrochemistry is favoured by low ultrasonic frequencies. This suggests that the mechanical ultrasonic effect, the continuous activation of the electrode surface and mass transport, are the most important contributors of the ultrasound treatment. When 20 kHz ultrasonic waves are used in combination with electrochemical oxidation using BDD anodes, approximately 68% removal of TOC is achieved in only two hours of treatment. The high performance of this combination is a result of the significant oxidation power of the BDD electrode and the strong mechanical effects of low frequency ultrasound. However, the best system in terms of TOC removal is the US (800 kHz)/BDD system, where 80% of this parameter is removed. This may be due to the high amount of •OH radicals coming from both systems.

4. CONCLUSIONS

This study has shown that low frequency (20 kHz) ultrasound does not degrade CV, but its physical effect benefits electrochemical degradation in the coupled anodic oxidation/ultrasound system. At high a frequency (800 kHz) CV degrades, but mineralization is not achieved.

The electrolyte-electrode interaction plays an important and definitive role in the efficiency of the process. Depending on the electrolyte and electrode combination, different oxidant species are formed: hydrogen peroxide, peroxodisulfate, ozone, and chlorinated oxidizing compounds.

The presence of chloride, sulfate and carbonate anions favoured the IrO_2 electrochemical system, the BDD electrochemical system and the sonochemical system, respectively. Synergistic effects were found between the sonochemical and the electrochemical processes. The impact of the synergy depended on the ultrasonic frequency and anode used. Of all the different processes tested in this study, the US(800 kHz)/BDD system was most effective at mineralizing CV, achieving 80% mineralization in two hours of treatment.

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