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Sono-electrochemical degradation of Orange G in pure water, natural water, and seawater: effect of operating parameters

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ABSTRACT

Sono-electrochemical degradation of Orange G (OG) in acidic aqueous solutions using 22.5 kHz ultrasonic irradiation with platinum grid anode and carbon felt cathode was investigated. Effects of various operating parameters such as ultrasonic power, initial pH, initial dye concentration, electric current, and Fe(II) concentration on the degradation of OG were examined. Additionally, sono-electrochemical degradation of substrate was evaluated in natural mineral water and seawater. The obtained results show that the degradation increased with increasing ultrasonic power up to 15 W. Significant degradation was achieved at pH 3 with an applied current of 100 mA and a Fe(II) concentration of 0.05 mM. It was found that sonoelectrofenton process is an efficient technique for the degradation of OG even in complex matrices such as natural mineral water and seawater. Its high performance arises from the coupling between ultrasound irradiation and the *in situ* electrogeneration of Fenton's reagent. A significant synergy index of 4.5 was observed for the sono-electrochemical treatment of water contaminated by OG.

Keywords: Sono-electrochemical; Degradation; Orange G; Complex matrices; Synergistic effect

1. Introduction

Azo dyes represent the most important class of commercial dyes and are mainly used in textile and paper industries. They are very stable to ultraviolet and visible light irradiation. Moreover, they are resistant to aerobic degradation and can be reduced to potentially carcinogenic aromatic amines under anaerobic conditions [1,2]. The presence of low concentration of dyes in the effluent streams is highly visible and undesirable and it reduces the light penetration,

which leads to inhibiting photosynthesis. The release of dyes in the environment is a considerable source of eutrophication that can produce dangerous byproducts through oxidation, hydrolysis, or other chemical reactions taking place in the wastewater itself [3,4].

Dye removal from industrial effluents has been the subject of great attention in the last few years. Approximately, 10–15% of the overall production of dyes is released into the environment, mainly via wastewater [5]. A variety of physical, chemical, and biological techniques are presently available for the treatment of wastewater discharged from various industries. Conventional methods of the treatment of

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dye wastewater include adsorption [6] chlorination and ozonation [7,8], electrochemical methods [9,10], biological methods [11,12], and chemical oxidation [12,13]. However, because of high dye concentrations and the increased stability of synthetic dyes, these methods are becoming less effective for the treatment of colored industry effluents. To overcome the problems associated with these traditional methods, much attention has recently been focused on the so-called advanced oxidation processes (AOPs) for water and wastewater decontamination. In these processes, various techniques are applied to produce reactive species [14-16], principally, hydroxyl radicals (•OH), which are able to induce the degradation and mineralization of organic pollutants [17]. Sono-electrochemical oxidation has been investigated as a viable AOP for the destruction of various pollutants in water.

Sono-electrochemistry means the application of power ultrasound irradiation to electrochemical processes [18–20]. Sono-electrochemical treatment of wastewater is a promising technology having many advantages. For example, it has strong oxidation ability, fast reaction rate, and high efficiency. It can be used under mild reaction conditions, facilitates excellent mass transfer of reaction solutions, maintains electrode activity during the process, and is able to treat toxic pollutants over a wide range of concentrations [21]. This makes the sono-electrochemical process a safe and effective technology, which uses only electricity as a reactant [22].

Although some works were carried out for the sono-electrochemical treatment of dye solution [19,23-26], comprehensive studies on the effects of process variables are yet to be carried out. To the best of our knowledge, data on the sono-electrochemical removal of OG from contaminated water have not been reported previously. Additionally, it is of considerable practical interest to examine the degradation of OG in complex matrices such as natural mineral water and seawater. Hence, the purpose of this work was to study the sono-electrochemical degradation of OG dye using 22.5 kHz ultrasound. The effects of experimental conditions such as ultrasonic power, initial pH, initial dye concentration, electric current, and Fe(II) concentration on the degradation of OG were investigated. Finally, the degradation of the substrate contained in natural mineral water and seawater was also evaluated.

2. Materials and methods

2.1. Chemicals

Orange G (abbreviation: OG; C.I. number: 16230, synonym: Acid Orange 10; chemical class: azo;

molecular formula: $C_{16}H_{10}N_2Na_2O_7S_2$) was used as a model solute. OG [1-phenylazo-2-naphthol-6,8-disulfonic acid, disodium salt] (molecular weight: 452.37 g/mol) was purchased from Sigma–Aldrich and was used as received.

Sodium sulfate, sodium chloride, sodium nitrate, sulfuric acid, and ferrous sulfate were supplied by Sigma–Aldrich.

All reagents used in the present study were purchased among the products of high purity (analytical grade).

The solutions of OG were prepared by dissolving the corresponding amount of substrate into pure water, mineral water, or seawater.

2.2. Procedures

A schematic diagram of the applied device for the sono-electrochemical process is shown in Fig. 1. Experiments were performed in an open, undivided, and cylindrical glass cell of 250 mL capacity, with a double jacket for circulation of external thermostated water to regulate the solution temperature (20°C). The volume of the treated dye solution was 150 mL. Ultrasound was produced by an ultrasonic power generator operating at 22.5 kHz (Microson XL 2000). Ultrasonic irradiation was introduced into the reaction solution by a titanium horn (6 mm diameter) mounted at the top of the cylindrical glass cell. The ultrasonic generator had facility of power output control. The power control knob was set at 15 W during sonication, except when the effect of power was examined. The working electrode (cathode) was a 3D piece of carbon felt $(6 \times 2.5 \text{ cm}, 1.1 \text{ cm} \text{ in width})$. The counter electrode was a Pt grid (anode). Continuous O2 saturation at atmospheric pressure was assured by bubbling air through a frit, starting 10 min before sonoelectrolysis to reach a steady O_2 concentration. In all trials, the solution is vigorously stirred magnetically to enhance the mass transport toward/from the electrodes. A catalytic quantity (0.03-0.5 mM) of ferrous ion was introduced into the solution before the beginning of sonoelectrolysis. The applied current was 100 mA for degradation kinetics, except when the effect of electric current was investigated. The current and the amount of charge passed through the solution were measured and displayed continuously throughout sonoelectrolysis using a DC power supply. Prior to starting sonoelectrochemical treatment, the initial pH of dye solution was set to 3 by addition of aqueous H₂SO₄ in all experiments, except for those carried out to examine the effect of initial pH. The pH variation was negligible and remained stable during all the experiment.

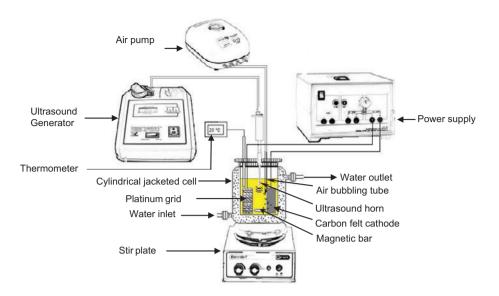


Fig. 1. Experimental setup used for sonocelectrochemical degradation of OG.

The ionic strength was maintained constant (50 mM) by the addition of Na_2SO_4 as a supporting electrolyte. Electrolysis was performed by applying a constant voltage of 4.0 V. Samples were withdrawn during sonoelectrolysis at pre-set time intervals to assess the concentration decay of OG.

Experiments with ultrasound irradiation alone were performed with the same setup, but without application of current to the electrodes.

2.3. Analytical method

A well-known procedure for determining OG concentrations, based on Beer's law calibration plots, was applied using a UV–vis spectrophotometer (Lightwave II). The wavelength resolution and the bandwidth were, respectively, 1 and 0.5 nm. The length of the optical path in glass cell was 1 cm. The maximum absorption wavelength was determined as equal to 482 nm. Then, the calibration plot was constructed. The calibration was repeated five times during the period of measurements. The linearization of this plot usually provided determination coefficient close to 99.99%. These data were used to determine the remaining OG concentration in aqueous solution. In some cases, a proper dilution was necessary to obtain a well measurable absorption.

2.4. COD measurement

Chemical oxygen demand (COD) was measured using a dichromate solution as the oxidizer in a strong

acid medium. Test solution (2 mL) was transferred into the dichromate reagent and digested at 150 °C for 2 h. The optical density for the color change of dichromate solution was determined with a UV–vis spectrophotometer (Lightwave II). In order to avoid the interference of the residual hydrogen peroxide, samples were neutralized with sodium hydroxide and treated with catalase previous to COD analysis.

3. Results and discussion

3.1. Effect of ultrasonic power

The degradation of OG was performed under different experimental conditions that include ultrasound alone, electrofenton alone, and a combination of ultrasound and electrofenton (sonoelectrofenton) at different ultrasonic powers. The effect of ultrasonic power on the sono-electrochemical degradation of OG was studied for an initial dye concentration of 0.04 mM, a Fe(II) concentration of 0.05 mM, a solution volume of 150 mL, a supporting electrolyte concentration (Na₂SO₄) of 0.05 M, and an electric current of 100 mA. The obtained results are shown in Fig. 2. As a single process, only 3% degradation of OG was achieved after 30 min during sonication alone for an ultrasonic power of 15 W. Whatever the used ultrasonic power, OG degradation by sonolysis does not exceed 3% after 30 min of sonication. However, 90% OG was removed by the electrochemical method after 30 min of treatment. When both ultrasound and electrofenton are combined (sonoelectrofenton), a significant enhancement in the degradation of OG was

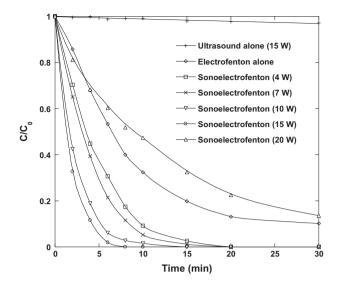


Fig. 2. Effect of ultrasonic power on sono-electrochemical degradation of OG (conditions: volume: 150 mL, initial OG concentration: 0.04 mM, pH 3, Na₂SO₄ concentration: 0.05 M, ultrasonic power: 4–20 W, Fe(II) concentration: 0.05 mM, electric current: 100 mA, voltage: 4.0 V).

observed, especially for an ultrasonic power of 15 W. As can be seen from Fig. 2, a considerable improvement in the sono-electrochemical degradation rate was observed when the ultrasonic power was increased from 4 to 15 W. For example, complete removal (100%) was obtained after 20 min at 4 W, 15 min at 10 W and 8 min at 15 W. This higher degradation degree is attributed to the synergistic effect.

For any hybrid technology, it is obviously expected that the efficiency of the hybrid system should be higher than the sum of the efficiencies of the two single technologies. The synergistic index may be calculated by the following equation:

Synergy index =
$$\frac{R_{\text{US-EF}}}{R_{\text{US}} + R_{\text{EF}}}$$
 (1)

where R_{US} , R_{EF} , and $R_{\text{US-EF}}$ are initial degradation rates by ultrasound, electrofenton, and sonoelectrofenton, respectively.

A synergy index of 1 means the overall efficiency is mere addition of individual efficiencies. A synergy index greater than 1 means there is a positive synergy effect and less than 1 means a negative effect.

From Fig. 2, it can also be observed that the initial degradation rate increases with an increase in ultrasonic power until 15 W and then decreases afterward. For example, for an ultrasonic power of 15 W, the initial rates of OG degradation are $0.1 \,\mu\text{M/min}$ by ultrasound, $2.9 \,\mu\text{M/min}$ by electrofenton, and

13.5 μ M/min by sonoelectrofenton, giving a synergy index of 4.5 demonstrating a large positive synergy for the combined system. The synergistic indexes for ultrasound powers of 4, 7, and 10 W were 2, 2.3, and 3.8, respectively. For an ultrasonic power of 20 W, the synergy index was 1.3. Considering that this value is only slightly greater than 1, and within experimental error of the measurements, it suggests that there is an additive effect in combining ultrasound and electrofenton, rather than a synergistic effect.

The reason for the observed synergistic enhancement in the sono-electrochemical degradation rate may be explained as follows. Ultrasound irradiation has both chemical and physical effects on heterogeneous processes. The chemical effects of ultrasound are due to acoustic cavitation, where the high temperatures and pressures can be reached inside the cavitation bubbles, leading to the thermal decomposition of water molecules into 'OH and H' [27,28]. In this case, sonication alone leads to very low degradation rate indicating that the chemical effect associated with ultrasound not be the key point for the OG degradation, because the yield of 'OH radicals produced at low frequency sonolysis is quite low [29]. Therefore, the physical effects of cavitation induced by sonication play an important role for the enhancement of degradation efficiency by sonoelectrofenton process. It seems that the enhancement of electrofenton process by ultrasound is due to increased mass transport and electrode activation by elimination of the impurity layer at the surface of electrode [25,30-32]. Additionally, ultrasound may enhance the electrocatalytic oxidation and the production of free radicals, resulting in the generation of additional hydroxyl radical to react with the substrate [25,30-32].

To clarify the changes in molecular and structural characteristics of OG as a result of sono-electrochemical degradation, representative UV-vis spectra changes in the dye solution as a function of reaction time were observed and the corresponding spectra are shown in Fig. 3. As can be observed from these spectra, before the oxidation, the absorption spectrum of OG in water was characterized by two main bands in the ultraviolet region, with their maximum absorption at 235 and 314 nm, and by one other band in the visible region located at 482 nm. Following a period of sono-electrochemical treatment, these characteristic absorption bands decreased in intensity and underwent a change in their spectral shape, indicating the degradation of the dye and the formation of an absorbing product in the UV-vis region. It is noteworthy that the absorption of the visible band at 482 nm decreased with increasing treatment time. The rapid decrease of the absorption maximum indicates the

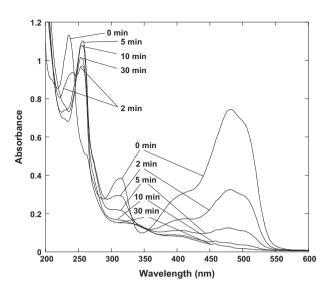


Fig. 3. Changes in the UV–vis absorption spectra observed during sono-electrochemical degradation of OG (conditions: volume: 150 mL, initial OG concentration: 0.04 mM, pH 3, Na₂SO₄ concentration: 0.05 M, ultrasonic power: 15 W, Fe(II) concentration: 0.05 mM, electric current: 100 mA, voltage: 4.0 V).

complete removal of the conjugate structure of the dye. The absorbance peaks at 314 and 235 nm have obviously declined, which indicates that the entire conjugated chromophore structure of OG has been destroyed. In addition to rapid decolorization effect, the decay of the absorbance at 314 nm, related to absorbance of poly-aromatic rings, was considered as evidence of aromatic fragment degradation in the dye molecule and its intermediates. Hence, the rapidly increased mass of aromatic intermediates likely to absorb in UV region is clearly reflected by the appearance of a new absorption peak at 256 nm, indicating the increase in the concentration of the OG byproducts.

3.2. Effect of initial pH

It is well known that pH of solutions markedly influence the sono-electrochemical degradation of organic pollutants [33–35]. Hence, the effect of this parameter on the sono-electrochemical degradation rate of OG was investigated. Different initial pH values ranged between 2.0 and 6.0 were tested at 0.04 mM of substrate concentration, 15 W of ultrasound power, 100 mA of current intensity, 0.05 mM of Fe(II), and 20 °C. The results showed in Fig. 4 indicated that sono-electrochemical degradation at pH 3 is higher than that obtained at pH 2. The increase in pH from 3 to 6 reduced the OG degradation. This is due to the decrease in oxidation potential of 'OH radicals with an increase in pH [33]. On the other hand, at high pH, the generation of 'OH was lowered due to the formation of insoluble ferric hydroxo complexes. It should also be noted that at very low pH value (<3), hydrogen ion acts as 'OH radical scavengers [34]. At low pH, the reaction is slowed down due to the formation of complex species $[Fe(H_2O)_6]^{2+}$, which reacts more slowly with peroxide compared to that of [Fe $(OH)(H_2O)_5]^{2+}$ [35]. In addition, the peroxide gets solvated in the presence of high concentration of H⁺ ions to form stable oxonium ion $[H_3O_2]^+$ [35]. An oxonium ion makes peroxide electrophilic to enhance its stability and substantially reduces the reactivity with Fe²⁺ ion [34,36]. Hence, it was decided to sustain pH 3 in all other experiments.

3.3. Effect of initial dye concentration

OG sono-electrochemical degradation was evaluated using different initial concentrations, from 0.02 to 0.8 mM, under the same experimental conditions. Fig. 5 illustrates the results of experiments. As shown in this figure, the removal efficiency of OG decreased with increasing initial dye concentration. OG was completely degraded within 6 and 8 min with initial concentrations of 0.02 and 0.04 mM, respectively. At higher initial concentrations, such as 0.6 and 0.8 mM, the degradation efficiency reached 92 and 87% after

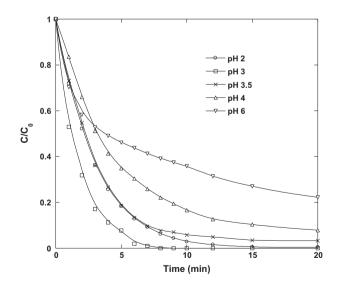


Fig. 4. Effect of initial pH on sono-electrochemical degradation of OG (conditions: volume: 150 mL, initial OG concentration: 0.04 mM, pH 2–6, Na_2SO_4 concentration: 0.05 M, ultrasonic power: 15 W, Fe(II) concentration: 0.05 mM, electric current: 100 mA, voltage: 4.0 V).

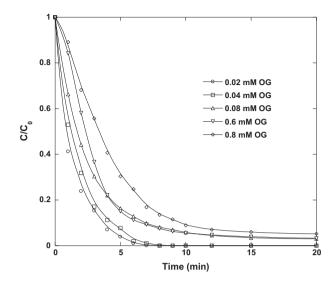


Fig. 5. Effect of initial OG concentration on substrate sonoelectrochemical degradation (conditions: volume: 150 mL, initial OG concentration: 0.02-0.8 mM, pH 3, Na₂SO₄ concentration: 0.05 M, ultrasonic power: 15 W, Fe(II) concentration: 0.05 mM, electric current: 100 mA, voltage: 4.0 V).

10 min, respectively. Higher degradation efficiencies of OG were observed at lower initial concentrations.

In the reaction system, identical levels of oxidants are generated under the same treatment conditions. At low initial concentrations, the produced oxidants are sufficient to oxidize the amount of OG in solution. Thus, higher degradation efficiency was observed. Whereas at higher initial concentrations, the oxidants formed are not sufficient to drive the oxidation with the same speed for the higher level of dye. Additionally, the lower removal efficiency at high OG concentrations was attributed to the competition between various OG molecules and/or the intermediate products formed during the oxidation process. Both OG and its transformation products can compete for hydroxyl radical generated in the system.

3.4. Effect of electric current

The electric current is an important factor for the sono-electrochemical process. Higher electric current is favorable for the combined system. Different electric currents ranging from 30 to 200 mA were applied in an experiment series under otherwise identical experimental conditions, and the obtained results are shown in Fig. 6. The data indicate that the increase in electric current from 30 to 100 mA offered faster OG degradation. This may be due to the fact that an increase in electric current increased the amount of electro-generated H_2O_2 and promoted the degradation process.

From Fig. 6, it can be also observed that the increase in electric current beyond 100 mA decreased the removal of OG dye, which is due to the slower generation of 'OH radicals. This may be due to the occurrence of following at higher electric current: hydrogen peroxide is anodically oxidized to yield intermediate HO₂ radicals; Fe²⁺ present in the solution is anodically oxidized to Fe³⁺; and OH is dimerized H_2O_2 $(2 \cdot OH \rightarrow H_2O_2)$ and destruct H_2O_2 to $(OH + H_2O_2 \rightarrow HO_2 + H_2O)$ [37]. It should be noted that the dimerization generally occurs at higher concentration of hydroxyl radicals and such higher concentration is possible with the higher electric current. Therefore, an electric current of 100 mA was selected for further studies in this work.

3.5. Effect of Fe(II) concentration

The sono-electrochemical degradation of OG solution at initial dye concentration of 0.04 mM in the presence of various concentrations of Fe(II) ranging from 0.03 to 0.5 mM at pH 3, an ultrasonic power of 15 W, and an electric current of 100 mA was studied. The obtained results are shown in Fig. 7. The degradation increased with increasing Fe(II) concentration from 0.03 to 0.05 mM. An initial removal rate of 8 μ M/min was attained for Fe(II) concentration of 0.03 mM, while in the presence 0.05 mM of Fe(II), the constant defining the initial degradation rate of the substrate increased to 13.6 μ M/min. This is due to

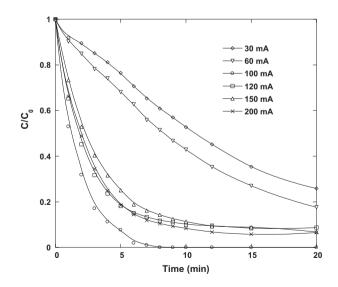


Fig. 6. Effect of electric current on sono-electrochemical degradation of OG (conditions: volume: 150 mL, initial OG concentration: 0.04 mM, pH 3, Na_2SO_4 concentration: 0.05 M, ultrasonic power: 15 W, Fe(II) concentration: 0.05 mM, electric current: 30–200 mA).

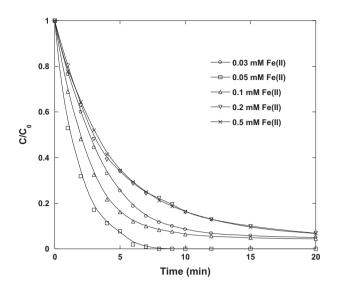


Fig. 7. Effect of Fe(II) concentration on sono-electrochemical degradation of OG (conditions: volume: 150 mL, initial OG concentration: 0.04 mM, pH 3, Na_2SO_4 concentration: 0.05 M, ultrasonic power: 15 W, Fe(II) concentration: 0.03–0.5 mM, electric current: 100 mA, voltage: 4.0 V).

the enhanced production of hydroxyl radicals by ultrasound and electrofenton. The enhancement of degradation by Fe(II) addition in a catalytic amount was due to H_2O_2 decomposition and hydroxyl radical generation in the Fenton (Fe(II)/ H_2O_2) process. An increase in Fe(II) concentration from 0.05 to 0.5 mM leads to decrease in OG degradation. The initial degradation rates were 10.4, 7.4, and 7.2 μ M/min for Fe(II) concentration is due to the direct scavenging effect of the hydroxyl radical by the excessive quantity of Fe(II). Consequently, a concentration of Fe(II) of 0.05 mM was chosen throughout this work.

3.6. Effect of real complex matrices

Several studies have been investigated on the degradation of pollutants by electrofenton but a limited number of them involve water matrices effects. Hence, the evaluation of the effect of inorganic compounds and organic species present in natural mineral water and seawater on the sono-electrochemical degradation of pollutant is of special interest. In order to assess this and to evaluate the applicability of the sono-electrochemical treatment to a real water treatment, OG dye was dissolved in a natural mineral water and in seawater. The main characteristics of the natural mineral water are: Ca^{2+} : 57.9 mg/L, Mg^{2+} : 16.3 mg/L, Na^+ : 12 mg/L, K^+ : 0.5 mg/L, SO_4^{2-} :

 $31 \text{ mg/L}, \text{ HCO}_3^-$: $210 \text{ mg/L}, \text{ Cl}^-$: $15 \text{ mg/L}, \text{ NO}_3^-$: 8 mg/L, pH 7.6, salinity: 300 mg/L. The seawater has a high salinity (\sim 35 g/L), which is composed mainly of Na⁺: 11 g/L, Mg²⁺: 1.3 g/L, Ca²⁺: 0.4 g/L, Cl⁻: 20 g/L, SO_4^{2-} : 3 g/L. Fig. 8 shows the comparative degradation of OG in pure water, natural mineral water, and seawater. From this figure, it can be seen that the matrices in seawater accelerate the degradation of OG (0.04 mM) compared to that obtained in pure water. The degradation of OG in natural mineral water was not affected for the first minutes of treatment, but it was slightly inhibited afterward. In natural mineral water, even after 20 min of sonoelectrochemical treatment, the destruction of OG dye was not complete (94%). The degradation of substrate in pure water and seawater was complete after 8 min of treatment. Hence, sono-electrochemical treatment represents a very interesting advanced oxidation technique for the removal of OG in complex matrices such as natural water and seawater.

Because the major component of seawater is sodium chloride and in order to explain the enhancement of degradation of OG in seawater, the effect of supporting electrolyte type in pure water was studied. The influence of the presence of 0.05 M of different supporting salts namely sodium sulfate, sodium chloride, and sodium nitrate on the degradation of OG was investigated. The obtained results, shown in Fig. 9, indicate that the degradation rates showed the following tendency: sodium chloride > sodium

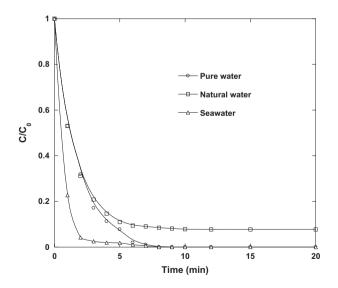


Fig. 8. Sono-electrochemical degradation of OG in pure water, natural mineral water and seawater (conditions: volume: 150 mL, initial OG concentration: 0.04 mM, pH 3, ultrasonic power: 15 W, Fe(II) concentration: 0.05 mM, electric current: 100 mA, voltage: 4.0 V).

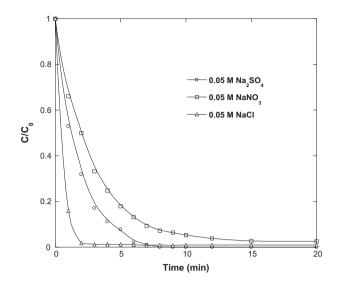


Fig. 9. Effect of supporting electrolyte type on sono-electrochemical degradation of OG (conditions: volume: 150 mL, initial OG concentration: 0.04 mM, pH 3, ultrasonic power: 15 W, Fe(II) concentration: 0.05 mM, electric current: 100 mA, voltage: 4.0 V).

sulfate > sodium nitrate. The higher degradation in the presence of sodium chloride may be due to the *in situ* production of hypochlorite ions that having higher oxidation potential [24,38]. However, sodium sulfate and sodium nitrate are less effective electrolyte for degradation. This may be due to formation of

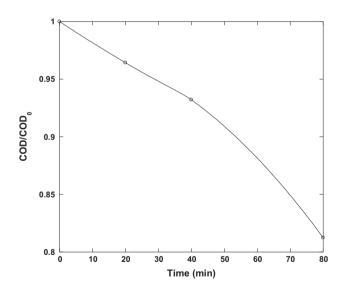


Fig. 10. COD removal of OG solution by sono-electrochemical degradation process (conditions: volume: 150 mL, initial OG concentration: 0.04 mM, pH 3, Na_2SO_4 concentration: 0.05 M, ultrasonic power: 15 W, Fe(II) concentration: 0.05 mM, electric current: 100 mA, voltage: 4.0 V).

adherent film on the anode surface, which poisoned the electrode process, and these electrolytes do not contain chloride ions that are the main source of production of hypochlorite [38]. Therefore, it seems that the enhancement of degradation rate in seawater in comparison to that obtained in pure water was probably due to the presence of high concentration of sodium chloride.

3.7. COD abatement

COD differences along the time are exclusively related to the degree of oxidation of the organic matter as a whole. To determine the overall treatment efficiency of the sono-electrochemical process, the degradation of organic matter (OG and its intermediates) was determined by COD analysis. The best experimental conditions have been used to record the COD abatement as a function of time. Fig. 10 shows that 19% of COD removal was achieved after 80 min of treatment time.

4. Conclusions

The combination of sonochemical and electrochemical treatments for the removal of OG in aqueous media shows an attractive synergistic effect. The sono-electrochemical treatment carried out for an ultrasonic power of 15 W was synergistic with a synergy index of 4.5. Experiments carried out using natural mineral water and seawater demonstrated that sono-electrochemical process is an efficient technique for the degradation of OG even in complex matrices such as natural mineral water and seawater. The rapid and effective degradation of OG in sono-electrochemical system suggested its great potential in wastewater treatment contaminated by dyes.

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22542

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