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Degradation of Rhodamine B dye in aqueous medium using electro-Fenton and sono-electro-Fenton process

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ABSTRACT

The electrochemical degradation of tetraethylrhodamine, commonly known as Rhodamine B (RhB) in acidic aqueous solutions, was examined utilizing a platinum grid anode and a stainless steel cathode. This dye is a substance used to impart color to cotton, silk paper, bamboo, weed, leather, and other materials as well as to prepare carbon paper, ball pen, stamp pad inks, paintings, etc. In case of being swallowed by humans and animals, this chemical compound causes an irritation to the skin, eyes, gastrointestinal and respiratory tract, in addition to phototoxic and photoallergic responses. Experimental evidence of carcinogenicity, reproductive and developmental toxicity, neurotoxicity, and chronic toxicity in people and animals has been established. The effects of various experimental parameters on the RhB dye degradation were investigated. The optimum conditions are: a current of 100 mA, Fe(II) = 10 mg/L, and Na_2SO_4 = 10 mg/L. All the experiments were carried out at pH = 2.5. The % removal = 98.75 after 120 min. The combination of electro-Fenton and ultrasonic irradiation with a low frequency (sono-electro-Fenton process) was also studied. Sonoelectrochemical treatment of RhB-contaminated water yielded a significant, considerable percentage of 99% after 90 min at a current of 100 mA.

Keywords: Degradation; Electro-Fenton; Operating factors; Rhodamine B (tetraethylrhodamine); Complex matrices; Sono-electro-Fenton

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1. Introduction

Freshwater represents 1% of the total amount of water on the planet. This percentage is available for human usage as well as the environment as a whole. However, the quality of the available quantity that might be used by humans (0.1%) has been irrevocably deteriorating. The increased amount of liquid, solid, and gaseous harmful discharges have caused the production capacity to be exceeded [1]. Water is a special type of aqueous system. Precipitation, pollutant breakdown, and pollutant dilution are three natural ways for it to purify itself. On the other hand, these self-purification mechanisms in water can only take effect when the contaminant is relatively diluted when the concentration of contaminants in water is high, the water ability to self-purify is compromised. This is the case with coloured effluents from chemical production [2]. The nature of the pollutants being emitted during the onset of industrial growth was such that the problem was contained within nature's assimilation capability. However, as the complexity of the toxins discharged has increased, the ecosystem's natural assimilation capability has begun to be exceeded. The textile sector, which ranks first on the list of the most polluting industries, is one of the businesses that releases harmful chemicals into the environment [3].

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The two basic types of dyes are natural dyes along with chemical and synthetic dyes. Mineral dyes were the first used by humans (colored earth), which were made from plant or animal dyes. The majority of dyes used were from vegetable origin, extracted from plants, trees and lichens; or animal origin, collected from insects like kermes or molluscs like purple. On the other hand, Natural dyes, have never had more than a few dozen copies. However, synthetic dyes have over 7,000 copies. A range of various materials are colored with dyes, such as textile fibres, papers, leathers, furs, woods, polymers, and elastomers. The use of dyes goes to color food and medicinal items, as well as to produce paints, printing inks, and varnishes, in addition of being used in cosmetics, metal colouring (anodized aluminium), photography (sensitizers), biology (colouring of microscopic preparations), color indicators, and medicines (antiseptics, antimalarial, etc.). In order to maintain their structure and color, modern textile dyes must have a high level of chemical and photolytic stability. They are designed to resist decomposition due to time and solar exposure, as well as biodegradation, hence generate major ecological and environmental difficulties [4].

The utilization of dyes increased pollution load, and enterprises were compelled to implement particular processes to decolorize effluents before dumping to surface water or land. Coagulation, flotation, chemical oxidation, solvent extraction, hyper filtration, along with other physical and chemical procedures, have been investigated for their ability to remove color from wastewater [5]. However, investigations have shown that all of these solutions are either ineffective on a large scale, or they are cost-intensive, and they may become a source of secondary pollution (sludge production) [1]. Nonetheless, since the contaminant is simply transferred from water to a solid matrix, these procedures are non-destructive [6]. Furthermore, the membrane process is associated to difficulties including operation and maintenance challenges, filter clogging, and high maintenance and investment costs [4].

For environmental conservation and lower water consumption, recycling 91% of wastewater is becoming increasingly significant [3]. Recent years have seen the development of advanced oxidation processes (AOPs) and electrochemical technologies for treating pollutants in drinking water and industrial effluents. Almost all advanced oxidation methods rely on the production of reactive species such as hydroxyl radicals ($^{\bullet}OH$), which instantly and non-selectively destroy a wide spectrum of organic contaminants. Despite claims that additional species are involved, the unstable and highly hydroxyl radical ($^{\bullet}OH$), appears to be the active species responsible for the removal of pollutants in the majority of cases. Because the $^{\bullet}OH$ radical is unstable, it must be continually created *"in-situ"* by chemical or photochemical processes. As soon as $^{\bullet}OH$ is produced, the hydroxyl radical attacks the organic matter (OMs) in the solution, as shown in the following equation [7]:

$$^{\bullet}\mathrm{OH} + \mathrm{OM} \rightarrow \text{intermediates} \rightarrow \text{harmless spices} \left(\mathrm{CO_2}, \mathrm{H_2O}, \text{etc}\ldots\right) \tag{1}$$

The important advanced oxidation processes include H_2O_2/Fe^{2+} (Fenton's reagent) [H_2O_2/Fe^{+3}] (Fenton-like reagent), electro-Fenton and H_2O_2/O_3 as chemical procedures, UV/H_2O_2/Fe^{+2} UV/H_2O_2/Fe^{3+}, UV/H_2O_2, UV/O_3 and photo-electro-Fenton as photoelectrochemical treatment, and UV/TiO_2, UV/TiO_2/O_3 and UV/ZnO as photocatalytic methods. The adaptability of AOP is further improved by the fact that they provide a variety of methods for producing hydroxyl radicals, facilitating better compliance with specific treatment requirements [7]. The $^{\bullet}OH$ radicals are highly reactive species that have a high-oxidizing power [6].

Direct electrolysis may be used to achieve electrochemical oxidation of organic for wastewater treatment, where the pollutants are oxidized after adsorption on the anode surface without the need of any chemicals other than the electron, which is a "clean reagent" [8]. Theoretically, direct electro-oxidation is feasible at low potentials prior to oxygen release; however, the intoxication effect causes the reaction rate to be slowed and the catalytic activity to be diminished owing to the creation of a polymer layer on the anode surface. Due to the inclusion of intermediates of oxygen evolution [Eq. (2)], this electrode deactivation may be prevented by executing the oxidation at high potentials in the water discharge region [8]:

$$\mathrm{H_2O} \rightarrow {}^{\bullet}\mathrm{OH} + \mathrm{H^-} + e^- \tag{2}$$

However, while operating at high anodic potentials, the current efficiency is reduced by the secondary oxygen evolution process that occurs during oxidation, as given by Eq. (3) [8]:

$$\mathrm{H_2O} \rightarrow \tfrac{1}{2}\mathrm{O_2} + 2\mathrm{H^+} + 2e^- \tag{3}$$

Other sophisticated oxidation processes are based on Fenton methods. Fenton's reagent is a mixture of ferrous ions (Fe^{+2}) and hydrogen peroxide (H_2O_2) that produces the hydroxyl radical ($^{\bullet}OH$) *in situ* according to Eq. (4) [7]:

$$\mathrm{Fe^{2+}} + \mathrm{H_2O_2} \rightarrow \mathrm{Fe^{+3}} + \mathrm{OH^-} + {}^{\bullet}\mathrm{OH} \tag{4}$$

Fe(III) can catalyse the oxidation of H_2O_2. The creation of the hydroperoxyl radical $HO^{2\bullet}$ [Eq. (5)] in the reaction of H_2O_2 with Fe(III) (also known as the Fenton-like reagent) [7]:

$$\mathrm{Fe^{3+}} + \mathrm{H_2O_2} \rightarrow \mathrm{Fe^{2+}} + \mathrm{HO^{2\bullet}} + \mathrm{H^+} \tag{5}$$

Hydroxyl radicals, which have a standard potential of 2.8 V and a half-life of around 10^{-9} s, may rapidly and non-selectively oxidize a wide spectrum of compounds of environmental significance. The development of an electrochemical technique capable of manufacturing the Fenton reagent at specific cathodes has addressed the major limitations of requiring vast quantities of chemicals and producing excessive quantities of iron-containing sludge. Because of the positive findings, this technique has advanced fast, with applications including the treatment of dyes, pesticides, herbicides, explosives, surfactants, pharmaceuticals, actual effluents, and wasted adsorbent regeneration [9].

$^{\bullet}OH$ radicals are formed in the majority of the solution by the reaction of electro generated H_2O_2 and Fe^{2+} in the electro-Fenton technique [Eq. (4)]. According to the following equation [Eq. (6)] [7], hydrogen peroxide is created electrochemically by reducing oxygen with two electrons on various electrodes (mercury pool, graphite, carbon polytetrafluoroethylene O_2^- fed cathodes):

$$O_2 + 2e^- + 2H^+ \rightarrow H_2O_2 \quad (6)$$

Fe^{2+} regeneration, which is primarily accomplished by reducing Fe^{3+} species with electro generated H_2O_2, may propagate catalytic reactions in this system [Eq. (5)] and reducing it on the cathode surface [Eq. (7)] [7]:

$$Fe^{+3} + e^- \rightarrow Fe^{+2} \quad (7)$$

This method has been used successfully to decolorize a variety of organic pigments [7].

Another feature of electro-Fenton processes is the simultaneous occurrence of iron regeneration via cathodic reduction, which allows for the use of quasi-catalytic levels of this reagent with little sludge creation and significant cost savings [Eq. (8)] [9]:

$$Fe^3 + e\text{-} \rightarrow Fe^{2+}\ E0\ (Fe^{3+}/\ Fe^{2+})\ ð = 0,\ 77\ V\ vs\ SHE \quad (8)$$

In order to achieve rapid oxidation, it is required to favour the reduction of iron(III) to iron(II) by accelerating this reaction, which is much slower than the reverse process. As a result, when evaluating a cathode material for electro-Fenton processes, two different abilities should be considered: the ability to reduce oxygen to electro generate hydrogen peroxide and the ability to reduce ferric ions to restore ferrous ions, thereby promoting the reaction leading to $^{\bullet}OH$ production [9].

Electro-Fenton process is one of the alternative methods for wastewater treatment, benefiting from advantages such as versatility, environmental compatibility and potential cost effectiveness [9].

Integration of the electro-Fenton process with other oxidation processes is a possible treatment method that has benefits like high efficiency, fast response rate, and high oxidation capacity. Ultrasonic radiation degradation is one of the most commonly used degradation methods. The ultrasonic radiation degradation method is derived from cavitation bubbles generated by liquid under ultrasonic radiation. After entering the cavitation bubbles, water molecules will decompose to produce highly oxidizing active substances [Eq. (9)] that are conductive to inducing organic degradation. Additionally, water molecules on the surface of cavitation may form supercritical water, which is conductive accelerating chemical reaction rates [Eq. (10)].

$$H_2O + US \rightarrow OH^{\bullet} + H^{\bullet} \quad (9)$$

$$H^{\bullet} + O_2 \rightarrow HO_2 \quad (10)$$

Sonochemistry and electrochemical oxidation (sono-electro-Fenton process) is a hybrid technology developed for the treatment of variety of water pollutants. The utilization of this method has various advantages including treatment of wastewater under moderate conditions, high efficiency and fast reaction rate. Sono-electro-Fenton is an eco-friendly process (only electricity as a reactant).

Several recent studies have investigated the sono-electro-Fenton process for the treatment of dye solutions such as Reactive Red 195 (RR195), Sandolan Yellow, and Orange G. In addition, Hasani et al. studied the improvement of electro-Fenton process combined with ultrasonic sonochemistry for different dye compounds and they observed efficiency decolourization [22].

In this study the degradation of Rhodamine B (RhB) dye using electro-Fenton and sono-electro-Fenton process was studied.

Rhodamine B is an industrial and commercial cationic dye. Possible adverse effects include skin irritation, sarcoma, digestive tract irritation, neurotoxicity, and reproductive toxicity. As a result, it is vital to remove Rhodamine B from wastewater created by Rhodamine B-using enterprises before disposing it into any water body [3].

Various physical and chemical treatment processes have been used for RhB dye elimination in wastewater.

Adsorption of (RhB) dye was investigated using raw *Elaeis guineensis* frond fiber [10], raw and chitosan supported mesoporous adsorbents [11]. The effects of various additives such as iron (elemental, bivalent, and trivalent), carbon tetrachloride, hydrogen peroxide, tert-butyl alcohol, salt (Na_2SO_4), sucrose, and glucose on the sonochemical destruction of RhB, in the aqueous phase, was studied by Marouani et al. [12]. The present paper questions the electro-Fenton procedure and a combination of electro-Fenton and ultrasonic irradiation (sono-electro-Fenton) in order to examine the performance of the platinum grid (Pt) as anode and stainless steel plate as the cathode, using Na_2SO_4 as electrolyte and under acidic aqueous solutions. The effect of the primary operational parameters such as applied current, temperature, Fe(II) concentration, electrolyte (Na_2SO_4) concentration and initial dye concentration.

Also, effect of real complex matrices has been investigated. In order to improve the degradation efficiency and reaction rate, the degradation of RhB using sono-electro-Fenton process was realized.

The impact of ultrasonic power on the sonoelectrochemical degradation of RhB, at room temperature was investigated.

The rest of the paper is structured as follows, materials and methods are presented in Section 2, results are presented and discussed in Section 3, and finally the conclusion Section.

2. Materials and methods

2.1. Chemicals

All of the chemicals were of analytical grade and were used as received, without any further purification. The characteristics of the selected dye are summarized in Table 1.

RhB powder was perched from (Sigma-Aldrich, USA) and used as received.

The molecular structure of RhB is shown in Fig. 1. Through the whole experiments, all required solutions

Table 1
Characteristics of Rhodamine B

Tetraethylrhodamine (Rhodamine B)	Abbreviation RhB*
Molecular weight	479.01 g/mol
CI number	45710
Synonym	Basic Violet 10; Brilliant Pink B_RhO_Tetrathyl rhodamine
Chemical class	Xanthene
Molecular formula	$C_{28}H_{31}N_2O_3Cl$
IUPAC name	N_[9_ortho_carboxylphenyl_6_(diethylamino)_3H_xanthen_3_ylidene]diethl ammonium chloride, which is a highly water soluble

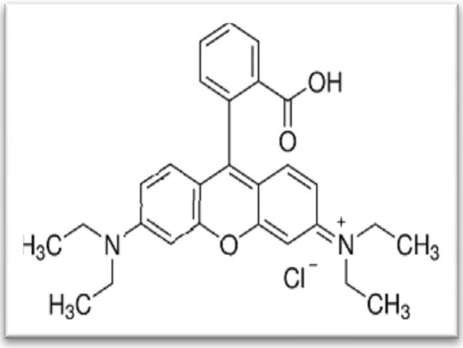

Fig. 1. Chemical structure of Rhodamine B (RhB), (Basic Violet 10).

were prepared by dissolving the corresponding amount of substrate into pure water, mineral water, spring water and seawater. Ferrous sulfate powder and sodium sulfate powder were purchased from Sigma-Aldrich (USA), sulfuric acid was supplied by biochem_lab (France).

2.2. Experimental procedures

The initial concentration of RhB solution was 10 mg/L for all experiments, except for those carried out to examine dye concentration. The setup we used can be found in [4].

Various aqueous solutions of RhB (10 mg/L) containing different additives were prepared by adding the required amount of the agents and stirring using a magnetic bar.

Experiments of the electro-Fenton process were performed in 300 mL cylindrical glass reactors with indirect current generated by the power generator and operated at 100 mA, unless the effect of power was examined. In addition, ultrasonic irradiation was introduced into the reaction by ultrasonic bath (YX-2080) at very low frequency and very low puissance.

An inoxidable steel plate (2.5 cm × 2.5 cm) was used as the working electrode (cathode). The counter electrode was platinum grid (Pt) (anode) (2.5 cm × 2.5 cm), and the distance between the two electrodes was fixed at 2 cm throughout the experiments. Continuous O_2 saturation at atmospheric pressure was assured by air bubbling through a frit before electrolysis. The current was supplied to the electrodes using Kleinspannungs Stelltrafo 52135 current generators. Rhodamine B is mixed with a supporting electrolyte to improve the conductivity of the mixture.

The initial Rhodamine B concentration was 10 mg/L. During the post-optimisation process, the solution was mechanically stirred with 10 mg/L of Fe(II) powder and 10 mg/L Na_2SO_4 as a supporting electrolyte. Except for assessing the effects of temperature, all experiments were carried out at room temperature. Before turning on the power supply, the initial pH of the dye solution was set to 2.5 by the adding pure H_2SO in all experiments in order to fixe pH during reactions (Fig. 2).

Experiments with ultrasound irradiation and the combination of ultrasounds and electro-Fenton process were performed with the same setup, the general framework of which is given in Fig. 3.

In the EF process, the electrode materials play a significant role. Hydrogen peroxide (H_2O_2) can be electrogenerated by the two-electron reduction of dissolved O_2 [Eq. (11)], as well as by the concomitant ferrous ion (Fe^{+2}) regeneration through (Fe^{+3}) reduction, depending on the cathode materials used [Eq. (12)]. The Fenton reaction causes both reagents to produce hydroxyl radicals (${}^{\bullet}OH$) in bulk solution [Eq. (13)] [10].

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{11}$$

$$Fe^{+3} + e^- \rightarrow Fe^{+2} \tag{12}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \tag{13}$$

Nadais et al. [16] improved that for all the compounds studied, a decrease in apparent reaction rate was observed at pH values above 2. Previous electro-Fenton studies indicate that the optimum pH is between 2.8 and 3.0. Where the ${}^{\bullet}OH$ may be propagated by the Fe^{+3}/Fe^{+2} catalytic behaviour couple. The available Fe^{+2} in the reaction medium is highest at a pH of 2.8. As a result, the Fenton reaction has the highest rate. At a pH 5, the Fe(III) species may precipitate as $Fe(OH)_3$, reducing the amount of catalyst in the solution and breaking down H_2O_2 into O_2 and H_2O.

This information was used to approximate the optimal pH, which can be influenced by the cathode material's composition. Hence, it was decided to sustain pH 2.5 in all other experiments [13].

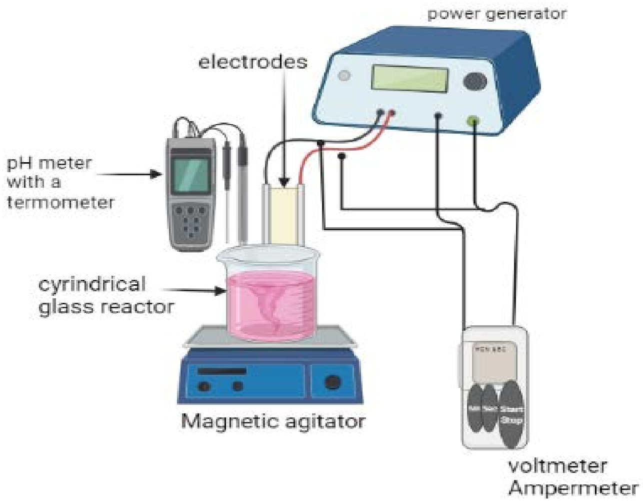

Fig. 2. Experimental setup used for electrochemical degradation of RhB.

2.3. *Analytical methods*

The concentration of Rhodamine B during the reactions was determinate by using UV-VIS (6705 UV/Vis Jenway Spectro, UV, France); adsorption spectra were acquired from 200 to 800 nm, revealing the desorption spectra of unmediated aqueous solution of RhB at varied concentrations. The absorption band is in the visible range, peaking 555 nm, which corresponds to pink color. The % removal was determined as it is shown below [15]:

$$\% \text{ Removal } = \frac{C_i - C_f}{C_i}$$

where C_i: initial dye concentration and C_f: final dye concentration.

3. Results and discussion

3.1. *Influence of temperature*

In order to clarify the effect of temperature during the treatment, dye solutions with initial pH = 2.5, 10 mg/L and Fe(II) were electrolyzed at 100 mA at different temperatures; the results are depicted in Fig. 4.

As the temperature rises between 25°C and 35°C ± 1°C, the rate of dye degradation increases, which can be attributed to a rise in the rate of organic reactions involving hydroxyl radicals. Probably because hydrogen peroxide produced at the cathode self-decomposes at high temperatures [Eq. (14)].

$$H_2O_2 \rightarrow H_2O + ½O_2 \tag{14}$$

The result obtained by increasing the temperature (over 35°C) appears to be the same as that obtained by increasing the electric current (over 200 mA). An increase in parasitic reactions, in particular, may explain this phenomena. At the anode, turning O_2 to H_2O has a negative impact on the formation of H_2O_2 and the development of H_2 [12].

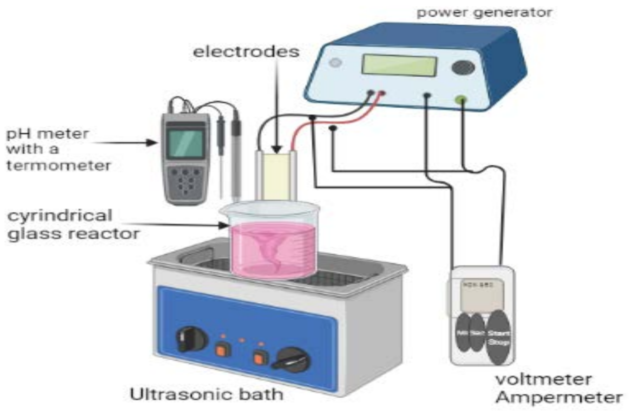

Fig. 3. Experimental setup used for sonoelectrochemical degradation of RhB.

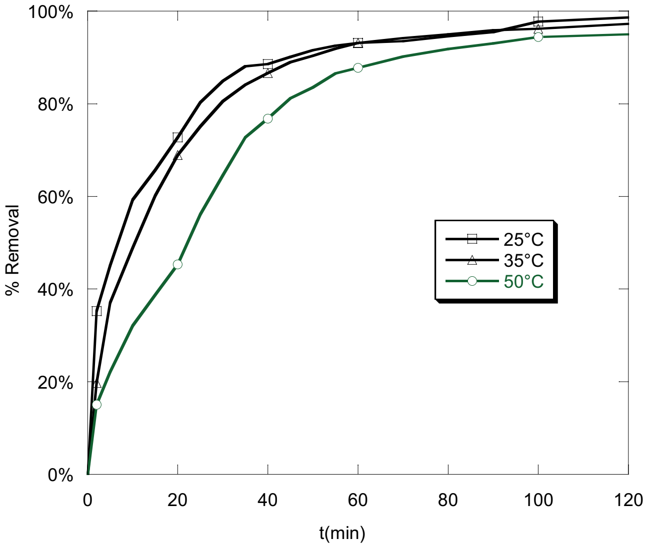

Fig. 4. Influence of temperature on electrochemical degradation of RhB (conditions: initial RhB concentration: 10 mg/L; pH 2.5; Na_2SO_4 concentration: 10 mg/L; electric current: 100 mA).

However, it is advisable to limit the temperature to 25°C ± 1°C in order to prevent the excessive release of hydrogen and other gases and to minimize other negative effects, including higher operating costs. It should be noted that the influence of temperature is less significant than other factors [16] and ambient temperature has been frequently used in many electro-Fenton process with good efficiencies.

As a result, 25°C ± 1°C is the optimal electrolysis temperature under our working conditions.

3.2. *Effect of Fe(II) concentration*

Catalyst concentration (i.e., Fe^{2+} ions) is an important parameter influencing EF process efficiency.

The degradation of RhB solution with an initial dye concentration of 10 mg/L was studied in the presence of different Fe(II) concentrations ranging from 5 to 20 mg/L at pH = 2.5, 10 mg/L of Na_2SO_4, and electric current of 100 mg/L. The results obtained are shown in Fig. 5.

The % removal in Fig. 5 shows that the catalyst concentration increases as the catalyst mass increases up to 10 mg/L. Beyond this value, a decrease in % removal is observed.

Thus, it is important to mention that the degradation rate of RhB dye was enhanced as the catalyst concentration increased up to 10 mg/L. This contrast could be justified by the fact that, in the degradation study, electrolysis requires a long time to oxidize the organic matter and, therefore, an important catalyst concentration in order to enhance the production of hydroxyl radicals. On the other hand, when the catalyst concentration is high in the medium, it accelerates the consumption of hydrogen peroxide, which is responsible for the production of hydroxyl radicals, reagents that improves the dependence of the production of hydroxyl radicals on the Fe^{2+}/Fe^{3+} catalytic cycle. For a catalyst concentration above 10 mg/L, the % removal decreases and becomes slow. This low elimination is due to the consumption of hydroxyl radicals by excess iron in solution, which promotes competitive reactions between hydroxyl radicals and excess ferrous ions according to Eq. (15).

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{2+} + OH^{-} \tag{15}$$

Thus, a concentration of catalyst Fe(II) equal to 10 mg/L was selected for the duration of this study.

3.3. Effect of applied current

The applied current controls the rate of H_2O_2, production, a critical parameter in the EF process, as well as the regeneration rate of the catalyst, thus affecting the wastewater efficiency. Several studies were conducted to investigate the effect of this parameter on the oxidative degradation of RhB. Experiments were carried out at various current levels ranging from 20 to 200 mA, and Fig. 6 depicts the obtained results.

This figure shows that, RhB was completely degraded by $^{\bullet}OH$ radicals at all applied currents between 20–200 mA, and the degradation rate increased with applied current.

This faster oxidation rate at higher current could be explained by an increase in the rate of H_2O_2 electro-generation as well as an acceleration of Fe^{2+} regeneration, resulting in greater Fe^{2+} production [17].

When the current intensity exceeded 200 mA (300 mA), the degradation rate decreased, this result is explained by an increase in parasitic reactions, particularly when O_2 is converted to H_2O, the formation of H_2O and the development of H_2 at the anode are impeded [12].

According to Lounis et al. [4], the increase in synthesis of the Fenton reagent is responsible for the increase in the rate of degradation with increasing current intensity up to 100 mA. The reaction mechanism is shown in Fig. 7. Similar results were reported by Özcan et al. [18] who indicated that the degradation kinetics of picloram (0.125 mM/150 mL) increased with increasing current intensity up to 300 mA, above this value no ameliorative effect was observed.

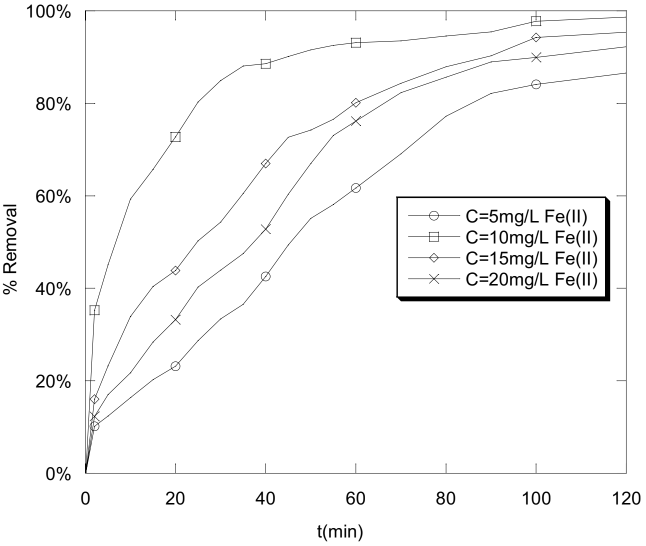

Fig. 5. Effect of Fe(II) concentration on electrochemical degradation of RhB (conditions: initial RhB concentration: 10 mg/L; pH 2.5; Na_2SO_4 concentration: 10 mg/L; electric current: 100 mA; temperature 25°C).

It was observed that at a current intensity of 20 mA, RhB degradation efficiency was 90% after 120 min of treatment (Fig. 6). But at 100 and 200 mA, the degradation efficiency was improved to near 100% (99%). In light of these findings, any increase in current is pointless, since it generates an overconsumption of electrical energy without improving the deterioration kinetics. Consequently, electrochemical oxidation of RhB, using a platinum grid as anode and stainless steel as the cathode is favoured at current equal to 100 mA.

3.4. Effect of Na_2SO_4 concentration

Based on previous documented information, we decided that the supporting electrolyte used in our research is the Na_2SO_4; Ghoneim et al. [19] found that when comparing Cl electrolytes of the same concentration, aqueous solutions containing SO_4^{2-} decolorized the Sunset Yellow azo dye at the fastest rate. This is consistent with previous research, which found that the efficiency of Fenton-like oxidation is decreased in the presence of Cl ions, whereas in the presence of SO_2^{2-} the effect is marginal. This is due to the higher conductivity of SO_2^{2-} electrolyte compared to Cl [14].

Because oxidation of the analysed RhB by electro-generated Fenton's reagent was faster in a 10 mg/L Na_2SO_4 solution, it was studied in Na_2SO_4 solutions of varied concentrations (5, 10, 15, and 30 mg/L) using the previously optimized operating parameters. With 10 mg/L Na_2SO_4 as a supporting electrolyte, the oxidation of the studied RhB by electro-reagent Fenton's was substantially faster and more efficient.

The obtained results are presented in (Fig. 8). The % removal is estimated to 92.73%, 98.75%, 97.64% and 96.78% at 5, 10, 15 and 30 mg/L.

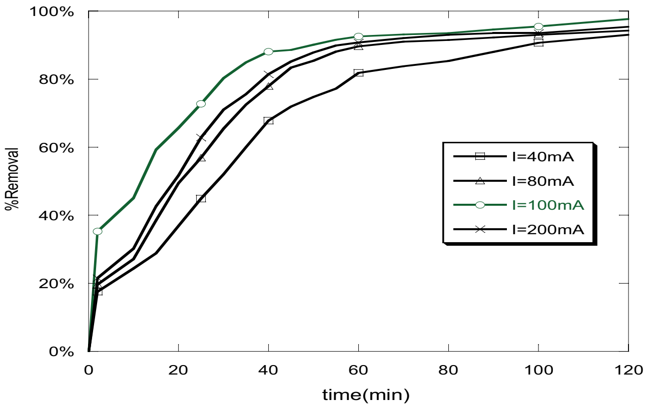

Fig. 6. Effect of applied current on electrochemical degradation of RhB (conditions: initial RhB concentration: 10 mg/L; pH 2.5; Na_2SO_4 concentration: 10 mg/L; Fe(II) concentration: 10 mg/L; temperature 25°C).

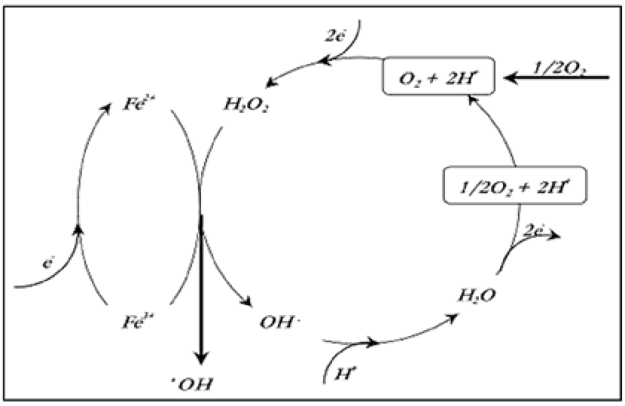

Fig. 7. Electro-Fenton reaction mechanism.

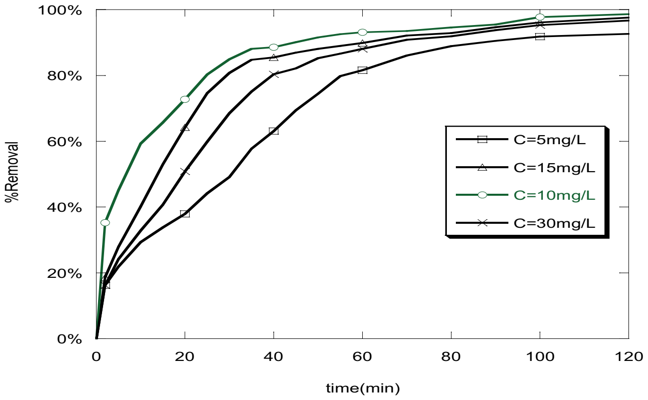

Fig. 8. Effect of Na_2SO_4 concentration on electrochemical degradation of RhB (conditions: volume: 200 mL; initial RhB concentration: 10 mg/L; pH 2.5; Fe(II) concentration: 10 mg/L; temperature 25°C).

Eq. (16) can account for the possibility of high SO_4^{2-} concentration consuming the generated hydroxyl radical [14].

$$^\bullet OH + SO_4^{2-} \rightarrow OH^- + SO_4^{\bullet -} \tag{16}$$

At 10 mg/L, the Na_2SO_4 concentration would be optimal (Fig. 7). As a result, it was chosen as a supporting electrolyte for the remainder of the current study.

3.5. Effect of initial dye concentration

The effect of the initial dye concentration on the rate constant at an optimum pH of 2.5, a Fe^{2+} concentration of 10 mg/L and Na_2SO_4 concentration of 10 mg/L is shown in Fig. 9. The current density was kept constant at 100 mA, with RhB concentrations of 5, 10 and 20 mg/L.

The results show that the initial RhB concentration has a clear impact on the degradation efficiency.

This tendency can be explained by the development of intermediate products that are more difficult to oxidize than RhB and so require more $^\bullet OH$ to degrade [19]. In addition, while the amount of RhB in solution increased, the amount of $^\bullet OH$ generated remained constant. As a result, the quantity (steady state concentration) of $^\bullet OH$ in RhB oxidation becomes the limiting reagent [20]. The reason for this is the energy expenditure, which is related to the amount of organic and the number of electrons engaged in the conversion of organic matter to CO_2 in the treatment process [15].

Under the same conditions, equivalent amounts of oxidants are created in the reaction system. The generated oxidants are adequate to oxidize the quantity of pollutants in solution at low beginning concentrations. As a result, the deterioration efficiency was found to be greater. On the other hand, the oxidants generated at greater beginning concentrations are insufficient to induce the same rate of oxidation as the higher dye concentration. Furthermore, the decrease in removal efficiency at higher concentrations was attributed to competition between various pollutant molecules and/or intermediates produced during the oxidation process. Both the contaminant and its transformation products could compete for the hydroxyl radical produced [4]. Molla Mahmoudi et al. [20] studied the effect of initial diazinon concentration on diazinon degradation efficiency, according to their interpretation. When the concentration of diazinon goes up, it breaks down less. This can be explained as follows:

- Because all samples were subjected to the same conditions, the amount of hydroxyl radicals produced at each starting concentration of diazinon was identical. As a result, at low diazinon concentrations, the hydroxyl radicals may quickly eliminate a substantial proportion of the pollutants in the reaction chamber, but as the contaminant concentration rises, the number of radicals available will be inadequate to further degrade them.
- The creation of intermediates at higher diazinon concentrations may result in competition between diazinon molecules and intermediates with hydroxyl radicals, resulting in a reduction in removal efficiency; this is in line with our results [21].

These findings suggest that a relatively the initial dye concentration 10 mg/L was more effective for degradation of RhB dye.

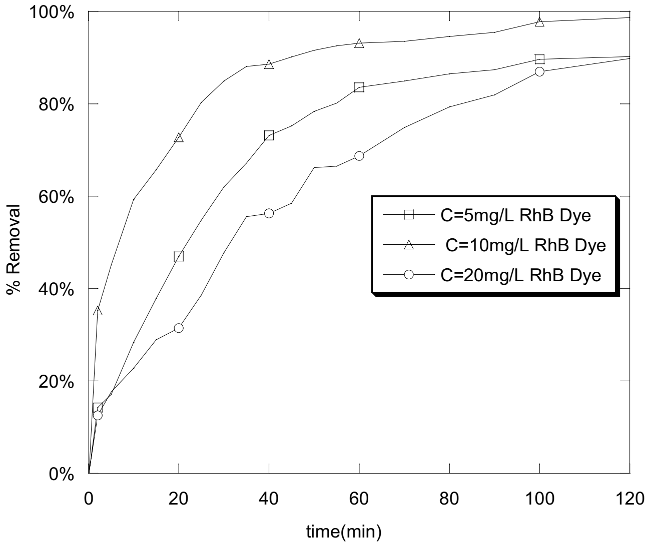

Fig. 9. Effect of initial dye concentration on electrochemical degradation of RhB (conditions: pH 2.5; Na_2SO_4 concentration: 10 mg/L; Fe(II) concentration: 10 mg/L; temperature 25°C).

3.6. Effect of real complex matrices

Several studies have investigated the degradation of pollutants by electro-Fenton, but only a few have investigated the impacts of water matrices. As a result, determining the impact of inorganic compounds and organic species present in natural mineral water, spring water and saltwater on pollutant EF process degradation is of particular interest. To test this and assess the applicability of the electrochemical therapy to real-world water treatment, although research on the degradation of pollutants by electro-Fenton has been conducted, only a small number of studies have looked at the impacts of water matrices [4].

The RhB dye was dissolved in natural mineral water and saltwater to examine the applicability of electrochemical treatment to real-world water treatment.

The main properties of 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 mg/L, HCO_3: 210 mg/L, Cl^-: 15 mg/L, NO_3: 8 mg/L, pH 7.6, salinity: 300 mg/L.

The seawater has a high salinity (~35 g/L), which is composed mainly of Na^+: 11 g/L, Mg^{+2}: 1.3 g/L, Ca^{2+}: 0.4 g/L, Cl^-: 20 g/L, SO_4^{2-}: 3 g/L [4].

Fig. 10 shows the comparative degradation of RhB in pure water, natural mineral water, spring water and seawater.

It can be observed that natural matrices have no effect on the electro-Fenton degradation of RhB. As a result, it appears that the reduced degradation rate in saltwater compared to pure water is most likely attributable to high concentration of sodium chloride as well as organic matter.

3.7. Effect of ultrasonic power

Different experimental parameters were used to degrade RhB, including ultrasound alone, electro-Fenton alone, and a combination of ultrasound and electro-Fenton (sono-electro-Fenton) at ultrasonic powers. For an initial dye concentration of 10 mg/L, a Fe(II) concentration of 10 mg/L, a solution volume of 200 mL, a supporting electrolyte concentration (Na_2SO_4) of 10 mg/L, pH = 2.5 and an electric current of 100 mA, in room temperature, the impact of the ultrasonic power on the sonoelectrochemical degradation of RhB was investigated. Fig. 10 depicts the acquired results.

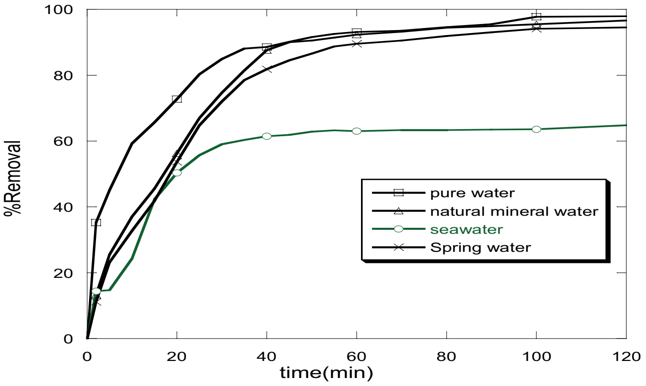

Fig. 10. Effect of real complex matrices on electrochemical degradation of RhB (conditions: pH 2.5; Na_2SO_4 concentration: 10 mg/L; Fe(II) concentration: 10 mg/L; temperature 25°C).

Only 15% degradation of RhB was achieved after 90 min of sonication at very low ultrasonic power as a single procedure. On the other hand, the electrochemical approach, eliminated 90% of RhB after 90 min of treatment. A considerable improvement in RhB degradation was reported when ultrasound and electro-Fenton were combined (sono-electro-Fenton). Complete removal (100%) was obtained after 90 min, which is schematized in Fig. 11.

The following is an explanation of the synergistic enhancement of the sonoelectrochemical degradation rate. Ultrasonic irradiation has chemical and physical impacts on sanitary processes. Ultrasound has chemical consequences due to acoustic cavitation. In this process, high temperatures and pressures can be generated inside cavitation bubbles, leading to the thermal decay of water molecules into OH^- and H+ [4].

Because the yield of OH radicals produced during low-frequency sonolysis is so low, sonication alone results in a very low degradation rate, demonstrating that the chemical impact associated with ultrasound is not the most important factor in RhB degradation.

As a result, the physical consequences of sonication-induced cavitation have a substantial impact on the decreasing efficiency of the sono-electro-Fenton process. It appears that ultrasonic improves the electro-Fenton process by increasing mass transport and electrode activation by eliminating the impurity layer on the electrode surface. In addition, ultrasound can assist in electro catalytic oxidation and free radical reduction. Trabelsi et al. [21] confirmed that low frequency ultrasound increases mass transfer values. They calculated that at 20 kHz (20 W), mass transfer is 120 times greater than diffusion, with a maximum on the reactor axis (area between the electrodes). It was claimed that ultrasound can improve the efficiency of H_2O_2 electro generation via cathodic O_2 reduction. Li et al. [22] observed that the electrochemical production

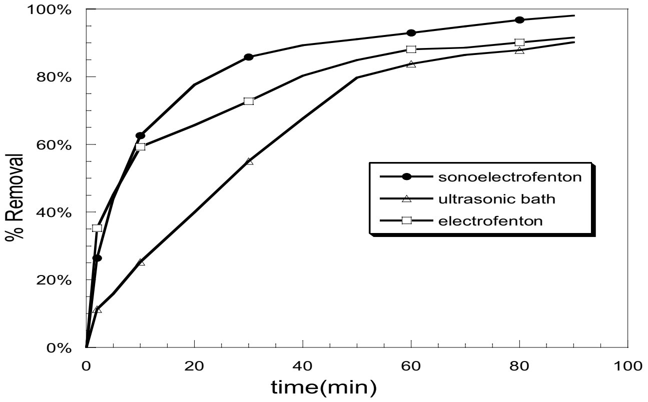

Fig. 11. Effect of ultrasonic power on electrochemical degradation of RhB (pH 2.5; Na_2SO_4 concentration: 10 mg/L; Fe(II) concentration: 10 mg/L; temperature 25°C).

of H_2O_2 rises in the presence of ultrasound at 20 kHz (80–160 W). In this context, Oturan et al. explained how rapid mass transfer Fe^{3+} and O_2 to the cathode, as well as Fe^{2+} and H_2O_2 to the solution, improved the electro-Fenton process in the presence of ultrasonic irradiation, resulting in an increase in the rate of production of $^{\bullet}OH$ and thus accelerating the degradation of organic matter. However, because of the improved hydrodynamic conditions, the $^{\bullet}HO$ develop more rapidly. It can be deduced that the sono-electro-Fenton method promotes the generation of a greater number of $^{\bullet}OH$ than the electro-Fenton method, without the need for a prior increase in the applied current intensity. This indicates the effectiveness of this process for the treatment of organic pollutants [22].

4. Conclusion

The removal of Rhodamine B (RhB) from an aqueous medium by sonochemical and electrochemical treatments has a promising synergistic effect. The synergistic effect of sonoelectrochemical treatment in a low-frequency, low-power ultrasonic bath with a 100 mA platinum electrode has been demonstrated. Experiments with natural mineral water and seawater have shown that the electrochemical method is ineffective in degrading RhB in complex matrices such as natural mineral water and seawater. Because of the speed and efficiency with which RhB is broken down in the electro-Fenton system, this is an intriguing method for treating wastewater containing the dye. The obtained results shown the efficiency of the experimental method carried out. However, the present study has only investigated electro-Fenton and combination between electro-Fenton process and the sono-electro-Fenton for degradation of azo dye RhB. Thus, in order to achieve a closely exhaustive investigation, further studies, which take the kinetic of degradation into account, will need to be undertaken. The results obtained demonstrate the effectiveness of the experiment conducted. However, the present study has only examined electro-Fenton and a combination of electro-Fenton and sono-electro-Fenton for the degradation of the azo dye RhB. For a complete analysis, more research is needed that takes into account the kinetics of degradation.

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