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Designing a simple electrochemical method for ozone generation and using for removal of C.I. Reactive blue 203 (RB 203) from textile wastewater

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Abstract

Textile wastewater is one of the most important environmental pollutants. These wastewaters are containing different kinds of dyes, chemicals and salts. Therefore, it is required to remove these dyes and chemicals from wastewaters before discharging them into the environment. One of the best methods to remove these dyes and chemicals from wastewater is using oxidation agents such as H_2O_2, O_3 and etc. Ozone is an important and eco-friendly oxidizing agent that is widely used in the purification of wastewater, water disinfection and decomposition of organic materials. The main aim of this study is the investigation of the degradation of RB 203 (textile dye) from aqueous solutions by using electrochemical ozone generation with a titanium anode electrode modified with a mixture of nickel, antimony and tin oxides. Some parameters such as the pH of the solution, current density and ozonation time were optimized and finally, the kinetics of the removal of RB 203 was investigated. The results showed that removal of the dye (100 ppm) from the solution increased by increasing ozonation time at a constant current density of 20 mA/cm^2 for 40 min electrolysis and it was removed from solutions with an efficiency of 99%.

Keywords: Electrochemical ozone generation, Modified titanium electrode, Wastewater treatment, Degradation of textile dye, C.I. Reactive blue 203 (RB 203)

1. Introduction

Water is one of the most important substances in the world. In general, the lack of healthy water in the environment is harmful to industry, humans, and other organisms. In most industries, water is the start point of the production process and can affect the quality and quantity of the product directly or indirectly. For example, it is widely used in the textile industry for washing, dyeing, bleaching, and printing (at least 200 to 400 liters per kilogram of finished textile). According to

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the annual reports, 700,000 tons of dyes are produced and used for the textile process, which an average of 280,000 tons of them include 8,000 types of dyes and 6,900 kinds of other chemicals which are discharged into the factory's wastewaters. Also, it is estimated that for 100 kilograms of finished textile products, an average of 100 kilograms of dye and other additives is used [1-3]. RB 203 is one of the most important textile dyes, which have widely used in dyeing cellulosic fibers [4]. This dye has a conjugated diazo structure, and the maximum wavelength absorbance of this dye is 594 nm (Figure 1).

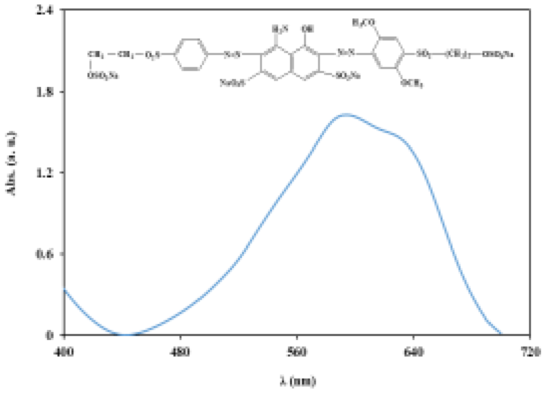

Fig. 1. UV-Vis spectrum and the structure of RB 203 dye with (100 ppm)

The RB 203, existing in textile wastewater, must be degraded before discharged into the environment. One of the best ways to remove this group of dyes (azo structures) is the use of ozone. Ozone is one of the most important gases in the earth's atmosphere. It is an allotrope of oxygen with O_3 formula, which has a nasty smell. This gas naturally produced in nature from some sources such as lightning and sunlight. Also, it is generated by a lot of methods such as cold corona discharge, photochemical, electrochemical, etc. [5]. Ozone was used first-time as a germicidal in water purification, and then due to high oxidation potential, it was used in wastewater purification, bleaching of paper etc. According to this point that ozone is an unstable molecule, it was necessary to produce ozone at the consumption place [6]. Therefore, some new research have been improved for ozone generation. In this study, the electrochemical method was used due to some advantages such as low cost, simple design, low required voltage, easy cooling of the electrode in water, the possibility of removing the toxic pollutants, high production efficiency, low repair cost and maintenance, the possibility of application in continuous processes, non-production of NO_x gas during the process and production of ozone solution with high concentration [7]. The most important challenge in the electrochemical method for ozone generation is the selectivity of the water decomposition reaction. Because the potential of the oxygen production reaction from water oxidation (1) is lower than the ozone production reaction (2) thermodynamically so, the reaction of ozone generation will be accompanied by the production of some oxygen [8].

$$2H_2O \longrightarrow O_2 + 4\,H^+ + 4\,e^- \qquad V_0 = +1.23 \text{ V vs RHE} \qquad (1)$$

$$3H_2O \longrightarrow O_3 + 6\,H^+ + 6\,e^- \qquad V_0 = +1.51 \text{ V vs RHE} \qquad (2)$$

Recently, various electrodes have been used for dye and chemicals degradation. In 2014, Parsa et al. performed the degradation of acid red 33 from dye solution (94% dye degradation) using titanium electrode modified with tin dioxide [9]. Subsequently, this group performed the degradation of acid red 33 from dye solution with a titanium electrode modified with carbon nanotubes [10] and titanium dioxide [11]. Clematis et al. in 2017 applied a boron-doped diamond electrode for degradation of Safranin-T [12]. Chavez and coworkers performed the degradation of methyl orange dye with a titanium electrode modified with Ir-Pb, Ir-Sn and Pt-Pd-Ru oxides, while the slowest dye degradation was related to titanium electrode modified with platinum and palladium and rhodium oxide [13].

2. Experimental procedure

2.1. Materials and instruments

Titanium plate (98% purity) was purchased from Boaji China and other chemicals such as sodium hydroxide, acetone, oxalic acid, tin tetra-chloride ($5H_2O$), nickel di-chloride ($6H_2O$), antimony tri-chloride, absolute ethanol, phosphoric acid, hydrochloric acid, nitric acid, 2 butanol and tetrabutyl orthotitanate were prepared from Merck. Textile dye C.I. Reactive blue 203 by the commercial name of Ramazol blue was purchased from Dye Star company of Germany.

In order to prepare the anode electrode, spin-coat V-coat 3, ultrasonic bath Ultra, oven (Paat Ariya Sanat), furnace (Exciton, 2 Liters), Sartiorius scale (accuracy of ±0.1 mg) and wire-cut (DK-7740) were used. Also for investigation of the electrochemical properties of the fabricated electrode a potentiostat/galvanostat device (Autolab PGSTAT302 N) and NOVA software of 2.1, Sama 500 for coulometry tests while Ag/AgCl/KCl saturated electrode was used as reference and platinum electrode as counter electrodes. SEM and EDX devices (X-PRO) were used for investigation of the surface morphology and the analysis percentage of material on the electrode surface. For determination of the dye concentration and produced ozone concentration, an analytical spectrophotometer (Analytik Jena – Specord 250) was used. The pH was measured with a Metrohm 691 device and a magnetic stirrer of Hediolph Hei-Mix S.

2.2. Procedure

Electrode preparation

In this study, a titanium plate (with a thickness of 0.2 mm and a geometric area of 64 mm^2, width of 2 mm and a length of 42 mm handles for connection) with an accuracy of 0.01 mm was cut. One of the important factors in the quality of coverage and stability of this electrode is the initial cleaning of their surface. Therefore, the electrode surface was washed in two steps, at first, the electrode was placed for 1 h in sodium hydroxide (40 % w/v) at 90 ˚C and then the titanium electrode was rinsed with acetone for 15 min. After these two steps, the electrode surface was etched for 1 h with boiling oxalic acid solution (15% w/w), to rough the surface of the electrode and increase the adhesion of metal salts on the electrode surface. Finally, the etched titanium electrode was subjected to an ultrasonic wave for 1 h, in this step, the remaining material on the surface of the titanium electrode was separated from the surface due to the cavitation phenomenon and the surface was cleaned. After this step, the electrode was dried for 10 min at 110 ˚C [14].

To improve the adhesion of the modifier on the electrode surface, a solution of 2 butanol and tetrabutyl orthotitanate (20/80 v/v) in nitric acid (0.1 M) was prepared. Then, 10 µL of the prepared solution was injected at the titanium substrate and layered in two steps spin-coat. The initial layer process was set for 20 s and 500 rpm and the second layer process was done for 30 s and 1500 rpm.

After coating, the electrode was dried at the oven at 110 ˚C for 15 min and finally calcined in the furnace at 520 ˚C for 20 min. The fabricated electrode was placed in a two-electrode system with a counter electrode of platinum wire in an electrolyte containing sodium sulfate (5%) for 5 min and application of the cathodic current of 5 mA/cm^2 thus the prepared titanium dioxide layer was reduced to titanium hydride [15].

In order to modify the electrode surface, first a solution of metal salts of tin tetra-chloride, antimony tri-chloride and nickel di-chloride with a molar ratio of 1: 8: 500 in ethanol was made. Then, 10 µL of the prepared solution was layered in two steps by the Spin-coat method (20 s at 500 rpm and 30 s at 1500 rpm). The electrode was then dried for 15 min at 110 ˚C and finally calcined for 15 min at 520 ˚C.

To ensure the complete coverage of the surface, this step was repeated 22 times and in the last step, the electrode was calcined at 520 ˚C for 1 h. The electrochemical characterization of the modified electrode was performed according to the method reported by Wang et al. and the ozone generation was done by the UV-Vis spectroscopy method at the wavelength of 258 nm [8].

Electrochemical degradation of RB 203

In order to investigate removal of the RB 203 (textile dye), the dye solution was prepared and then the dye degradation was done in a two-electrode system containing a modified electrode as an anode and platinum electrode as a cathode in an electrochemical cell. The electrochemical cell contained 4 mL of dye solution (3 different groups of dye solution was prepared: without adjusting pH, the dye solution in deionized water at 100 ppm of dye concentration, with adjusting pH, for adjusting pH, the dye solution was prepared in different pH of phosphate buffer at 100 ppm of dye solution and for optimization of the initial concentration of dye, different dye concentration was made in phosphate buffer pH=4) and a constant current density of 20 mA/cm^2 was applied at different times using the coulometry technique to electrochemically ozone generation. Then, the absorption of samples at different times was tested using a UV-Vis spectrophotometer. To evaluate the degradation efficiency of dye at various times, the equation 1 was used [16], while C_0 is the initial dye concentration and C_t is the dye concentration at time t.

$$\text{C.R.E (\%)} = 100\times \frac{(C_0 - C_t)}{C_0} \qquad (1)$$

The constant rate of dye degradation reaction during the time was calculated by using the equation 2 [17], while (dC/dt) is the changes of dye concentration vs. time, n is the different orders of reaction (0, 1 and 2) and k is the constant rate of reaction. All experiments were performed 3 times.

$$dC/dt = k.C^n \qquad (2)$$

3. Results and discussion

3.1 Characterization of the modified electrode

First, the electrochemical characteristics and the modification of the titanium electrode surface with mixed metal oxides, tin, antimony, and nickel, and the titanium electrode were investigated. Then, to find the optimal conditions for ozone generation the current density was optimized, then for optimizing the dye degradation the various parameters such as pH of the solution adjust by phosphate buffer, electrolysis time, initial dye concentration and kinetics order of dye degradation were investigated.

Figures 2 (A) and (B) show the SEM images of non-modified titanium after washing and chemical etching, and modified titanium with nanocatalysts (mixed metal oxides). As can be seen, the electrode before modification has a porous and rough surface while after modification of the electrode, the porous are filled with nanocatalysts and create a new surface with small cracks which increases the effective surface area and consequently more electron transfer in the solution.

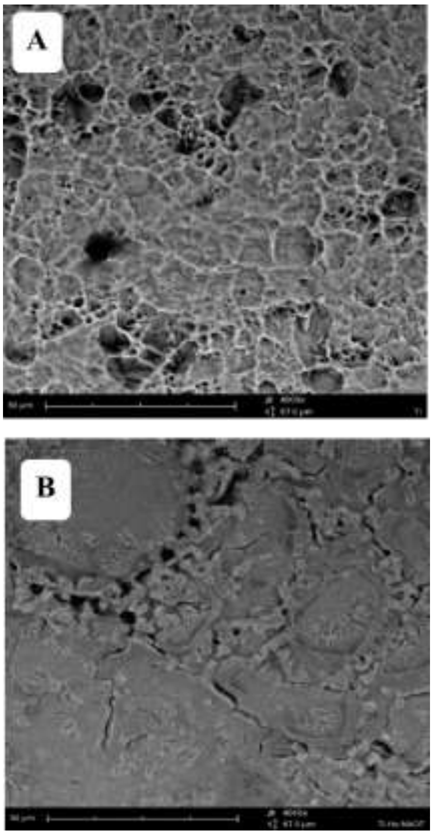

Fig. 2 (A) and (B) the SEM images of non-modified and modified electrodes with magnification of 30 µm

Figures 3 (A) and (B) shows the EDX spectra and the percentage of elements on the surface of the non-modified and modified electrodes. Figure 3 (B) shows that the elements properly covered the surface with specified percentages. In the taken spectrum, the titanium peak appears in the area of 3-4 keV [18], which overlaps with the tin oxide peaks [19] and the antimony [20]; also, the nickel peak appears in the area of 7-8 KeV [21]. The percentages of available elements are shown in inset figure 3 (A) and (B) by EDX which confirm these results.

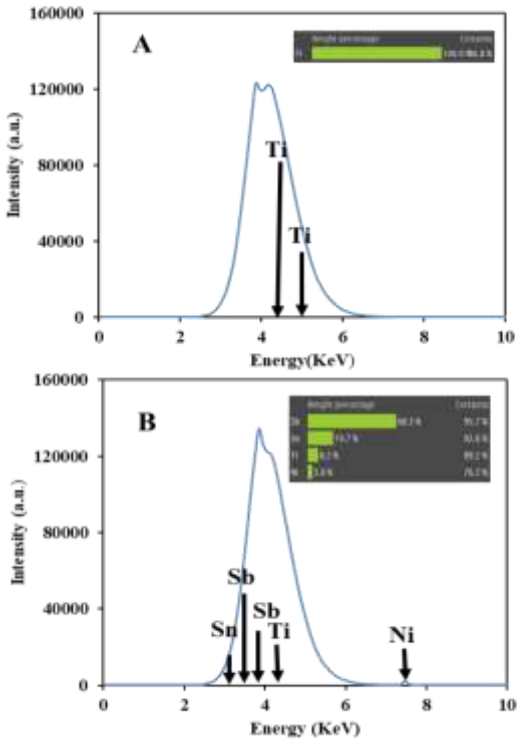

Fig. 3 (A) and (B) the EDX images of non-modified and modified electrodes and insets the percentage of available elements, respectively.

For the characterization of the modified and non-modified electrodes, their cyclic voltammograms in a three-electrode system containing the work electrodes of modified titanium and non-modified titanium electrodes, the platinum wire and (Ag/AgCl) as counter and reference electrodes, respectively in phosphoric acid (0.1M, pH 1.54) at a scan rate of 50 mV/s, at room temperature were plotted. Figure 4 (A) shows that the oxidation of water does not show a significant current on the bare titanium electrode (non-modified). Also, shows the modification of the electrode surface, significantly increases the anodic current density at a potential of 1.9 V. So, the oxygen production is stopped kinetically, and the initial potential for the oxidation of the water is over potential of oxygen production. Therefore, the electrode has good selectivity for ozone generation. Due to this point that ozone has an absorption peak in 258 nm, the ability of ozone generation by modified and non-modified electrodes was tested by electrolysis process (the current density of 20 mA/cm^2 for 25 min at room temperature) in a two-electrode system containing the modified titanium and non-modified titanium electrodes as an anode (working) electrodes and platinum as a cathode (counter) electrode in phosphoric acid solution (0.1 M). Figure 4 (B) shows the UV-Vis spectrum of ozone at a wavelength of 258 nm for two electrodes (modified and non-modified). As can be seen, the ability of ozone generation for the modified electrode has been increased significantly compared to the non-modified electrode (0.098 Abs.= 1 mg/L O_3) [8].

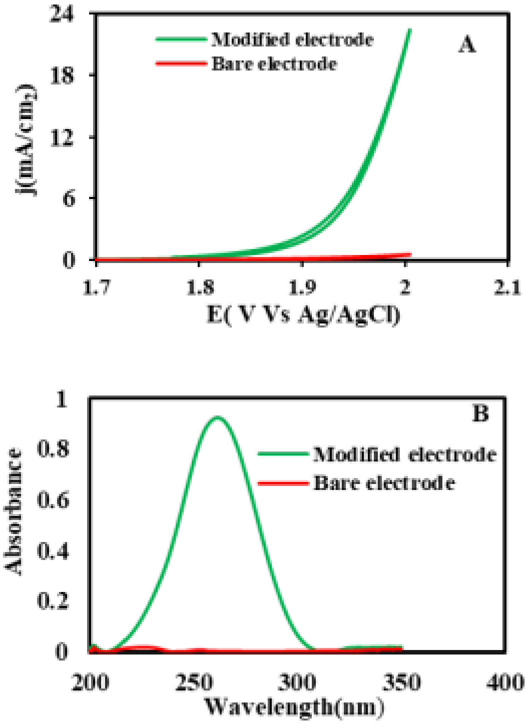

Fig. 4 (A) The cyclic voltammograms of the modified and non-modified electrodes in phosphoric acid solution (0.1M) and a scan rate of 50 mV/s and (B) the absorption spectrum of phosphoric acid solution (0.1M) after electrolysis with modified and non-modified electrodes during electrolysis process (25 min and a current density of 20 mA/cm^2 at room temperature)

3.2 The optimization of the effective parameters

In this study, first the current density for ozone generation was optimized and then for RB 203 degradation, some parameters such as pH of the solution (using phosphate buffer solution), initial concentration of dye, electrolysis time and kinetics order of dye degradation were investigated.

Optimize current density for ozone generation

To improve the performance of the electrode, the current density for ozone generation was optimized. The current density in the range of 5 to 60 mA/cm^2 during 2 min of electrolysis in the phosphoric acid (0.1 M) was done. The results showed that by increasing the current density up to 20 mA/cm^2, the current efficiency of the ozone generation was increased and then slowly decreased. This is probably related to the competition between ozone production and oxygen production or increasing the electrode temperature during the electrolysis process, which can lead to ozone degradation. Therefore, the optimum value of the current density for dye degradation process was selected 20 mA/cm^2.

Optimize pH for electrochemical dye degradation

One of the effective parameters on the dye degradation efficiency is the pH of the solution. To study the dye degradation in ozone process, at first the dye solution was prepared in deionized water (100 ppm). During the electrolysis it was observed that the pH of the dye solution changed versus time during the ozone degradation process (from 5.9 to 3.1). This is due to the oxidation of water and the ozone generation which is associated with protons production (according to Equation (1)). However, other reason for this change is due to the breaking of the dye azo bond and forming the organic acids with smaller molecules [22-24]. So for this purpose, the dye solution was prepared (100 ppm) in phosphate buffer with different pHs of 2.0, 4.0, 5.0, 7.0, 9.0 and 12.0 and then the electrolysis was done by applying a current density of 20 mA/cm^2 in 25 min. The results showed that the dye degradation efficiency at pH= 4.0 is higher than other pHs. As a result, the pH of 4.0 was selected as the optimum value of pH (Figure 5).

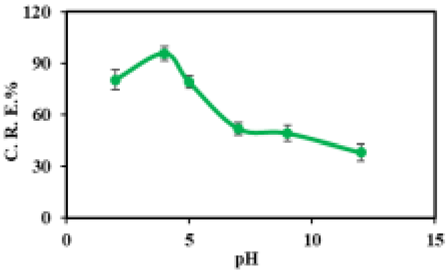

Fig. 5 The effect of pH of solution on the dye degradation efficiency at 25 min at room temperature

The initial concentration effect study

The initial concentration of the dye is an important factor in the efficiency of the dye degradation process. For this purpose, the selected dye (RB 203) was prepared in various concentrations of 5, 10, 20, 50, 100, 200, and 300 ppm in phosphate buffer solution (pH = 4.0), then electrolysis process was done (current density of 20 mA/cm^2 for 10 min). As shown in Figure 6, by increasing the dye concentration from 5 to 300 ppm, the dye degradation efficiency values are decreased (from 97% to 47%). This phenomenon is depending on the amount of generated ozone which is limited and it can be degraded a constant mole of dye in solution, thus by increasing the concentration of the dye the dye degradation efficiency is decreased. Since the amount of remained dye in the wastewater after dyeing is more than 100 ppm and also there was not a big difference between the dye degradation efficiency of the solution with the dye concentration of 100 ppm to 300 ppm, the concentration of 100 ppm was chosen for the investigation of the kinetics of dye degradation. This has been confirmed in other studies [16].

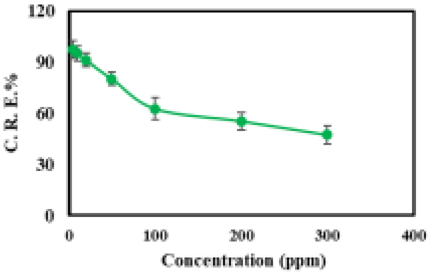

Fig. 6 The diagram of the percentages removal of the RB 203 efficiency at 10 minutes' electrolysis at room temperature versus the initial dye concentration

The effect of electrolysis time on the dye degradation

For the investigation of the electrolysis time effect on the dye degradation during ozonation process, the dye was prepared in phosphate buffer pH=4 and dye with initial concentration of 100 ppm. Then, the electrochemical dye degradation was performed in a two-electrode system (with the modified electrode as anode and Pt electrode as cathode) with a current density of 20 mA/cm^2 in an electrochemical cell (volume of 4 mL) in the time range of 0 to 40 min and the changes in dye concentration and kinetics order of the dye concentration at different contact times were examined.

In order to determine the dye concentration after degradation process, first, the absorption spectra of RB 203 in the concentrations of 1, 2, 4, 5, 8, 10, 20, 30 and 40 ppm were measured and the calibration curve was plotted. And then, using the calibration curve the dye concentration after degradation was measured (Figure 7).

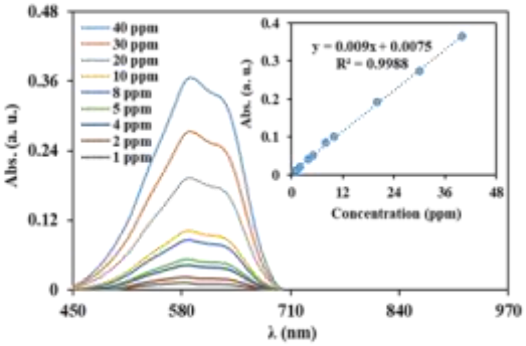

Fig. 7 The absorption spectra of the RB 203 dye at concentrations of 1, 2, 4, 5, 8, 10, 20, 30, and 40 ppm, Inset: the calibration curve (dye absorption values vs. dye concentration)

Figure 8 shows the absorption spectra of the RB 203 after dye degradation at different times. As can be seen, the absorption value decreases with increasing the electrolysis time and the percentage of dye degradation efficiency increases to 99% after 40 min electrolysis (inset figure 8). This is directly related to the amount of produced ozone during the electrolysis process.

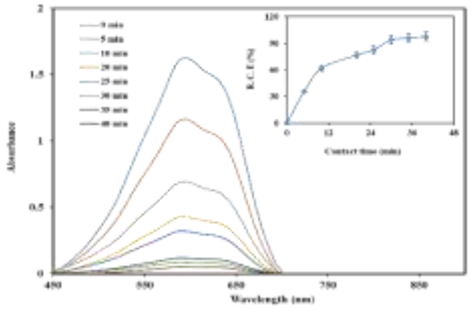

Fig. 8 The absorption spectra of RB 203 after dye degradation at different electrolysis times, inset: the percentage of dye degradation efficiency at different electrolysis times

The investigation of the kinetics order of dye degradation

To investigate the kinetics order of dye degradation, first the dye solution was prepared in phosphate buffer pH=4 and dye with initial concentration of 100 ppm and concentration of dye after different times of electrolysis was measured and then the kinetic orders of zero, one and two under the optimum conditions were examined. According to the calculated correlation coefficient in three kinetic models, it is observed that the kinetic process of dye degradation follows the first-order kinetics (Table 1).

Table 1 Investigation of the kinetic order of RB 203 degradation

Kinetic order	k	R^2
0	2.299	0.9252
1	0.0927	0.9901
2	0.0058	0.7982

To calculate the kinetics order of dye degradation the equation 3 was used. In this equation, C_0 is the initial concentration of dye, C_t is the concentration of dye at t and k is the constant rate of dye degradation reaction. The obtained slope from drawing the diagram of $\ln C_0/C_t$ versus time of ozonation is equal to the constant rate of the dye degradation process (Figure 9).

$$C_t = C_0 \exp(-Kt) \quad (3)$$

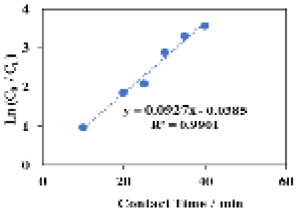

Fig. 9 The kinetic diagram of the RB 203 degradation using the modified electrode.

4. Conclusion

In this study, ozone was generated electrochemically using a modified titanium electrode and it was used for degradation of the RB 203 from dye solution. First, titanium electrode was modified with nickel, antimony and tin salts by spin coat layering and pyrolysis, then it was used as an anode electrode in a two-electrode system in an electrochemical cell containing dye solution (100 ppm) and electrolysis process was applied (current density of 20 mA /cm^2 for 40 min). The results revealed that the dye degradation efficiency increases with decreasing the initial concentration of dye and the prepared electrode has a good potential for complete removing the RB 203 dye (99% dye degradation efficiency). Also, this method for dye degradation is inexpensive and nearly simple.

Acknowledgments

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