



ISSN: 0975-833X

RESEARCH ARTICLE

ELECTROCATALYTIC DEGRADATION OF ACID BLUE 113 AZODYE VIA Rh/RhO/TITANIUM THERMALLY ACTIVATED MODIFIED ELECTRODE

*Mona A. Abdel-Fatah, Nabila H. Hussien and H. H. Shaarawy

Department of Chemical Engineering and Pilot Plant, National Research Center, Dokki, Cairo, Egypt

ARTICLE INFO

Article History:

Received 18th July, 2015
Received in revised form
05th August, 2015
Accepted 05th September, 2015
Published online 20th October, 2015

Key words:

Titanium,
Modified Electrodes,
Noble Metals,
Dyestuffs Electro-catalytic,
Oxidation.

ABSTRACT

The Removal of undesirable organic or dyestuff impurities from water through electrochemical processes is based on the selecting the suitable electrodes and potential/current conditions required for the degradation of these impurities. In this investigation the rhodium/rhodium oxide/titanium thermally activated modified electrode was used for the electrochemical degradation blue 113 azo dye in its aqueous solutions. The results of oxidation process electro generated Fenton's agent were expressed in terms of the remaining dye concentration and COD removal, which were determined instrumentally. The different operating conditions of treatment process were studied which include: current density, pH, and temperature, time of electrolysis, conductive electrolyte concentration, and initial dye concentration. The optimum operating conditions for each dye were determined. The under-test modified electrode gave good results for the complete removal of dye and COD.

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Citation: Mona A. Abdel-Fatah, Nabila H. Hussien and H. H. Shaarawy, 2015. "Electrocatalytic degradation of acid blue 113 azodye via Rh/Rho/tithermally activated modified electrode", *International Journal of Current Research*, 7, (9), 21191-21197.

INTRODUCTION

Water pollution is a prominent environmental problem witnessed across the globe. A large number of organic substances like dyes, phenols, pesticides, fertilizers, detergents and other chemical products are disposed of directly into the water system from various sources such as industrial effluent, agricultural runoff and chemical spills. Their toxicity, stability to natural decomposition and persistence in the environment has been the cause of much concern to society and regulation authorities around the world. The textile industry is one of the most polluting industries in term of discharge volume and effluent composition. The non-biodegradable dye effluent is characterized by strong color, high chemical oxygen demand (COD) with pH varying from 2 to 12. The removal of color and COD reduction poses greatest problems in textile industry (Ruth and Adrian, 1995; Naumczyk et al., 1996; Weixing et al., 1999). Also the improper handling of hazardous chemicals in textile water have some serious impact on the health and safety of workers putting them into the high-risk bracket for contracting skin diseases like chemical burns, irritation, ulcer etc. and even leads to respiratory problems.

*Corresponding author: **Mona A. Abdel-Fatah**,
Department of Chemical Engineering and Pilot Plant, National Research Center, Dokki, Cairo, Egypt.

Treatment of dyestuffs using different techniques such as adsorption (Ruth and Adrian, 1995; Naumczyk et al., 1996; Weixing et al., 1999; Ruth and Adrian, 1995), biological treatment (Weixing et al., 1999; Meyer and Carlsson, 1992; Guolin and Water, 1991), catalytic wet air oxidation (Opdycke, 1997; Perkowski and Lech, 1996) and ion exchange (Philipps and Boardranan, 1997) has been widely reported. Due to the large variability of the composition of textile wastewater, most of the traditional methods are becoming inadequate (Hao et al., 2000; Fernandes et al., 2004; Sakalis et al., 2005). In generally electrochemical oxidation and specifically The advanced oxidation using electrogenerated Fenton's agent for wastewater treatment has recently attracted a great deal of attention, mainly because of the ease of control and the increased efficiencies provided by the use of compact bipolar electrochemical reactors and by the large surface area of three dimensional electrodes (Lei et al., 1997; Lin et al., 1996; Joseph, 1996; Drower and Reed, 1987; Paprowicz and Slodczyk, 1988; Gatirel and Kirk, 1990). In electrocatalytic oxidation treatment of dye wastewater, Electrode material is the most important component in the electro-degradation system. Transition metal oxides can be used as the electrode by coating on inert inexpensive material (ArisMukimin, 2010).

On traditional electrode materials, such as Au, Pt, and C whilst the oxidation reaction by oxygen transfer is spontaneous, it is

characterized by low reaction rate constant. Oxygen transfer is usually favored on an anode material with high oxygen evolution over potential. Lead dioxide, is characterized by high oxygen over potential, therefore it is one of the most commonly used anodes for electrochemical degradation for many pollutants (Morsia *et al.*, 2011) particularly when it is doped with metallic cations whose oxides have low oxygen evolution overvoltage which improve the transfer rate of oxygen atom. So doping PbO₂ with bismuth improved the oxidation kinetics of several organic compounds, due to the formations of a low surface density at the bismuth oxide (Bi₂O₃) sites (Morsia *et al.*, 2011).

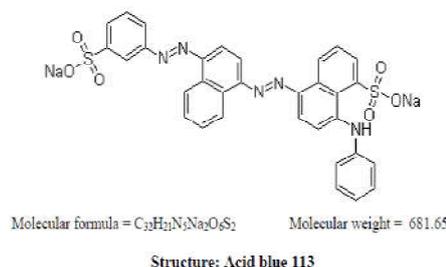
Active Metal oxides such as IrO₂ and RuO₂ electrodes have been studied (José *et al.*, 2008), achieving an incomplete oxidation of organic pollutants; whereas «non-active» oxides, such as Ti/SnO₂ and Pb/PbO₂ and their doped analogues are capable to oxidize organics to CO₂ (José *et al.*, 2008). Within this last group of electrode materials, boron doped diamond electrodes have received great attention due to the wide range of their electrochemical properties. In recent years, several scientific groups have investigated the application of diamond electrodes for removing dyes from wastewater (José *et al.*, 2008). These anodes produce a huge amount of hydroxyl radicals (OH[•]) formed by water oxidation on Si/ BDD surface, oxidizing the organic molecules in the proximity of the surface layer of OH[•]. Three modified electrodes (C/PbO₂, Pb+Sn/PbO₂+SnO₂ and Pb/PbO₂) were used as anode for electrochemical degradation of Reactive Red 24 (RR24) dye in aqueous solution. These electrodes containing lead dioxide which is characterized by high oxygen evolution over potential, inexpensive, consume less electrical energy and inert for acidic and basic media. The results of electrochemical oxidation process of RR24 dyes were expressed in terms of the remaining concentration and COD removal, which were determined instrumentally. After 15 min, nearly complete degradation of RR 24 was achieved; 97.84%, 96.82 and 95.95% using the three electrodes, respectively, at pH 2.23, current density 25 mA cm⁻² and in the presence of NaCl (6 g L⁻¹) at 25 °C (Abdalla *et al.*, 2012).

The treatment of Acid green V by an electrochemical oxidation using Ti/RuO₂ IrO₂ TiO₂ as anode and cathode and NaCl as supporting electrolyte in a tubular flow reactor under continuous single pass process was carried out (Kavitha, 2012). During the electrolysis, COD reduction, color removal, and energy consumption were investigated under different flow rates and current densities. The experimental results showed that at 10 l/h flow rate, 2.5 A/dm² current density, initial COD 960 mg/l (3000ppm), COD reduction, color removal and power consumption were found to be 87.5%, 100% and 3.2545 kWh/kg COD respectively. At the same flow rate and current density for an initial COD 480 mg/l (1500ppm), COD reduction, color removal and power consumption were found to be 100 %, 100% and 6.0417 kWh/kg COD respectively. Reactive blue 198 was electrocatalytic oxidized (Rajkumar *et al.*, 2013) using graphite electrode and nano cerium oxide as catalyst. At dye concentration 50mg/l and operating conditions 34.96mA/cm², with NaCl as supporting electrolyte TOC removal reached 46%.

The present work aims to study the possibility of use of rhodium/rhodium oxide/titanium thermally activated modified

electrode prepared by alternating current oxidation for the acid blue 113 azo dye electrochemical oxidation in their solutions.

Dye Structure



Synonyms: Sodium 8-phenylamino-5-(4-(3-sulphonophenylazo)-1-naphthyl azo) naphthalene sulphonate, Cyanine 5R

Figure 1. the acid blue 113 azodye structure

EXPERIMENTAL

Preparation of Modified Electrode

The development of Rhodium/Rhodium oxide thermally treated electrode which will be used in this study is shown in Fig. 2.

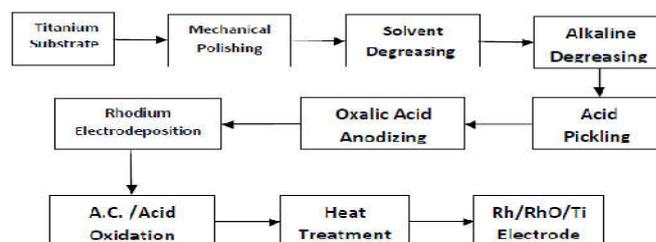


Figure 2. Flow chart for the preparation of Rhodium/Rhodium oxide thermally treated electrode

Titanium substrate was mechanically polished via different grades of sand paper followed by solvent degreasing via butyl glycol, water rinsing, and alkaline cleaning for complete removal of oil and grease. The substrate was then subjected to acid pickling for 5 minutes in 36% hydrochloric acid. Then acid pickled substrate was subjected to anodizing in 5% oxalic acid at 40°C for 5 minutes. The anodized titanium substrate was coated with rhodium thin film by the electro-deposition in rhodium sulfate bath with the composition and operating conditions as expressed above. The obtained coated titanium substrate with rhodium thin film is then subjected to oxidation process via alternating current (3A/cm², 30 volt, 50 Hz, for 60mins.) in concentrated sulfuric acid (98%). After completing the oxidation process, the electrode was rinsed in distilled water and then it was thermally treated with hot air at 450°C for 30mins. The details for the preparation of the modified electrode were explained via (26)Mixed oxidant generation electrochemical setup and procedure: Photograph 1 represents the experimental set-up used for the electrochemical degradation of acid blue 113 azodye in its solutions using mixed oxidants generated via sodium chloride solution electrolysis using Rh/RhO/Thermally activated modified electrode.

Electrode Morphology and Structure

The surface morphology and structure of obtained electrodeposited rhodium thin film over anodized titanium substrate and the acid oxidized rhodium thin film followed by thermal activation (Rh/RhO/Ti modified electrode) were examined using a scanning electron microscope (SEM) JEOL (Tokyo, Japan) JSM T330A equipped with KEVEX (Tokyo, Japan) electron diffraction equipped (EDAX) X-ray microanalyzer. The operating conditions were accelerating voltage of 25Kev. Beam/sample incidence angle of 900, and X-ray window incidence angle of 22.7°. The phases and crystal structure of the deposited rhodium and rhodium oxide on the pre-anodized titanium substrate were examined by x-ray diffraction (XRD). The measurements were carried out using a Philips (USA) diffractometer (40Kev, 30mA) with a nickel filter and copper radiation. The scanning angular range was from 4-90°. The diffraction pattern was recorded at room temperature.

Electrocatalytic oxidation

The cell used in these studies was made of transparent Perspex in the form of rectangular trough. The anode (Rh/RhO/Ti modified electrode) was supported in a vertical position midway between, and parallel to the graphite cathodes. The distance between each cathode and the anode was 3cm, and the electrolyte in each experiment was 50ml. all experiments were carried out with stirring (the liquid inside the cell and between the electrode is agitated). The electrical circuit used in this process is shown diagrammatically in photograph 1



Photograph 1. Electrolytic oxidation system

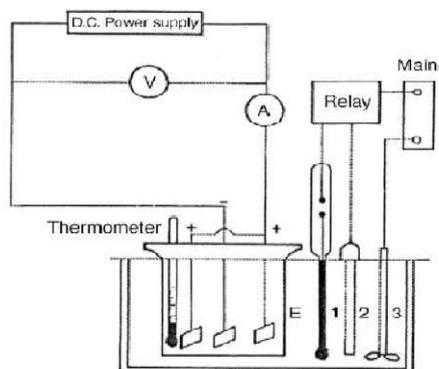


Figure 3. Electro-catalytic mixed oxidant preparation circuit

Analytical Measurements

Analytical parameters were measured to evaluate the treatment efficiency, these parameters were: (i) *remaining dye concentration* (mgL^{-1}), the phenomenon of the variation of the color of the dyestuff solution, as a result of electrocatalytic oxidation process, forms the basis of colorimetric analysis for determination of the remaining dye load concentration. (ii) *chemical oxygen demand COD* ($\text{mgO}_2\text{L}^{-1}$), which is a measure of the oxygen equivalent to the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. COD can be related empirically to organic matter. All required equipment including reagents, COD digestion reactor, used are supplied from *Hach Systems for Analysis, Hach Co., Loydand, Colorado, U.S.A*, the spectrophotometer (*model 552S Double-Beam UV-Visible, Bodenseewerk Perkin-Elmer Co. CMBH, Germany*) with microcomputer electronics was used in our investigation. Reactor digestion method, USEPA approved for reporting (27, 28), was used for the determination of chemical oxygen demand (COD).

This method for the determination of COD may be used where sample chloride concentration is known to be less than 2000mgL^{-1} . This means that, in the present investigations the interferences of Cl^- ions present in the solution and the electro generated species may occur. To eliminate the effect of these interferences, the measurements of COD of blank solutions were carried out. These blank solutions were treated under the same operating conditions used in the treatment of the dyestuff solutions. From the measurements of COD values of blank solution and dyestuff solution after treatment, the value of COD corresponding to the dye present in solution can be evaluated. The COD values obtained from the two methods were matched with each other. Studies were carried out for the investigation of optimum operation conditions for the degradation and removal of the above mentioned dye, from their synthetic solutions and COD removal by the electrocatalytic oxidation process. The studied operating conditions were: applied current density (mAcm^{-2}), time of electrolysis (min), pH, temperature ($^{\circ}\text{C}$), conductive electrolyte concentration (gL^{-1}) and initial dye load concentration mgL^{-1} . All materials used in this investigation are of analytical grade. NaOH and HCl were used for pH adjustments.

RESULTS

Electrode Quality Assessment

The produced Rhodium/Rhodium oxide thermally treated electrode was subjected to SEM to show its surface morphology with a magnification of 350. Figure3 (A) and (B) show, respectively, SEM photographs of the morphology of the electrodeposited rhodium metal of the pre-anodized titanium substrate and the oxidized rhodium oxide thin film formed due to the A.C. treatment of the rhodium thin film in concentrated sulfuric acid followed by thermal activation. As it is clear from the photograph that deposited was in the form of large crystal this large crystal divided into small porous structure with small-sized crystal particles with sharp boundaries and a very compact crystalline structure.

This gave the chance for the formation of active oxygen, hydroxyl radicals and hydrogen peroxide. Figure 4 (A) and (B) represents respectively the EDIX charts for the electrodeposited rhodium metal of the pre-anodized titanium substrate and the oxidized rhodium oxide thin film formed due to the A.C. treatment of the rhodium thin film in concentrated sulfuric acid followed by thermal activation. The presence of the Ti peak at 4.5Kev for the EDAX chart assure the porous structure of the electrodeposited rhodium thin film and the oxidized rhodium oxide thin film. Figure 5 (A) and (B) shows the XRD pattern for the electrodeposited rhodium thin film over the pre-anodized titanium substrate and that of oxidized rhodium thin film after treatment of concentrated sulfuric acid using A.C. followed by thermal activation. The peaks in this figure were represented for titanium, rhodium and rhodium oxide. The identification of the crystals is empirical: the

American Society for Testing and Materials (ASTM) provides Key sort and IBM cards that provides d-spacing and relative line intensities for pure compounds for over than 25000 crystalline materials. It is clear from the X-ray pattern that rhodium and rhodium oxide are present over the pre anodized titanium substrate. However the presence of titanium peaks could mean that the noble metal film is very thin may be 1 μm . Different current densities of values 5, 10, 15 and 20 mA/cm^2 were applied to investigate the electrocatalytic degradation of the acid blue 113 in 3 g/l NaCl solution at the following operating conditions: 100 mg/l initial dye load, pH of 3 and temperature of 25 °C for time period 20min.. Fig. 7 shows the remaining dye variation of COD removals % as a function of electrolysis time at different current densities for the investigated dye (b). Inspection of the plots of Fig. 3 indicates that:

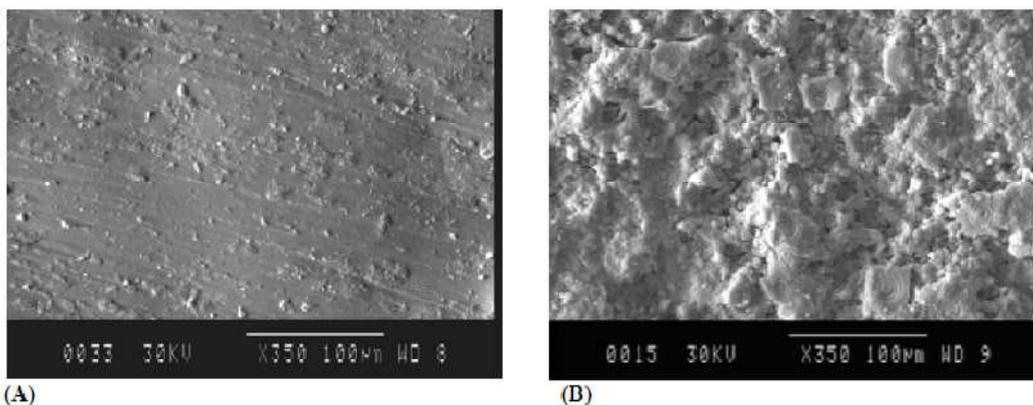


Figure 4. SEM photographs showing (A) rhodium thin film over titanium substrate(B) rhodium /rhodium oxide thin film over titanium substrate after chemical treatment with sulfuric acid using A.C. current and thermal activation (rhodium/rhodium oxide/titanium thermally activated modified electrode

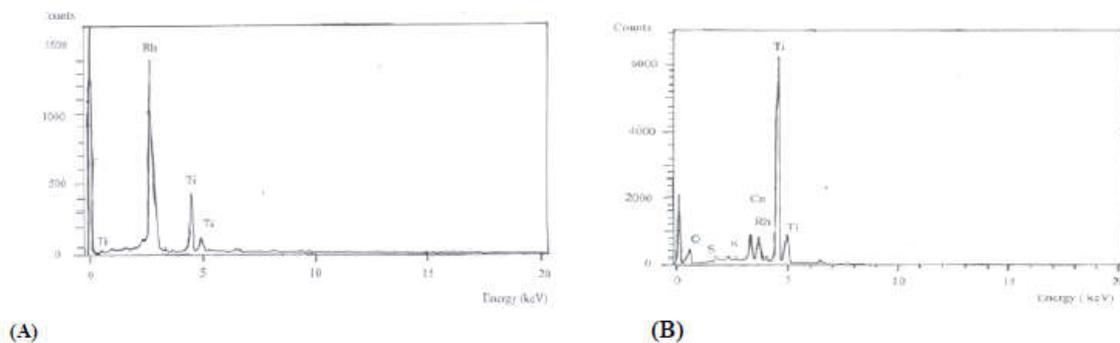


Figure 5. SEM-EDIX charts (A) for electrodeposited rhodium thin film over anodized titanium substrate, while (B) for the rhodium/rhodium oxide titanium mixed oxide modified electrode after treatment in sulfuric acid and heat treatment.

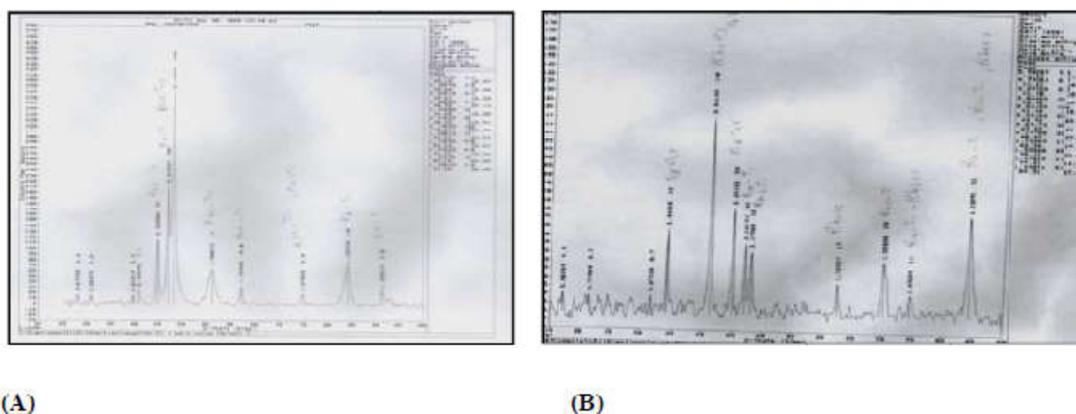


Figure 6. XRD patterns of (A) for the electrodeposited rhodium thin film over anodized titanium substrate, while (B) for the rhodium /rhodium oxide titanium mixed oxide modified electrode after treatment in sulfuric acid and heat treatment

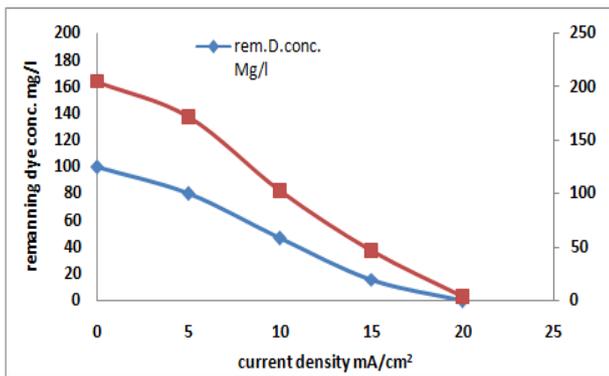


Figure 7. Effect of current density on the degradation of acid blue 113 in its solutions via electrogenerated Fenton's agent

At a given current densities, the COD removal % increases with increase of electrolysis time reaching complete dye and COD removal at current density 20mA/cm². At a given time of electrolysis, the COD removals % increased with increase of the applied current density till 20 mA/cm² and further increase in the current density did not bring any further effect. For this reason, the current density 20 mA/cm² was taken as optimum. The values of COD removals % at this optimum current density were; 98%, while the color removal efficiency was 100%. Fig. 8 shows the variation of the COD concentration as a function of electrolysis time at pH values of 1, 3, 5, 7 and 9 for the investigated dye the electrocatalytic degradation experiments were carried in 3 g/l NaCl solution at the following operating conditions: current density of 20 mA/cm², 100 mg/l of initial dye load and temperature of 25 °C for time period 20min.

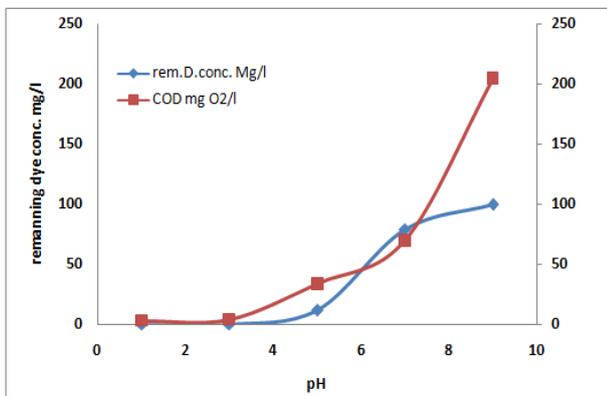


Figure 8. Effect of pH on the degradation of acid blue 113 in its solutions via electrogenerated Fenton's agent

As shown from the plots of Fig. 8 that, at a given pH values, the COD concentration decreased as the pH values decreased reaching to maximum removal at pH1. At a given electrolysis time, the maximum values of COD removal percentage were obtained at pH values of 1 and 3 and the increase of pH of solution greatly decreased the values of COD removal percentage of the investigated dyes. For this reason, the pH values of 2 and 3 were taken as optimum and from the economical point of view pH 3 was taken as optimum. As it is clear from Fig. 9 and at electrolysis conditions of 20mA/cm², pH 3, T°C 25, NaCl concentration 3g/l, initial dye load

100mg/l via Rh/RhO/Ti electrode it was found that, as the electrolysis time increases both of remaining dye and COD concentration decreases reaching to maximum removal at 20min. the color removal and COD removal efficiency were found to be 100% and 98%, respectively. So electrolysis time of 20min. was taken as optimum.

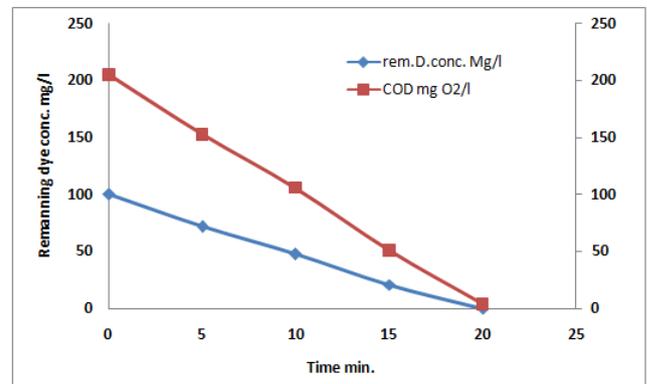


Figure 9. Effect of electrolysis time on the degradation of acid blue 113 in its solutions via electrogenerated Fenton's agent

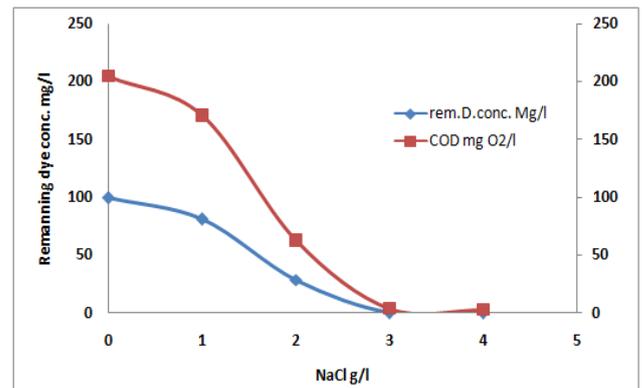


Figure 10. Effect of sodium chloride concentration on the degradation of acid blue 113 in its solutions via electrogenerated Fenton's agent

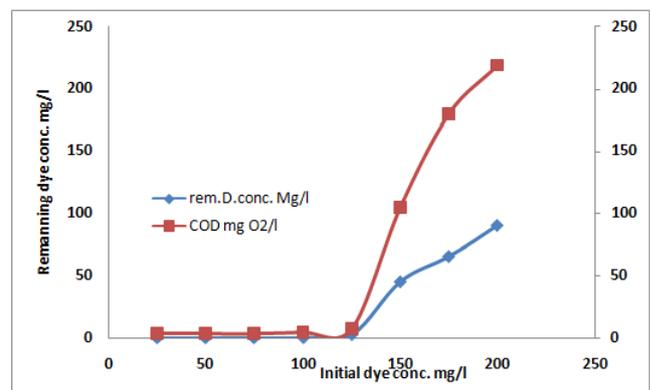


Figure 11. Effect of initial dye load on the degradation of acid blue 113 in its solutions via electrogenerated Fenton's agent

In this investigation, the concentration of NaCl was 1, 2, 3 and 3 g/l and the electrocatalytic degradation of the treated dyes was carried under the following operating conditions: current density of 20mA/cm², 25 °C, pH of 3 and the initial dye load

was 100 mg/l for time period 20min.. Fig. 10 shows the variation of COD concentration as a function NaCl concentration of 1, 3 and 5 gm/l for the electrocatalytic degradation of the investigated dye via Rh/RhO/Ti electrode at the above mention operating conditions. Inspection of the plots of Fig. 6, revealed that: At a given NaCl concentrations, the COD removal percentage increased with increase of electrolysis time reaching complete removal at NaCl concentration of 3, and 4 g/l. also the color removal greatly increased with the increase of NaCl concentrations to 3 and 4 g/l. At a given electrolysis time, the COD removal percentage of dyes in 3 and 4 g/l NaCl are almost equal to each other. So, the concentration of 3 g/l was taken as the optimum.

The results so far indicated that the optimum electrochemical degradation of the investigated dyes was attained at 20 mA/cm² current density, 3 g/l NaCl solution, pH 3, temperature 25°C and time period of 20min. Fig. 11 shows the effect of the investigated dye load variation on COD removal concentration and remaining dye concentration under the optimum operating conditions mentioned above. Inspection of the plots of Fig. 11, reveals that: 1. At a given time of electrolysis, the COD removal percentage decreased with increasing initial concentration from 100–250 mg/l respectively. 2. Complete COD removal percentage can be achieved in the presence of 100 mg/l as initial dye load. 3. Increasing the dye concentration resulted in a decrease in its electrochemical degradation rate. This might be explained that the ratio of mixed oxidant generated concentration is decreased with increase in initial dye concentration. Although, the degradation rate of the investigated dye decreased with increase the initial dyes dose, a good COD removal percentage was achieved at a relatively high dyes load as indicated from the plots of Fig. 11. It is found that, the COD removal percentage at initial dye load of 200mg/l was 50%.

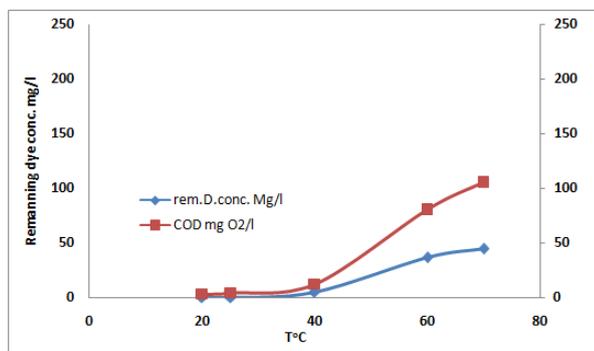


Figure 12. Effect of electrolysis temperature on the degradation of acid blue 113 in its solutions via electrogenerated Fenton's agent

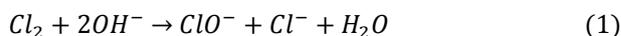
This investigation was carried out in 3 g/l NaCl solution at the following operating conditions: current density of 20mA/cm², 100 mg/l of initial dye load and about 20 min of electrolysis time for electrochemical degradation of the investigated dye. It is to be noted that, there are some conditions which ensure more or less complete electrocatalytic degradation of the treated dye as indicated from the results which so far. Fig. 5 shows the variation of the COD concentration as a function of temperature (25–70°C) for the investigated dye at the above mentioned operating conditions. It is clear from the plots of the

Fig. 12, that the change of temperature from 25–40°C had a slight effect on the efficiency of the degradation process, while more increment of the temperature increase the dye remaining dye concentration and COD concentration indicating bad removal of both dye and COD. For this reason, the temperature of 25°C was taken as optimum.

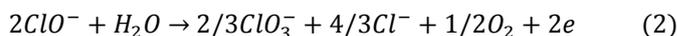
DISCUSSION

Generally, electrochemical oxidation of an organic compound in aqueous solution does not result from a direct transfer of electrons between the electrode surface and the reagent. In fact, it is a transfer reaction of one or more oxygen atoms. In the case of phenol, oxidation occurs in accordance with a complex mechanism involving both transfer of oxygen atoms and direct transfer of electrons (Rajkumar *et al.*, 2013). It is often assumed that the first step of oxygen transfer is a water molecule discharge at one electrode leading to the formation of a hydroxyl radical ($OH\cdot$) adsorbed on an active site of the anode surface (Shaarawy and Saied, 2012; Jirka and Carter, 1975; USEPA, 1980; Gattrell and Kirk, 1997; Cominnellis and Pulgarin, 1993). The second step is an electrophilic attack of the hydroxyl radical on the organic compound transported from the bulk of the solution at the electrode interface. Any organic compound can thus theoretically be oxidized on classical anode materials such as Au, Pt, C, etc., if the electrode potential value is sufficient to form the hydroxyl radicals. However, on these anode materials, the oxygen transfer reactions are slow and are characterized by low faradaic yields; in fact, a loss of current occurs with formation of molecular oxygen (Gattrell and Kirk, 1997; Cominnellis and Pulgarin, 1993; Brillas *et al.*, 1995).

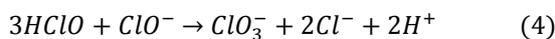
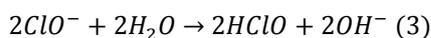
The removal of undesirable organic or dyestuff impurities from liquid (usually aqueous) phases through electrochemical processes is based on the possibility of choosing suitable electrodes and potential/current conditions selectively to degrade these impurities. Wastewater treatment by indirect electrochemical oxidation has been carried out. It was previously reported (Schinittinger and Chlorine, 1986) that, if NaCl solution is electrolyzed in an individual cell, Cl_2 formed at the anode disproportionate in the presence of OH^- ions generated at the cathode



The resultant hypochlorite can be further oxidized to chlorate:



However, this leads to the requirement of nine Faradays' per mole of chlorates; whereas only six are needed if a chemical disproportionate route is followed:



On the basis of the above reactions, we can see from reaction (2) that the hypochlorite is favored by keeping the chloride concentration as high as possible. In addition, high current

densities are employed owing to the fact that the current-voltage curve for reaction (2) is flatter than for chlorine evolution. Reactions (3, 4) can be suppressed by working at low temperature, and the resultant liquor can be used directly for bleaching and disinfection purposes. Noble metals and their oxides exhibit electrocatalytic activities for chlorine evolution and hypochlorite formation reactions (Meyer and Carlsson, 1992; Guolin and Water, 1991). Rhodium/rhodium oxide/titanium thermally activated modified electrode showed high efficiency for the removal of acid blue 113 dye in their solution.

Conclusion

Modified electrodes are of importance in the fields of chemical analysis and electrochemical industries. Rhodium/Rhodium oxide/Titanium thermally activated modified electrode prepared via alternating current oxidation of thin film of rhodium titanium coated substrate was chosen in the treatment of dyestuff effluents such as: acid blue 113 azodye in its solutions. It is concluded that, the prepared modified electrodes had a great efficiency in the removal of the above mentioned dyestuffs at low current densities, time and pH and in the presence of NaCl as a conductive electrolyte at temperature of 25°C. In addition, this modified electrode may be used in many applications such as: the electrocatalytic oxidation of different types of dyestuffs other than the above mentioned dye, bleaching of cotton fibers. Also, they could be used as electrocatalysts in fuel cells and electrolysis of water for hydrogen production.

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