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Decolorization of azo dye C.I. Acid Red 33 from aqueous solutions by anodic oxidation on MWCNTs/Ti electrodes

Farideh Nabizadeh Chianeh*, Jalal Basiri Parsa

Faculty of Chemistry, Department of Applied Chemistry, University of Bu-Ali Sina, Hamadan, Iran, Tel. +98 813 8282807; emails: nabizadeh_farideh@yahoo.com, f.nabizadeh@basu.ac.ir (F. Nabizadeh Chianeh), Parssa@basu.ac.ir (J. Basiri Parsa)

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ABSTRACT

In this study, a titanium electrode coated with multiwall carbon nanotubes was prepared by the electrophoretic deposition method. The electrode was characterized by field emission scanning electron microscopy and cyclic voltammetry. The electrochemical oxidation (EO) performance of prepared electrode was investigated using Acid Red 33 (AR33) as a model pollutant. The effect of initial pH of dye solution, current density, and type of supporting electrolyte on color removal efficiency were studied. High color removal efficiency (90%) was achieved for AR33 dye using a current density of 5.5 mA/cm^2 for 60 min. In addition, a comparison of EO, ozonation (O), and electrolysis combined ozonation (ECO) processes for decolorization of AR33 solution was performed. Results indicated that color removal efficiency follows the decreasing order: ECO > EC > O.

Keywords: MWCNTs/Ti electrode; Electrophoretic deposition; Decolorization; Acid Red 33

1. Introduction

In recent years, electrochemical techniques have attracted considerable attention in water treatment researches, due to their environmental compatibility, high energy efficiency, no production of sludge, small space requirement, and strong oxidation ability. In electrochemical methods, the reaction active sites and contacts between coating catalyst and reactant must be high to almost completely oxidize organics to CO_2 and H_2O. In addition, electrocatalytic efficiency process depends on the activity of coating materials on the electrodes [1,2].

Application of carbon nanotubes (CNTs) for modifying the electrode is a proper way to obtain materials with better properties. These materials have advantages over conventional materials in various environmental applications. CNTs are ideal coating to modify electrode because of their high aspect ratio, excellent mechanical strength, good conductance, and high chemical stability [3,4]. The electrical properties of CNTs including conductivity and charge accumulation decrease the electrode size, and modification of the surface can be a method to obtain the higher performance for the electrode.

The electrophoretic deposition (EPD) is a technique which includes covering conductive substrates with thin layers. This technique consists of two steps. In the first step, particles suspended in a liquid are forced to move toward an electrode under the effect of electric field. In the second step, the particles accumulate around the electrode and form a coherent deposit. Deposition occurs only on conducting surfaces [5,6]. In contrast to other coating techniques, EPD has a

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*Corresponding author.

number of advantages such as achievement of uniform coating thickness, relatively high speed of coating, applicability for a wide range of materials and to complex shape substrates, easy control of the coating composition, relative low cost and simple processing equipment as well as being environmentally adaptable. Owing to these advantages, the application of EPD in the development of a great variety of coatings is being continually reported [7,8]. In this research, a titanium electrode coated with multiwall carbon nanotubes (MWCNTs/Ti) was prepared by the EPD method and used to study the possibility of AR33 decolorization from aqueous solution. A few studies [9–12] have examined the application of CNTs electrode in wastewater treatment. Recently, research has focused on surface modification of the electrode anodes by CNTs [13,14]. The aims of this study are manufacturing of the layer made of multiwall carbon nanotubes (MWCNTs) deposited on the surface of titanium by EPD method and application as anode for oxidation of organic pollutants.

2. Experimental

2.1. Materials

An azo dye AR33, $C_{16}H_{11}N_3Na_2O_7S_2$, was selected as model solution, which was a commercial dye and used without further purification. This azo dye was provided by Alavan Sabet Company (Iran). Its structure and characteristics are given in Table 1. Sodium chloride and nickel(II) chloride were the products of the Merck Company with purity of more than 99.5%. MWCNTs were purchased from the Neutrino Corporation (Iran). Table 2 shows the characteristics of applied MWCNTs. The initial pH of model solution was adjusted using diluted sodium hydroxide and sulfuric acid solutions and sodium chloride was used as the supporting electrolyte. All solutions were prepared by using de-ionized water.

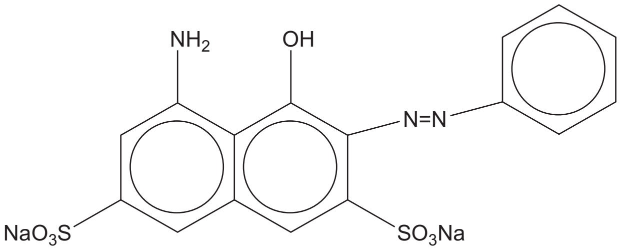
Table 2
COOH functionalized nanotubes (COOH-MWNTs) specifications

Outer diameter	8–15 nm
Inside diameter	3–5 nm
Purity	>95 wt%
Length	10–50um
Electrical conductivity	>100 S/cm
Specific surface area	233 m^2/g
COOH-MWNTs contain 2.5% COOH groups	

2.2. Electrode preparation

The suspensions for EPD were prepared using fresh de-ionized water and COOH-MWNTs. The concentration of COOH-MWNTs in the suspension was 0.166 mg/mL. In order to obtaining a surface charge on the MWCNTs with the aim of increasing deposition rate and improving adhesion of powder particles to substrate, the charger salt $NiCl_2$ was added to the suspension at a small amount (less than 1%). After adding $NiCl_2$, the suspension was put in ultrasonic for 60 min at room temperature. Then, the titanium mesh (2 cm × 2 cm) as the cathode, and a stainless steel substrate (3 cm × 6 cm) as the anode were immersed into the nanotubes suspension and were kept at a constant gap distance of 1 cm. A direct current voltage of 20 V was applied and MWCNTs deposition began to appear on the titanium cathode. The deposition time was kept at 5 min. After the deposition of COOH-MWCNTs, the cathode was dried in the air for 24 h and then was annealed at 300°C for 30 min in a furnace.

Table 1
Structure and characteristics of the AR33 dye

Structure	
Color index number	C.I.-17,200
λ_{max} (nm)	530
Mw (g/mol)	469.44
pH	5.2

2.3. Apparatus

A mixed reactor made of Pyrex glass with a total volume of 600 mL was used for all experiments. A magnetic stirrer (Alfa, HS-860) was used for mixing the solutions. The pH of solutions was measured using a pH meter (Denver, UB-10). In all experiments, the samples of AR33 were taken periodically from the reactor and analyzed by the UV–visible spectrophotometer (JASCO. v-630, Japan) via decrease of absorbance at 530 nm. The electric current was provided by a DC power supply (APS-1363P). Also, ozone was produced from air in an Onnic ozone generator (ES215A). Through a diffuser, the ozone–air mixture was introduced to the bottom of the reactor with a flow rate of 0.79 mg O_3/min and was measured iodometrically [15]. The morphology of the coating was examined by field emission scanning electron microscopy (FE-SEM). The cyclic voltammetry (CV) experiments were conducted using a three-electrode cell, with platinum wire as the counter electrode, Ag/AgCl as the reference electrode, and Ti or MWCNTs/Ti electrode as the working electrode. CV curves of the testing anodes were produced by potentiostat/galvanostat ATOLABS (Netherlands).

3. Result and discussion

3.1. Morphology of MWCNT films on titanium surface

The FE-SEM images of the Ti electrode surface with and without MWCNTs were shown in Fig. 1(a) and (b). Fig. 1(a) shows the fresh titanium surface. Fig. 2(b) presents the films of MWCNTs on titanium surface prepared by EPD method. The images in Fig. 1 demonstrate that all the surfaces of the MWCNTs coating are quite similar. As illustrated in Fig. 1, MWCNTs with a mesh-like structure were effectively interwoven around each other and made up an electric mesh with electrochemical sensitive sites on the interface. In other words, so many pores forming transition adsorption sites exist among interwoven MWCNTs, and capillarity provides fast penetration channels in the electrochemical degradation process [13].

3.2. Cyclic voltammetry

CV is a valuable characterization tool for evaluating electrode performance. The CV has been used as a standard electrochemical characterization for MWCNTs/Ti electrode. The CV is performed by connecting a potentiostat to an electrochemical cell. The single compartment cell contains a test solution (sulfuric acid) and three electrodes: working (MWCNTs/Ti), reference (A platinum wire), and auxiliary (Ag/AgCl electrode). The cyclic voltammograms were measured within a range of 0–2.5 V in 1.0 M sulfuric acid solution by three times repeated potential scanning with a rate of 0.1 V/s. Fig. 2 shows a representative cyclic voltammogram for a MWCNTs/Ti electrode. The behaviors of sample electrodes a (titanium) and, b (MWCNTs/Ti) implicated that the electron transfer rate in the MWCNTs/Ti electrode (b) is faster than that in the bare Ti electrode (a) [16].

3.3. Influence of current density

Fig. 3 displays the effect of current density on the color removal efficiency at initial dye concentration, initial pH of the solution, and NaCl concentration of 30 mg/L, 5.2 and 1 g/L, respectively. As can be seen in Fig. 3, the color removal efficiency increased with the increase of current density from $I = 2.5\ \mathrm{mA/cm^2}$ to $I = 5.5\ \mathrm{mA/cm^2}$, which was possibly due to the fact that a higher current density leads to a higher production of hydroxyl radicals originated from water oxidation. In other words, the reason of this observation can be related to the high production of active chlorine species (Cl_2(aq), Cl_3^-, HClO, and ClO^-) and hydroxyl radicals (OH·). Also, the results plotted in Fig. 3 clearly showed that the maximum color removal efficiency was achieved at $I = 5.5\ \mathrm{mA/cm^2}$. The greater color removal efficiency at $I = 5.5\ \mathrm{mA/cm^2}$ than $I = 7.5\ \mathrm{mA/cm^2}$ seems illogical because application of a greater current density results in more significant oxidation of dye. On the other hand, the increase of electrolytic gas bubble formation (anode-O_2/cathode-H_2) at a higher current density may disrupt the decolorization process by clogging pores and consequently electrocatalytic sites or breaking MWNT-MWNT contacts resulting in loss of electrochemical activity [9,17,18].

3.4. Comparison of NaCl vs. Na_2SO_4

The effects of two different supporting electrolytes, viz. Na_2SO_4 and NaCl for decolorization of AR33 dye were investigated. The operating conditions of treatment process were: current density of $5.5\ \mathrm{mA/cm^2}$, pH 5.2, $C_{\mathrm{NaCl}} = 1$ g/L, $C_{\mathrm{Na_2SO_4}} = 1$ g/L, $C_{\mathrm{AR33}} = 30$ mg/L, and MWCNTs/Ti electrode as anode. The reaction was allowed to proceed for 60 min. As can be seen in Figs. 4 and 5, the color removal rate was significantly enhanced using NaCl as supporting electrolyte. In the case of medium containing SO_4^{2-} ions, the color removal efficiency was comparatively poor and

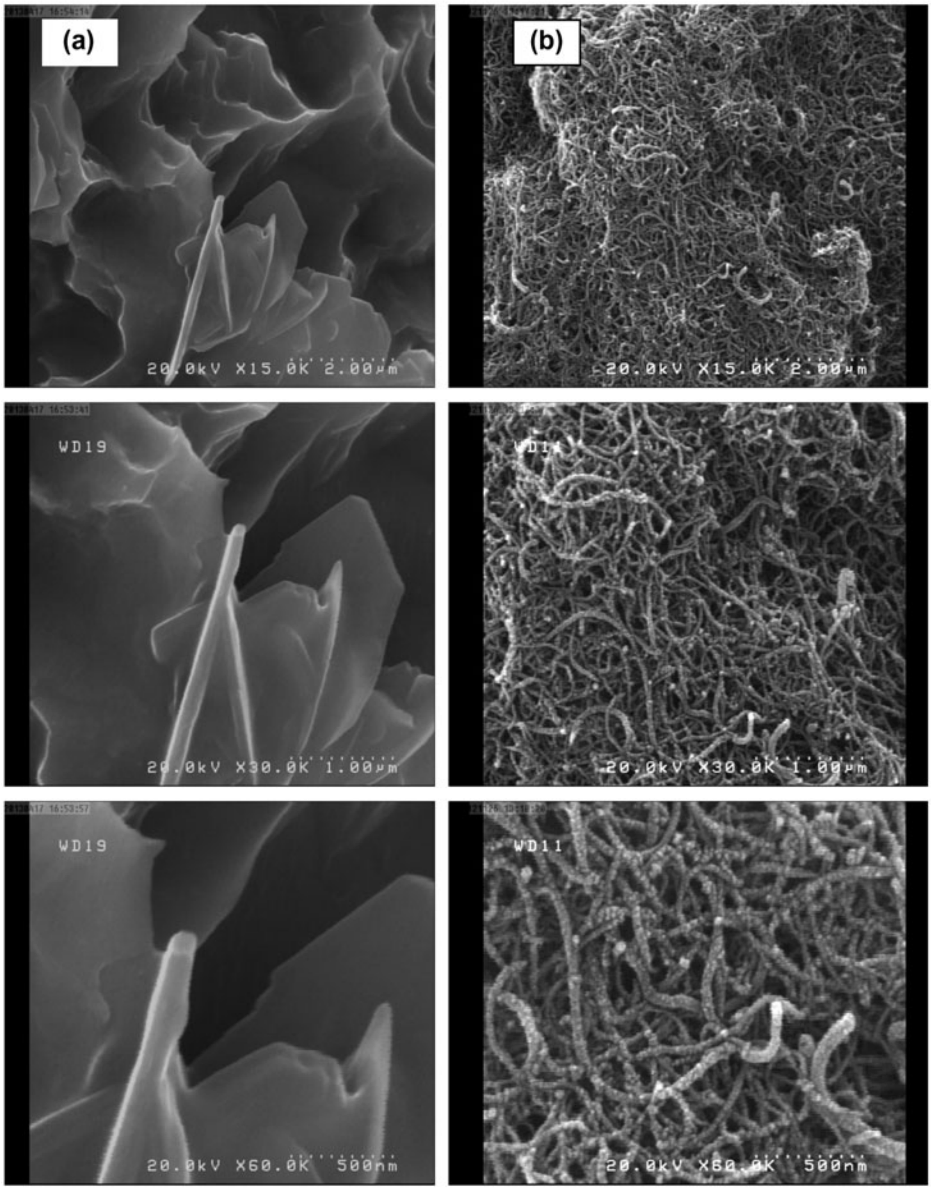


Fig. 1. The FE-SEM images of (a) Ti electrode without coating and (b) MWCNTs/Ti electrode.

required higher electrolysis time than in the medium containing Cl^- ion to attain about 79% decolorization. This is in accordance with the phenomenon in which the indirect oxidation process occurs during the electrolysis when the electrolyte consists of the SO_4^{2-} ion. The formation of $S_2O_8^{2-}$ from SO_4^{2-} ion can be illustrated from reaction (1):

$$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^- \quad (1)$$

It has also been demonstrated that $OH^\cdot$ is involved in the oxidation of sulfate to form peroxodisulfate based on reaction (2):

$$2HSO_4^- + 2OH^\cdot \rightarrow S_2O_8^{2-} + 2H_2O \quad (2)$$

Accordingly, a part of the $OH^\cdot$ produced on the MWCNTs/Ti surface is trapped by an oxidizable species like sulfate to form the corresponding peroxides. In fact, this peroxide formation indirectly helps to avoid the side reaction of oxygen evolution and can act as a mediator in the decolorization of the AR33 compound. The decomposition of peroxo disulfate produces hydrogen peroxide and other oxidants meaning that several oxidizing agents could be involved in the mediated oxidizing process. AR33 was

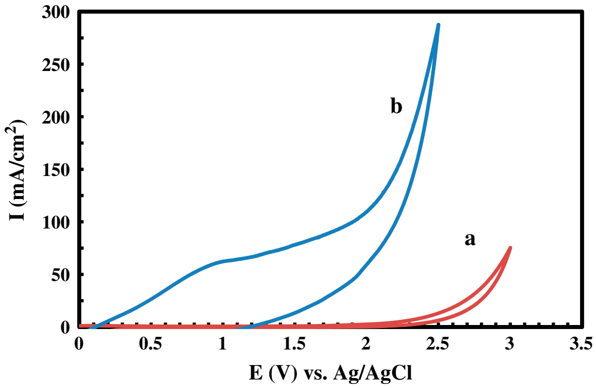


Fig. 2. Comparison of cyclic voltammograms obtained on different electrodes after reaching steady states; (a) Ti electrode without coating and (b) MWCNTs/Ti electrode.

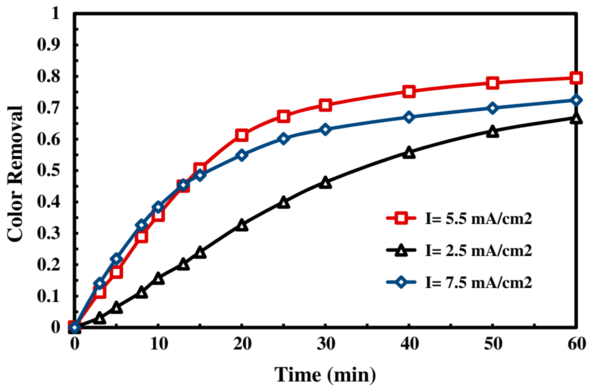


Fig. 3. The effect of current density on the color removal; C_{AR33} = 30 mg/L, C_{NaCl} = 1 g/L, pH 5.2.

decolorized with the electrolysis time 60 min when NaCl was employed as a supporting electrolyte. This rapid decolorization of AR33 could actually be attributed to the formation of a chlorinated AR33 molecule by interaction of electrogenerated chloro and/or oxychloro species. The previous studies have shown that the electrogeneration of chlorine-based oxidants such as ClO^- and Cl_2, can play an active role in the oxidation process of the organics. From these results, it was confirmed that the production of electrogenerated oxidants is also contributing to some extent for AR33 decolorization dependant on the supporting electrolyte used [19,20].

3.5. Influence of pH

The influence of pH on the removal of AR33 dye by MWCNTs/Ti anode was investigated at different values of pH including 3.0, 5.2, and 10. The experimental results were shown in Fig. 6. As can be seen in Fig. 6, the electrocatalytic activity and the efficiency of electrode on decolorization of AR33 were highly dependent on initial pH of the solution and enhanced in alkaline condition than in acid medium. The reason of this observation may be related to the differences in chemical properties of organic pollutant

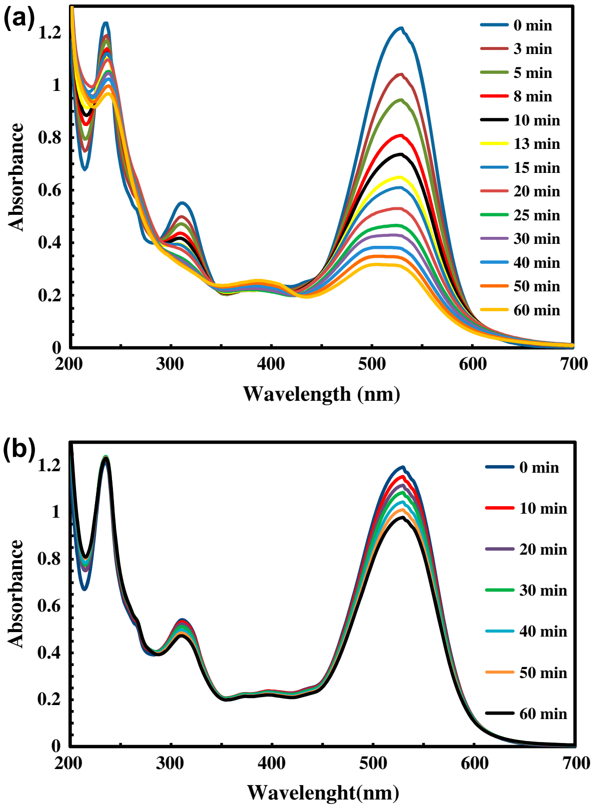


Fig. 4. Changes of UV–vis absorption spectra of AR33 during its EO in (a) NaCl and (b) Na_2SO_4 electrolytes; C_{AR33} = 30 mg/L, I = 5.5 mA/cm^2, pH 5.2.

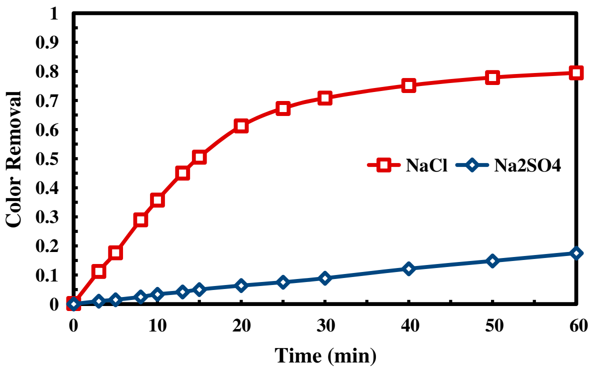


Fig. 5. The effect of consumed electrolyte on the color removal; C_{AR33} = 30 mg/L, I = 5.5 mA/cm^2, pH 5.2.

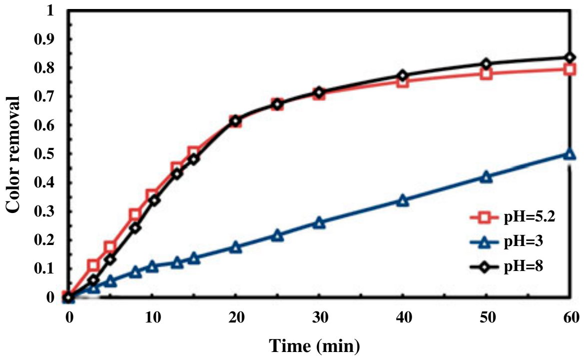


Fig. 6. The effect of initial pH on the color removal; $C_{AR33} = 30$ mg/L, $C_{NaCl} = 1$ g/L, $J = 5.5$ mA/cm^2.

degraded and the MWCNTs/Ti electrode employed. A rapid color removal efficiency at pH 10 may be attributed to the greater production hydroxyl radicals (OH$^\cdot$) (the increase of the solution pH favors HO$^\cdot$ formation) and higher adsorption of chemical forms of AR33 dye on MWCNTs/Ti electrode [21,22].

3.6. Decolorization of AR33 using different techniques

In recent years, the ozone production cost has decreased; however, the ozonation process still has a high cost. Due to this cause, wastewater treatment by ozonation may require a combination of methods to obtain satisfactory results, at reasonable cost [23].

The decolorization of AR33 with various techniques such as electrochemical oxidation (EO), ozonation (O), and electrolysis combined ozonation (ECO) are shown in Fig. 7.

This figure shows that the color removal efficiency during ECO process is higher than that in others and after 60 min reaction time is in the following order: ECO (%) > O > EO. This means that the destruction of azo groups is more rapid in ECO than that in others. In other words, these results demonstrate that electrolysis combined ozone has a synergistic effect on AR33 removal. This result can be associated with the mechanism included in each process.

Ozone reacts with dye molecules by two different mechanisms: directly and indirectly. In the direct oxidation, the molecular ozone directly reacts with an unsaturated bond through selective reactions, leading to a cleaving of the bond. In the indirect oxidation by ozone, a radical chain reaction takes place, during which OH$^\cdot$ radicals are produced and react with dye molecules. The indirect reaction can be performed in high pH solution. Therefore, some extra modifications should be combined to ozonation process to improve its effectiveness in wastewater treatment.

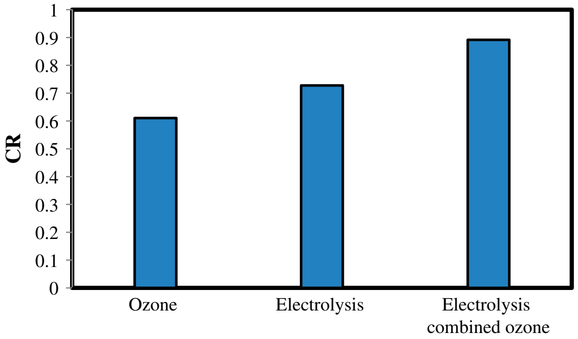


Fig. 7. Comparison of decolorization curves for AR33 with different techniques. Solution: $C_{AR33} = 30$ mg/l, $I = 5.5$ mA/cm^2, pH 5.2, $C_{NaCl} = 1$ g/L, reaction time = 60 min.

The main reactions during electrolysis combined ozone process are:

At the cathode, ozone reduction provides O_3^- as it is given by Eq. (3):

$$O_3 + e^- \rightarrow O_3^- \tag{3}$$

At the anode, reaction below can be suggested to be happened:

$$O_3^- + H_2O \rightarrow OH^\cdot + O_2 + OH^- \tag{4}$$

3.7. Degradation mechanism

The degradation mechanism of AR33 dye molecules has two parts. The first part of the dye molecules removal may occur through two primary mechanisms; the direct oxidation of AR33 dye molecules, in contact with the MWCNTs/Ti anode, and the indirect oxidation of AR33 dye molecules via anodic production of an aqueous oxidant (e.g. HO$^\cdot$). The first step in the direct oxidation mechanism involves deposition or adsorption of the AR33 dye molecules onto the MWCNTs/Ti anode:

$$\begin{aligned}&\text{MWCNTs/Ti} + \text{dye}\,[\text{AR33}]\\&\quad\rightarrow \text{MWCNTs/Ti}\,\text{dye}\,[\text{AR33}]\end{aligned} \tag{5}$$

The second step involves oxidation of the dye adhered to the MWCNTs/Ti anode, which is likely a multielectron process:

$$\text{MWCNTs/Ti}\ (nh^+)\ \text{dye}\ (ne^-) \rightarrow \text{MWCNT dye}_{(Ox)} \tag{6}$$

The indirect oxidation of dye also involves two steps, the first being the anodic one-electron production of an oxidant:

$$\begin{aligned}&\text{MWCNTs/Ti (h}^+) + \text{Ox}^- \ [\text{H}_2\text{O}]\\ &\quad\rightarrow \text{MWCNTs/Ti} + \text{Ox}^{\bullet}\ [\text{HO}^{\bullet}]\end{aligned} \tag{7}$$

The dye was subsequently oxidized and inactivated by produced oxidant:

$$\text{Ox}^{\bullet} + \text{dye} \rightarrow \text{Ox}^- + \text{dye}_{(\text{Ox})} \tag{8}$$

This reaction between dye and oxidant may have occurred in the solution, or one or both of the reactants may be absorbed by the MWNT/Ti surface [17].

In the second part of the degradation mechanism, AR33 dye molecules can degrade in a bulk solution by indirect electrolysis, generating *in situ* chemical oxidants from the NaCl electrolyte. In other words, the *in situ* generated active chlorine species such as hypochlorous acid/hyperchlorite (HClO/OCl^-), chlorine radical ($\text{Cl}^{\bullet}$), and/or dichloride radical anion ($\text{Cl}_2^{\bullet-}$) from direct oxidation of chloride ions at the MWCNTs/Ti anode surface can oxidize AR33 dye molecules [19,23].

4. Conclusion

In the present study, it has been demonstrated a novel method for fabricating a binder-free MWCNTs film electrode using the EPD technique. Deposited MWCNTs film showed reasonably good adhesion strength and electrical conductivity on the titanium surface. These results confirmed that the proposed electrolysis cell equipped with MWCNTs/Ti anode had a high efficiency for decolorization of AR33 from aqueous solution. It can be regarded as a potential technique to treat wastewater polluted with dye. The decolorization of azo dye using MWCNTs/Ti anode was affected by initial pH, current density, and type of supporting electrolytes. AR33 decolorization was 90%, when MWCNTs/Ti was used as anode under the conditions of initial pH of 10, initial dye concentration of 30 mg/L, current density of 5.5 mA/cm^2, concentration of 1 g/L sodium chloride, electrolysis time of 60 min, and distance of 1 cm between the electrodes. Moreover, the result showed that the color removal efficiency during ECO process is higher than that in others and after 60 min reaction time is in the following order: ECO (%) > O > EO.

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