

## Determination of the Efficiency of Different Modified Electrodes in Electrochemical Degradation of Reactive Red 24 dyes in Wastewater Dyestuff Solutions

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Present work concerns with preparation of three modified electrodes (C/PbO<sub>2</sub>, Pb+Sn/PbO<sub>2</sub>+SnO<sub>2</sub> and Pb/PbO<sub>2</sub>) which can be 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 overpotential, 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. The different operating conditions of treatment process were studied which include: current density, pH, temperature, type of conductive electrolyte and pH. The different operating conditions were studied and optimized. 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<sup>-2</sup> and in the presence of NaCl (6 g L<sup>-1</sup>) at 25 °C.

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**Keywords:** Electrochemical degradation; Reactive Red 24; electrodes; electrodeposition; electrocatalytic oxidation.

### 1. INTRODUCTION

Wastewater from textile industry is the major source of color and aromatic amines into the environment[1]. The color from textile industries is mainly due to dyeing process. There are more than 10,000 dyes used in textile industry and 280,000 t of textile dyes are discharged every year [2]. Degradation of dyes especially azo dyes, which contribute to about 70% of all used dyes, is difficult due to their complex structure and synthetic nature. Azo dyes are characterized by nitrogen to nitrogen double bond (–N=N–). The color of dyes is due to azo bond and associated chromophores [3]. Color in

the textile mill effluent is one of the most obvious indicators of water pollution and the discharge of highly colored synthetic dye effluents is aesthetically displeasing and can damage the receiving water body by impeding penetration of light [4,5].

Decolonization of C.I. Reactive Red 24 (RR 24) with initial concentrations ranging from 150 to 2400 mg/L was investigated. Decolonization efficiencies obtained were 98.9% for with initial concentration of 2400 mg/L after 24 h incubation period [6]. At its natural pH (6.95), the decolonization of Reactive red 24 in ultrasound, ultrasound/H<sub>2</sub>O<sub>2</sub>, exfoliated graphite, ultrasound/exfoliated graphite, exfoliated graphite/H<sub>2</sub>O<sub>2</sub> and ultrasound/exfoliated graphite/H<sub>2</sub>O<sub>2</sub> systems were compared. An enhancement was observed for the decolonization in ultrasound/exfoliated graphite/H<sub>2</sub>O<sub>2</sub> system. The effect of solution pH, H<sub>2</sub>O<sub>2</sub> and exfoliated graphite dosages, and temperature on the decolonization of RR24 was investigated. The sonochemical treatment in combination with exfoliated graphite/H<sub>2</sub>O<sub>2</sub> showed a synergistic effect for the decolonization of RR24. The results indicated that under proper conditions, there was a possibility to remove RR24 very efficient from aqueous solution [7]. Different parameters were investigated to evaluate their effect on the process removal efficiency of reactive dye from simulated spent reactive dye bath, by solar/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>, including H<sub>2</sub>O<sub>2</sub> concentration, TiO<sub>2</sub> loading and pH. As a result 99% of reactive dye can be removed at a TiO<sub>2</sub> loading of 400mg/l, H<sub>2</sub>O<sub>2</sub> concentration of 150 mg/l and of pH: 5.2 [8].

Three different techniques were employed for oxidation of the Reactive Red 198(RR198) dye on Ti/Ru<sub>0.3</sub>Ti<sub>0.7</sub>O<sub>2</sub> electrode: photocatalytic, electrochemical and photoelectron-chemical. The effect of temperature and current density were investigated [9]. In advanced oxidation processes (AOPs), UV/TiO<sub>2</sub>, UV/ZnO and photo-Fenton, were applied in order to degrade C.I. Reactive Red 45 (RR45) dye in aqueous solution. The effects of key operating parameters, such as initial pH, catalyst and hydrogen peroxide dosage as well as the effect of initial dye concentration on decolonization and mineralization extents were studied [10]. The photocatalytic degradation of Reactive Red 239, has been studied. TiO<sub>2</sub> P25 Degussa was used as catalyst and photodegradation was carried out in aqueous solution under artificial irradiation with a 125 W mercury vapor lamp. The effects of the amount of TiO<sub>2</sub> used, UV-light irradiation time, pH of the solution under treatment, initial concentration of the azo dye and addition of different concentrations of hydrogen peroxide were investigated [11]. The accelerated sonophotocatalytic degradation of Reactive Red (RR) 120 dye under visible light using dye sensitized TiO<sub>2</sub> activated by ultrasound has been carried out. The effect of sonolysis, photocatalysis and sonophotocatalysis under visible light has been examined [12]. The effectiveness of nanoscale zerovalent iron (NZVI) to decolorize (RR198) in synthesized wastewater were determined and the effects of the iron particle size, iron dosage and solution pHs on the destruction of RB5 and RR198 were investigated [13].

Photocatalytic decoloration kinetics of triazine (Reactive Red 11, Reactive Red 2, and Reactive Orange 84) and vinylsulfone type (Reactive Orange 16 and Reactive Black 5) of reactive dyes have been studied spectrophotometrically by following the decrease in dye concentration with time. At ambient conditions, over 90–95% decoloration of above dyes have been observed upon prolonged illumination (15 h) of the reacting system with a 150W xenon lamp [14].

The mechanism of electrochemical degradation of RR24 dye may be occurred by: (a) direct anodic oxidation where the dyes are adsorbed on the anode surface (M) and destroyed by the anodic

electron transfer reaction and (b) indirect oxidation in the liquid bulk which is mediated by the oxidants that are formed electrochemically. Anodic water discharge results in the formation of hydroxyl radicals that are adsorbed on the anode surface and can then oxidize the organic matter [15, 16].

Lead dioxide, is characterized by high oxygen evolution overpotential, therefore, it is one of the most commonly used anodes for electrochemical degradation of many pollutants particularly when it is doped with metallic cations whose oxides have low oxygen evolution overpotential [17].

The purpose of this study, is to remove the RR24 dye electrochemically using C/PbO<sub>2</sub>, Pb+Sn/PbO<sub>2</sub>+SnO<sub>2</sub> and Pb/PbO<sub>2</sub> electrodes, which are under the most inexpensive metal/metal oxide and high oxygen evolution overpotential anodes. Different factors including the pH, concentration of electrolyte, conductive electrolyte type, current density, time of electrolysis, initial concentration of RR24 solution, and temperature were studied and optimized. Two main parameters were measured to evaluate the electrochemical treatment efficiency, the remaining pollutant concentration and the COD.

## 2. EXPERIMENTS

### 2.1. Chemicals and Instrumentation

Sodium chloride, sodium fluoride, sodium carbonate, sodium sulphate, calcium chloride, potassium chloride, sodium hydroxide, sulphuric acid, potassium dichromate, silver sulfate were of analytical grade and purchased from Merck. Distilled water was used for the preparation of solutions. Standard solutions of potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) reagent with silver sulfate (Ag<sub>2</sub>SO<sub>4</sub>) and potassium hydrogen phthalate (KHP) were prepared to measure the COD. Different standard solutions of RR24 with concentration from 20–200 mg L<sup>-1</sup> were prepared to measure its degradation at different conditions. The double-beam UV-Vis spectrophotometer is from Shimadzu, the DC power supply is model GP4303D, LG Precision CO. Ltd. (Korea), a pH meter model AC28, TOA electronics Ltd., (Japan) to adjust pH of the solutions and a digital multi-meter is Kyoritsu model 1008, (Japan) for reading out the current and potential values. A closed reflux titrimetric unit was used for the COD determination [18].

### 2.2. Electrodeposition of Doped Lead Dioxide at Different Substrates

#### 2.2.1. Preparation of Pb/PbO<sub>2</sub> modified electrode

##### 2.2.1.1. Lead surface treatment

Pretreatments of the lead substrate were carried out before anodization to ensure good adhesion for lead dioxide film. Lead was first roughened to increase the adhesion of PbO<sub>2</sub> deposit via subjecting its surface to mechanical abrasion by sand papers of different grades, down to 40/0. Then, it was cleaned by acetone to remove sand particles or any other particles lodged in the metal surface. This process has a great application and good penetrating power. Then it was treated with an alkali solution,

a mixture of sodium hydroxide ( $50 \text{ g L}^{-1}$ ) and sodium carbonate ( $20 \text{ g L}^{-1}$ ), to remove any organic materials in the surface, and tri-sodium orthophosphate ( $20 \text{ g L}^{-1}$ ) and sulphuric acid ( $2 \text{ g L}^{-1}$ ) to remove any oxides. Uniform and well adhesive deposit necessitates a smooth surface with no oxide or scales. To confirm our preparation, the lead substrate was soaked for 2 min. in a pickling solution consisting of nitric acid ( $400 \text{ g L}^{-1}$ ) and hydrofluoric acid ( $5 \text{ g L}^{-1}$ ) and then chemically polished in boiled oxalic acid solution ( $100 \text{ g L}^{-1}$ ) for 5 min [19].

### 2.2.1.2. Electrochemical deposition of $\text{PbO}_2$

$\text{PbO}_2$  was deposited galvanostatically on the pretreated lead substrate by electrochemical anodization of lead in oxalic acid solution ( $100 \text{ g L}^{-1}$ ). This acid solution was electrolyzed galvanostatically for 30 min. at ambient temperature using an anodic current density of  $100 \text{ mA cm}^{-2}$ . The cathode was stainless steel (austenitic type), and the two electrodes were concentric with the lead electrode axially. This arrangement gave the formation of a regular and uniform deposit [19].

### 2.2.2. Preparation of $\text{Pb+Sn/PbO}_2+\text{SnO}_2$ modified electrode

#### 2.2.2.1. Preparation and fabrication of Pb-Sn alloy electrodes

Binary Pb-Sn alloy with concentration (1:1 w/w) were prepared according the standard following procedure and the fabrication of the electrodes as discussed in detail elsewhere. Anodic oxidation of alloy electrodes was carried out and the film was characterized for its structure [20].

#### 2.2.1.2. Electrochemical deposition of $\text{PbO}_2+\text{SnO}_2$

Three electrodes assembly was used for making thin films, in which the working alloy electrodes was of  $1 \text{ cm}^2$  area with Pt (4 cm) as the counter-electrode and saturated calomel electrode (SCE) as the reference. Prior to oxidation, the working electrode surface was successively polished on 1000~ grit paper on roughing stone using water as lubricant and finally with methanol-acetic acid mixture. The alloy substrate was cleaned by acetone to remove greases or oils lodged in the metal surface, treated with an alkali solution, a mixture of sodium hydroxide ( $50 \text{ g L}^{-1}$ ) and sodium carbonate ( $20 \text{ g L}^{-1}$ ), to remove any organic materials in the surface, and tri-sodium orthophosphate ( $20 \text{ g L}^{-1}$ ), sulphuric acid ( $2 \text{ g L}^{-1}$ ) to remove any oxides. To confirm our preparation, the alloy substrate was soaked for 2 min. in a pickling solution consisting of nitric acid ( $400 \text{ g L}^{-1}$ ) and hydrofluoric acid ( $5 \text{ g L}^{-1}$ ) and then chemically polished in boiled oxalic acid solution ( $100 \text{ g L}^{-1}$ ) for 5 min. Potentiodynamic anodization of Pb-Sn alloy was carried out at  $80^\circ\text{C}$  in the potential range from  $-1.25 \text{ V}$  to  $+2.35 \text{ V}$  with a sweep rate  $200 \text{ mV s}^{-1}$ . After 20 min of continuous anodization,<sup>[20]</sup> the electrode was taken out of the electrolysis bath and washed thoroughly in doubly distilled water followed by drying in air at  $120^\circ\text{C}$  for 2 h.

### 2.2.3. Preparation of modified C/PbO<sub>2</sub> electrode

#### 2.2.3.1. Carbon surface treatment

Pretreatment of carbon rod (8 mm × 25 cm) was carried out following the procedure applied by Narasimham and Udupa.<sup>[21]</sup> The carbon rod was soaked in 5% NaOH solution, washed with distilled water, dried in furnace at 105 °C, and cooked with linseed oil to reduce the porosity of rod. After that the electrode is ready to receive doped PbO<sub>2</sub>.

#### 2.2.3.2. Electrochemical deposition of PbO<sub>2</sub>

The electrodeposition of PbO<sub>2</sub> was performed at constant anodic current of 20 mA cm<sup>-2</sup> in 12% (w/v) Pb(NO<sub>3</sub>)<sub>2</sub> solution containing 5% (w/v) CuSO<sub>4</sub>·5H<sub>2</sub>O and 3% surfactant. The role of the surfactant is to minimize the surface tension of the solution. Electrodeposition was carried out for 60 min. at 80°C with continuous stirring [21].

### 2.3. Electrolysis of Reactive Red 24 Degradation

Galvanostatic electrolyses were carried out at C/PbO<sub>2</sub>, Pb+Sn/PbO<sub>2</sub>+SnO<sub>2</sub> and Pb/PbO<sub>2</sub> electrodes, with current density ranging from 0 to 200 mAcm<sup>-2</sup> and electrical potential ranging from 1-12 volts. Runs were performed at 10 - 40°C. Solutions of 100 mg L<sup>-1</sup> of pure RR24 solution were used. The investigations of this study were carried out in the presence of sodium chloride (0.2-20 g L<sup>-1</sup>) and 6 g L<sup>-1</sup> of different conductive electrolytes such as; NaCl, CaCl<sub>2</sub>, KCl, Na<sub>2</sub>CO<sub>3</sub>, NaF, NaP O<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> with pH between 1.5 and 12. The electrolysis duration ranges from 0-30 min. The electrochemical degradation of the RR24 solutions was carried out in a 100 mL Pyrex glass cell where the prepared electrodes C/PbO<sub>2</sub>, Pb+Sn/PbO<sub>2</sub>+SnO<sub>2</sub> and Pb/PbO<sub>2</sub> work as anode and austenitic stainless steel as cathode. The electrodes were connected to a DC power supply while the current and potential measurements were read out using digital multi-meter.

### 2.4. Analysis

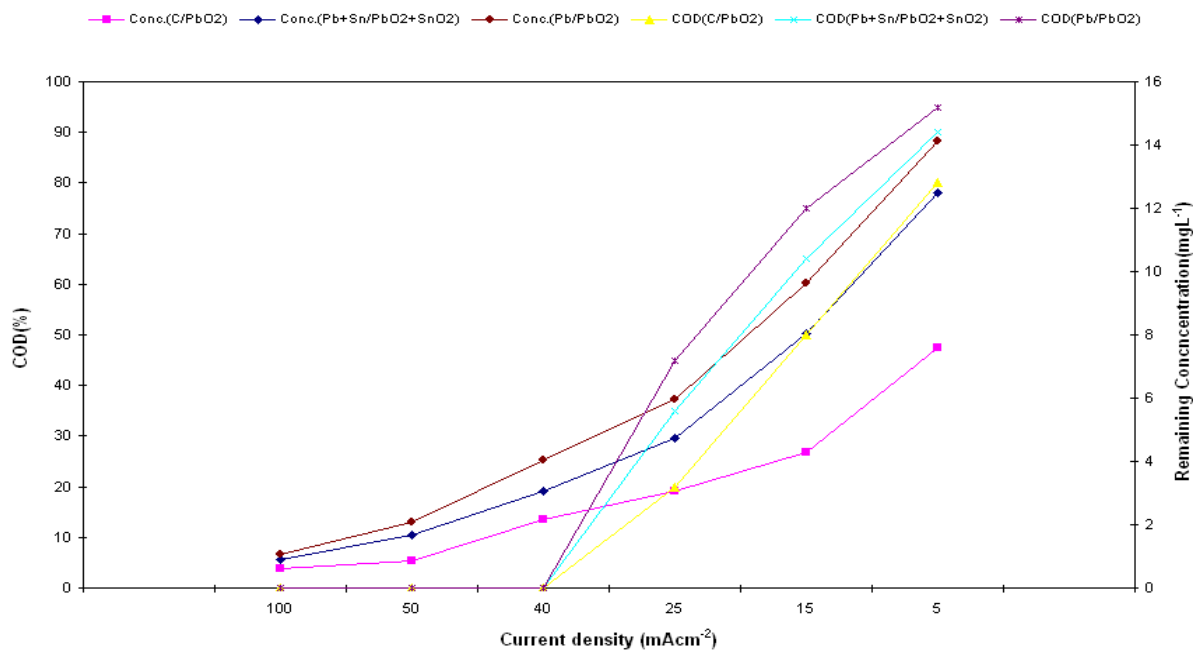
Two main parameters were measured to evaluate the electrochemical treatment efficiency, the remaining pollutant concentration and the COD. Remaining pollutants (RR24) concentration was measured with the double-beam UV-visible spectrophotometer from Shimadzu at  $\lambda_{\text{max}} = 500$  nm using calibration curve with standard error  $\pm 0.5$ . The COD was determined using a closed reflux titrimetric method [18].

## 3. RESULT AND DISCUSSION

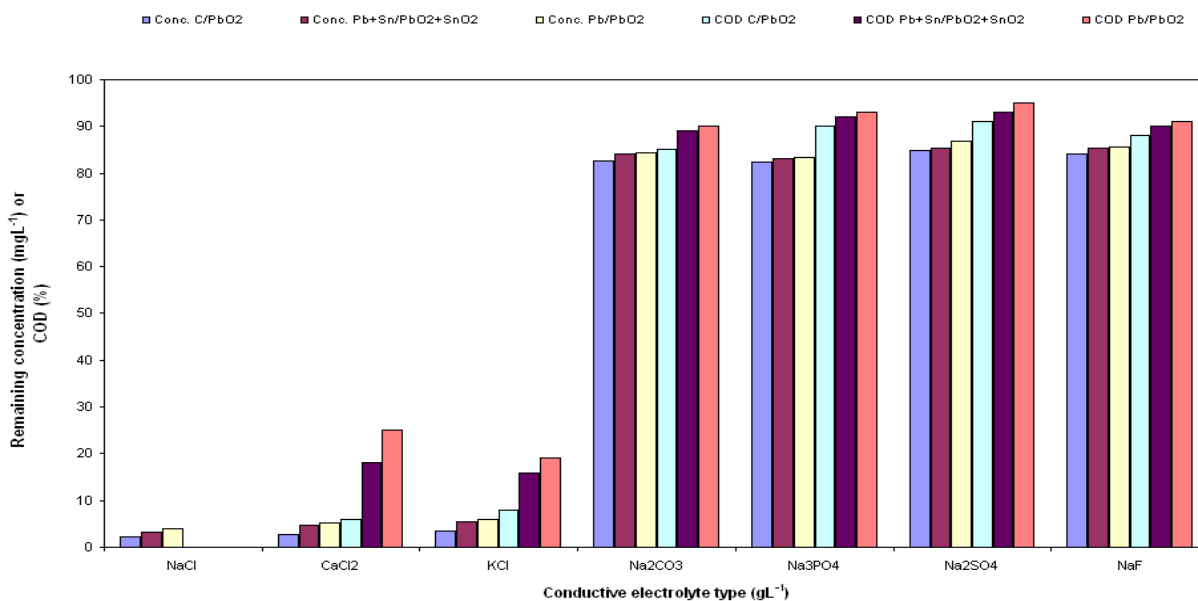
### 3.1. Effect of Various Factors on the Rate of Degradation

The effect of different operating conditions such as: type of conductive electrolyte, current density, pH of simulated solution, temperature, time interval of treatment, initial concentration, and

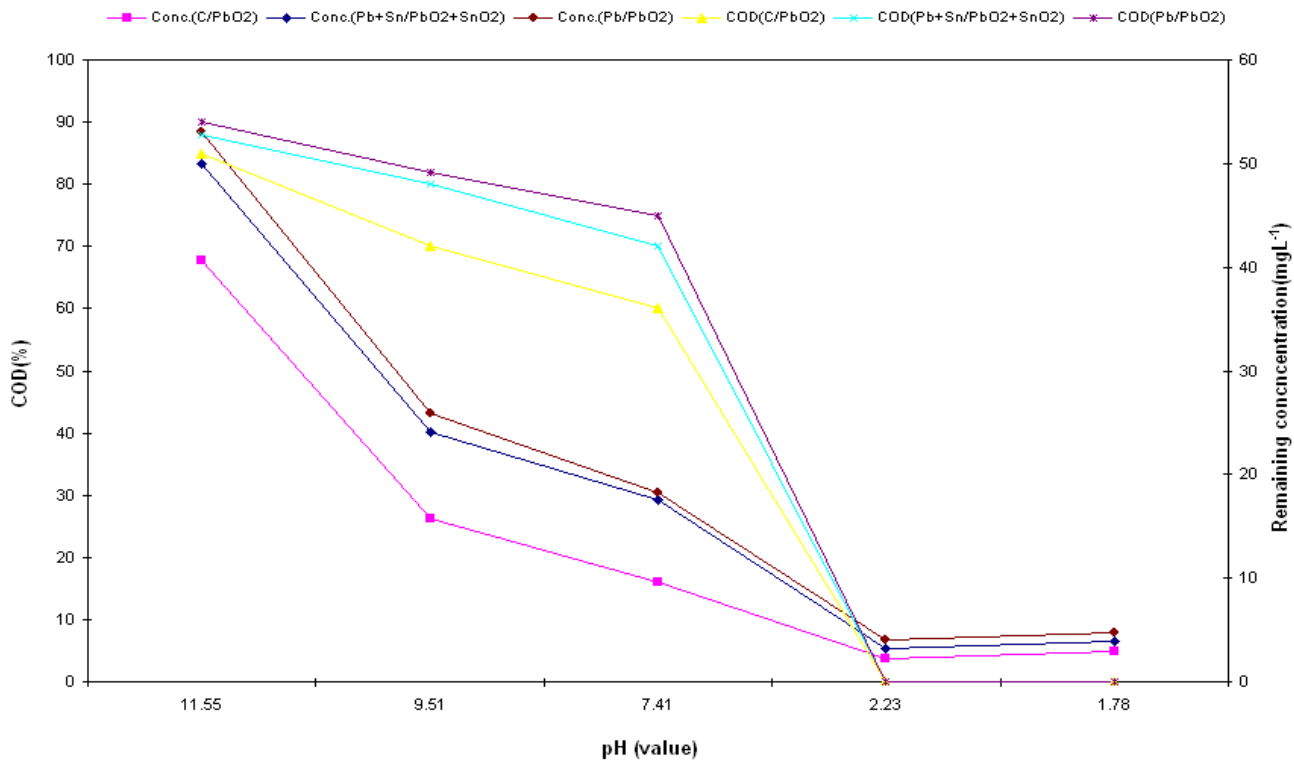
NaCl concentration were studied. The remaining concentration ( $\text{mg L}^{-1}$ ) and COD removal (%) were illustrated in Figs. 1-7.



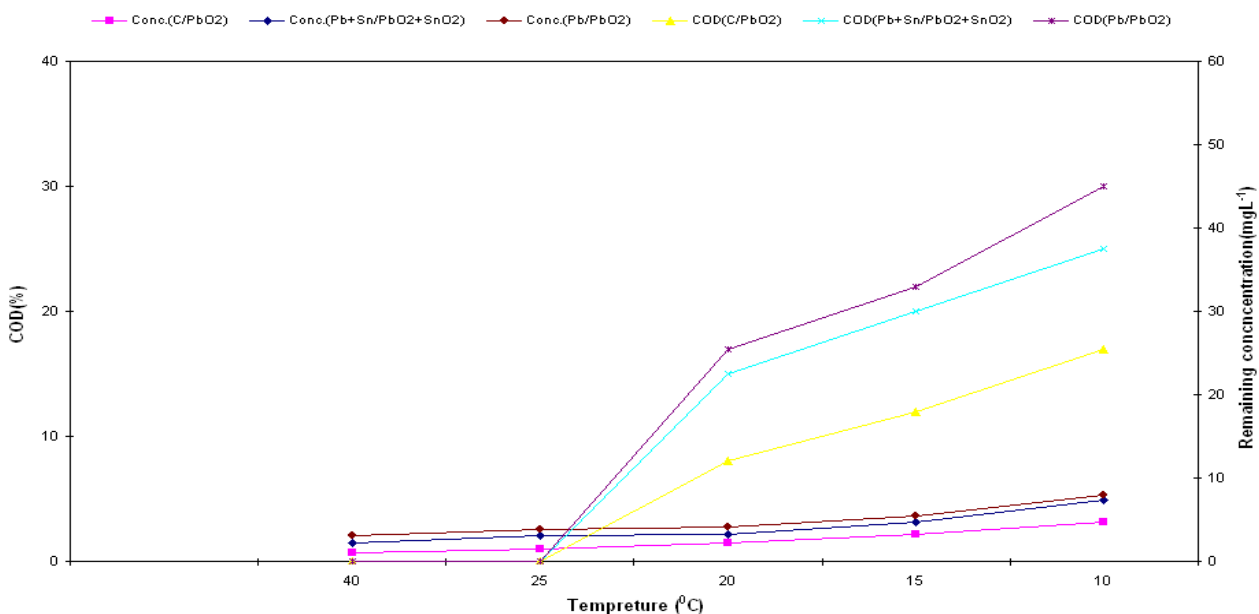
**Figure 1.** The effect of current density on **RR24** and COD removal using C/PbO<sub>2</sub>, Pb+Sn/PbO<sub>2</sub>+SnO<sub>2</sub> and Pb/PbO<sub>2</sub> electrodes.



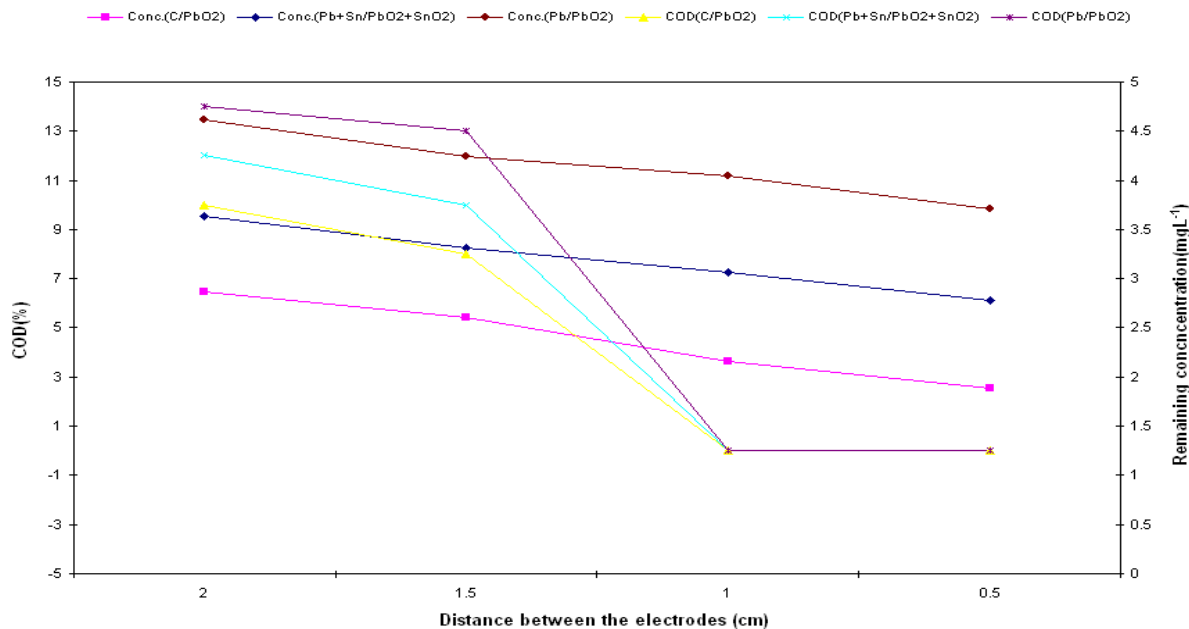
**Figure 2.** The effect of the conductive electrolyte type on **RR24** and COD removal using C/PbO<sub>2</sub>, Pb+Sn/PbO<sub>2</sub>+SnO<sub>2</sub> and Pb/PbO<sub>2</sub> electrodes.



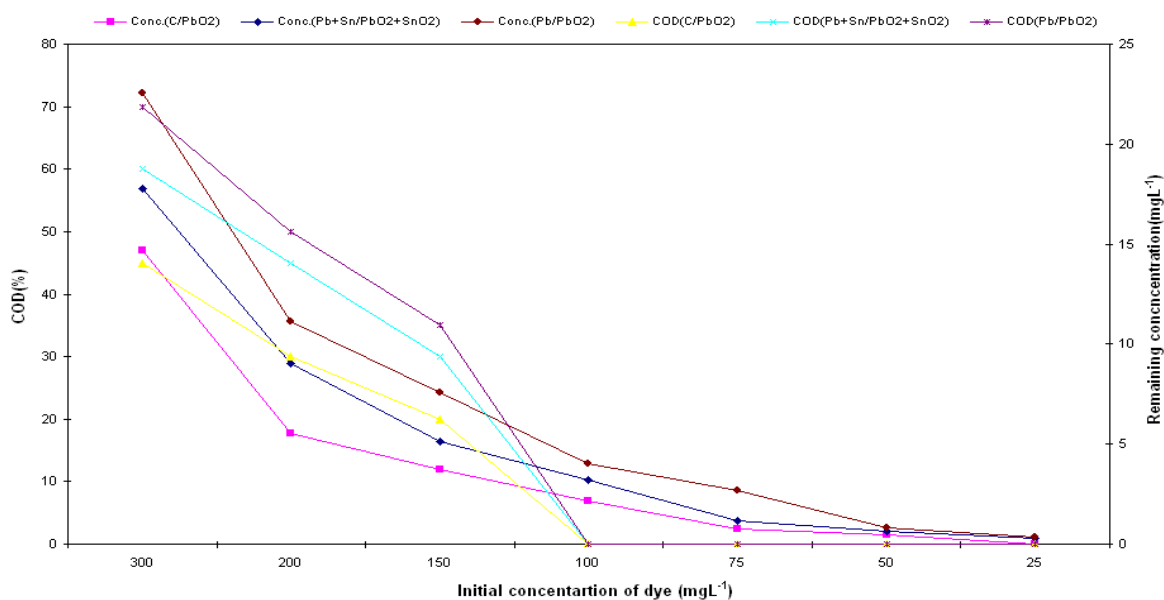
**Figure 3.** The effect of pH on **RR24** and COD removal using C/PbO<sub>2</sub>, Pb+Sn/PbO<sub>2</sub>+SnO<sub>2</sub> and Pb/PbO<sub>2</sub> electrodes.



**Figure 4.** The effect of temperature on **RR24** and COD removal using C/PbO<sub>2</sub>, Pb+Sn/PbO<sub>2</sub>+SnO<sub>2</sub> and Pb/PbO<sub>2</sub> electrodes.



**Figure 5.** The effect of distance between the cathode and anode on **RR24** and COD removal using C/PbO<sub>2</sub>, Pb+Sn/PbO<sub>2</sub>+SnO<sub>2</sub> and Pb/PbO<sub>2</sub> electrodes.



**Figure 6.** The effect of initial concentration on **RR24** and COD removal using C/PbO<sub>2</sub>, Pb+Sn/PbO<sub>2</sub>+SnO<sub>2</sub> and Pb/PbO<sub>2</sub> electrodes.

3.1.1. Effect of current density

As shown in Fig. 1, RR24 degradation and COD removal increase with increasing the applied current density up to 25 mA cm<sup>-2</sup> by using C/PbO<sub>2</sub>, Pb+Sn/PbO<sub>2</sub>+SnO<sub>2</sub> and Pb/PbO<sub>2</sub> electrodes. Further increase of the current density was followed by gradual decrease in RR24 degradation and



COD removal due to increase in temperature. Above a temperature 35°C, sodium hypochlorite tends to chemically decompose to sodium chlorate eq. (1).



So when temperature rises higher than 35°C, production of NaClO falls. But at higher current densities the rate of hypochlorite decomposition increases with increase in current density.

### 3.1.2. Effect of type of electrolyte

Electrolytes of 6 g L<sup>-1</sup> of the following salts; NaCl, CaCl<sub>2</sub>, KCl, Na<sub>2</sub>CO<sub>3</sub>, NaF, Na<sub>3</sub>PO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> were studied by three electrodes. As appears in Fig. 2, The NaCl, KCl and CaCl<sub>2</sub> were the most effective conductive electrolytes for the electrocatalytic degradation of the investigated RR24 and COD removal while NaF, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>3</sub>PO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> electrolytes show poor results. The Cl<sup>-</sup> anion is a powerful oxidizing agent. It enhances the degradation of pollutants. Therefore, addition of NaCl, KCl and CaCl<sub>2</sub> provides the effective Cl<sup>-</sup> ion. This behavior may be due to the small ionic size of K<sup>+</sup> and Na<sup>+</sup> which increases the ion mobility and the loss ability of Cl<sup>-</sup> ion. NaF, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>3</sub>PO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> electrolytes showed the least efficiency in the degradation of pollutant. This may be attributed to the formation of an adherent film on the anode surface which poisons the electrode surface. Also, these electrolytes do not contain chloride ion (Cl<sup>-</sup>) in their structures and may form stable intermediate species that could not be oxidized by direct electrolysis. These observations were also confirmed in other studies [19].

### 3.1.3. Effect of pH value

The pH of the solution was varied while the other conditions were kept constant. As shown in Fig. 3, maximum removal of RR24 and COD were achieved at pH 2.23 for C/PbO<sub>2</sub>, Pb+Sn/PbO<sub>2</sub>+SnO<sub>2</sub> and Pb/PbO<sub>2</sub>, respectively. The pH values of the solutions were adjusted by adding drops of H<sub>2</sub>SO<sub>4</sub> and NaOH. The reactions were carried out for 15 min for the three electrodes under the following conditions: the initial concentration of 100 mg L<sup>-1</sup>, a current density of 25 mA cm<sup>-2</sup>, a temperature of 25 °C and NaCl concentration of 6 g L<sup>-1</sup>. The distance between the two electrodes was adjusted to 1cm. It was found that the maximum rate of degradation using C/PbO<sub>2</sub>, Pb+Sn/PbO<sub>2</sub>+SnO<sub>2</sub> and Pb/PbO<sub>2</sub> electrodes was achieved in slightly acid medium as the optimal medium. The presence of protons capable of generating species of powerful oxidizing power and the conditions at the electrode surface play a paramount rule in the electrocatalytic degradation of organic pollutants on modified electrodes and this increase as the number of protons increase.

### 3.1.4. Effect of temperature

It is well known that the rate of diffusion of ions increases with increasing temperature. Fig. 4 represents the correlation between the concentration of the remaining RR24 dye and COD residual as a

function of the solution temperature. The rate of the RR24 degradation and COD removal increase significantly with increasing the solution temperature until 25°C. Therefore, 25°C was fixed as optimal electrolysis temperature under the same conditions mentioned respectively. From this figure, it is clear that the increasing remaining concentration and COD above 35°C may be attributed to decomposition of adsorbed film on anodic side. Also, the electrode is unstable at high temperature above 45°C [22]. Above a temperature 35°C, sodium hypochlorite tends to chemically decompose to sodium chlorate eq. (1). so when temperature rises higher than 35°C, production of NaClO falls and the degradation also decreases.

### 3.1.5. Effect of distance between the cathode and anode

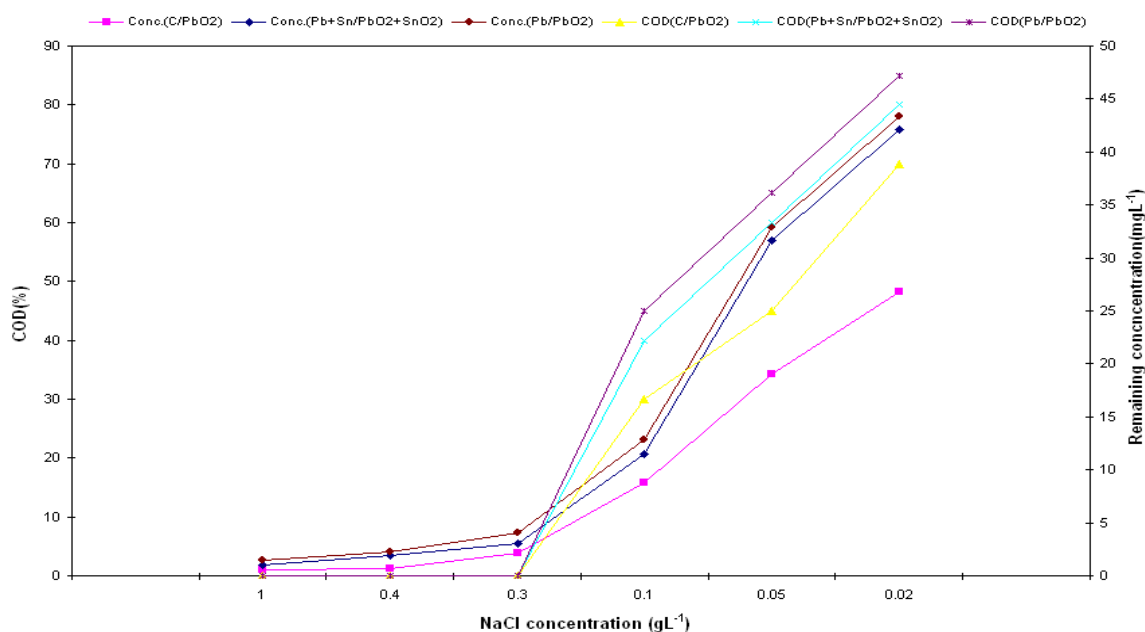
The effect of distance between the two electrodes of the cell was studied. It was found from Fig.5 that there was an increase of hypochlorite generation by decreasing the distance between the two electrodes up to 1cm for C/PbO<sub>2</sub>, Pb+Sn/PbO<sub>2</sub>+SnO<sub>2</sub> and Pb/PbO<sub>2</sub> electrodes. Therefore 1 cm was chosen as optimum distance between electrodes for sodium hypochlorite generation. The experiments were carried out under the following conditions; current density 25 mA cm<sup>-2</sup>, pH of 2.23, temperature of 25 °C and the concentration of NaCl 6 g L<sup>-1</sup>. The time of electrolysis was 15 min. It is clear that the sodium hypochlorite production increase with decreasing distance down to 1cm. This is due to drop of electrolyte ohmic potential, and hence the cell voltage [23]. The highest hypochlorite production was achieved with narrow distance between the cell electrodes of 1cm.

### 3.1.6. Effect of initial RR24 concentration

Fig. 6 shows the effect of different initial RR24 concentrations on the rate of R24 degradation and corresponding COD removal. Total removal of the RR24 and COD can be achieved in the presence of initial RR24 load up to 100 mg L<sup>-1</sup>. However, increasing the RR24 concentration above this level results in a decrease in the electro-catalytic rate of degradation. The removal efficiency of the RR24 by using C/PbO<sub>2</sub>, Pb+Sn/PbO<sub>2</sub>+SnO<sub>2</sub> and Pb/PbO<sub>2</sub> electrodes at 100 mg L<sup>-1</sup> was the optimum concentration for the initial load concentration of RR24. As the initial RR24 concentration increase, the degradation efficiency decrease. This evidence that the generation of the powerful oxidizing agent Cl<sup>-</sup> ions on electrode surface was not increased in constant current density. The optimum operating conditions for degradation RR24 dye for each electrode were determined and summarized in Table (2). At optimized conditions, the percentages of RR24 degradation and COD removal for C/PbO<sub>2</sub>, Pb+Sn/PbO<sub>2</sub> +SnO<sub>2</sub> and Pb/PbO<sub>2</sub> are 97.84%, 96.82 and 95.95% respectively. The results indicate that the C/PbO<sub>2</sub> electrode is more adequate than Pb+Sn/PbO<sub>2</sub>+SnO<sub>2</sub> and than Pb/PbO<sub>2</sub> modified electrode for the degradation of RR24. These behaviors may be attributed to the color and structure of tested electrodes. C/PbO<sub>2</sub> modified electrodes have a black color, while Pb+Sn/PbO<sub>2</sub>+SnO<sub>2</sub> and Pb/PbO<sub>2</sub> modified electrodes has a brown color. It was reported that PbO<sub>2</sub> film has two structures,  $\alpha$ -structure (brown color) and  $\beta$ -one (black color). The black one has a tetrahedral crystal structure which is a close-packed structure and more disorder in comparison with the close-packed structure of the brown

$\alpha$ -form (orthorhombic). Therefore, the surface area in case of tetrahedral structure is more than orthorhombic one, and hence the  $\beta$ -PbO<sub>2</sub> form will be more effective than  $\alpha$ -PbO<sub>2</sub> form. Because the over potential for oxygen evolution of  $\beta$ -PbO<sub>2</sub> is higher than that of  $\alpha$ -PbO<sub>2</sub> it is expected that the electrocatalytic properties for C/PbO<sub>2</sub> modified electrodes are more efficient than that of Pb/PbO<sub>2</sub> modified electrode [24]. In this work the degradation rate of RR24 was nearly completed and reached 97.84%, 96.82 and 95.95% using C/PbO<sub>2</sub>, Pb+Sn/PbO<sub>2</sub>+SnO<sub>2</sub> and Pb/PbO<sub>2</sub> electrodes respectively after 15 min.

### 3.1.7. Effect of the NaCl concentration



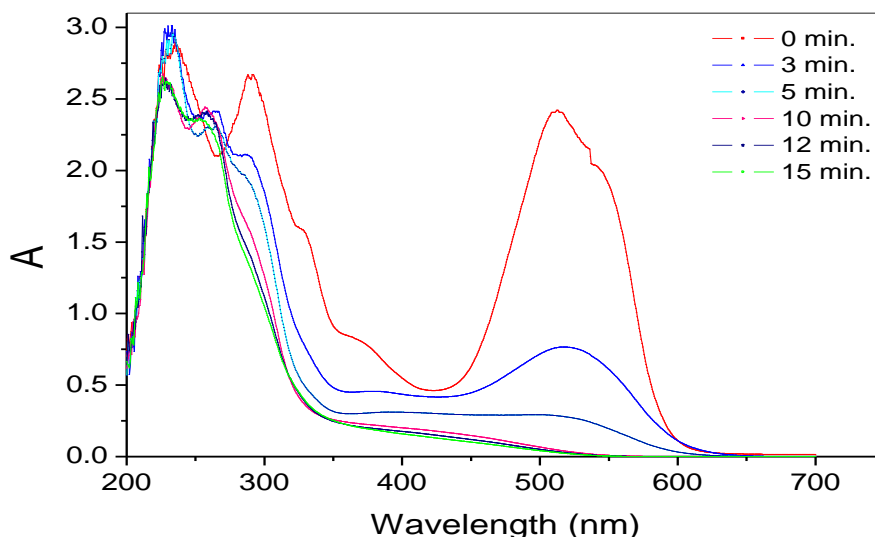
**Figure 7.** The effect of NaCl concentration on **RR24** and COD removal using C/PbO<sub>2</sub>, Pb+Sn/PbO<sub>2</sub>+SnO<sub>2</sub> and Pb/PbO<sub>2</sub> electrodes.

Different concentrations of NaCl were applied to study their effect on the removal of RR24 and the corresponding COD elimination as indicated in Fig. 7. The results indicate that an increase of the electrolyte concentration up to 6 gL<sup>-1</sup> lead to increase in the RR24 degradation rate and COD removal for three C/PbO<sub>2</sub>, Pb+Sn/PbO<sub>2</sub>+SnO<sub>2</sub> and Pb/PbO<sub>2</sub> electrodes. The NaCl solution liberates Cl<sub>2</sub> gas which is considered as the active species for the degradation of organic compound. Further increase of the NaCl concentration has slightly effect on the degradation rate of RR24 and COD removal. From this Figure it is clear that the less value of remaining concentration and COD was obtained in presence of NaCl. This indicates that NaCl is the most effective electrolyte in electrodegradation of wastewater. The OCl<sup>-</sup> anion is a powerful oxidizing agent. It enhances the degradation of pollutants. Therefore, addition of NaCl provides the effective Cl<sup>-</sup> ion which intern the main source for formation of OCl<sup>-</sup> ion. From the above Figures NaCl is considered as the most preferential electrolyte. This behavior observed may be due to the small ion size of Na<sup>+</sup> which increases the ion mobilities [25].

### 3.1.8. Effect of the electrolysis time

To assess the effect of electrolysis time, experiments were conducted with operating treatment conditions that were consistent with those described for C/PbO<sub>2</sub>, Pb+Sn/PbO<sub>2</sub>+SnO<sub>2</sub> and Pb/PbO<sub>2</sub> electrodes. The maximum removal of RR24 was achieved using C/PbO<sub>2</sub>, Pb+Sn/PbO<sub>2</sub>+SnO<sub>2</sub> and Pb/PbO<sub>2</sub> electrodes after at least 15 min. Therefore, this was taken as optimal degradation time for the removal of RR24. The optimal time for COD removal for three electrodes was 375, 430 and 460 min., respectively.

### 3.2. UV-Vis Spectra of Dyes



**Figure 8.** Time-dependent UV-Vis absorption spectra for decolorization of **RR24**.

The rate of decolorization was recorded with respect to the change in the intensity of absorption peak in visible region. Fig. 8 shows typical time-dependent UV-Vis spectrum of RR24 dye during electrochemical degradation using C/PbO<sub>2</sub> electrode. The prominent peak was observed at  $\lambda_{\max} = 500$  nm which decreased gradually and finally disappeared indicating that the dye had been degraded. The absorbance decreasing indicated that chromophore group, the basic functional group of dyes for its visible color, was broken down. Many previous experiments demonstrated that azo bond (N=N) was destroyed by the C/PbO<sub>2</sub> electrode.

### 3.3. Comparison with other Method of Treatment

It is resulted that the electrochemical degradation was the best when it was compared between each method using in literature and electrochemical method in this work, which represented in table 1.

The optimum operating conditions for degradation RR24 dye for each electrode were determined and summarized in Table (2). At optimized conditions, the percentages of RR24

degradation and COD removal for C/PbO<sub>2</sub>, Pb+Sn/PbO<sub>2</sub>+SnO<sub>2</sub> and Pb/PbO<sub>2</sub> are 97.66%, 95.33 and 94.60% respectively. The results indicate that the C/PbO<sub>2</sub> electrode is more adequate than Pb+Sn/PbO<sub>2</sub>+SnO<sub>2</sub> and than Pb/PbO<sub>2</sub> modified electrode for the degradation of RR24. These behaviors may be attributed to the color and structure of tested electrodes. C/PbO<sub>2</sub> modified electrodes have a black color, while Pb+Sn/PbO<sub>2</sub>+SnO<sub>2</sub> and Pb/PbO<sub>2</sub> modified electrodes has a brown color.

It was reported that PbO<sub>2</sub> film has two structures,  $\alpha$ -structure (brown color) and  $\beta$ -one (black color). The black one has a tetrahedral crystal structure which is a close-packed structure and more disorder in comparison with the close-packed structure of the brown  $\alpha$ -form (orthorhombic).

**Table 1.** Comparison of proposed electrodes and some decolonization technologies for (RR24) dye and its derivatives removal.

Method of treatment	Initial dye concentration (mg L <sup>-1</sup> )	Color removal efficiency (%)	Time	Literature
Anaerobic condition by mixed microbial culture	147.4	99.8	24 h	1
UV/TiO <sub>2</sub>	80	71	1 h	5
UV/ZnO	80	60.1	1 h	5
Photo-Fenton	80	Compleat decolorizat	1 h	5
Visible light irradiated TiO <sub>2</sub> (semiconductor photocatalyst)	50	93	15 h	9
Phytodegradation by water hyacinth	50	71.7	144 h	26
Electron beam irradiation	100	84	48 h	27
C/PbO <sub>2</sub> electrode	100	97.84	1/4 h	This work
Pb/PbO <sub>2</sub> electrode	100	95.95	1/4 h	
Pb+Sn/PbO <sub>2</sub> +SnO <sub>2</sub> electrode	100	96.82	1/4 h	

**Table 2.** Percentage of COD and concentration removal of RR24 on C/PbO<sub>2</sub>, Pb+Sn/PbO<sub>2</sub>+SnO<sub>2</sub> and Pb/PbO<sub>2</sub> electrodes.

Type of electrode	Removal percent of RR24 at 15 min	Removal percent of COD	Removal percent of COD for real samples
C/PbO <sub>2</sub>	97.84	Zero at 375 min	Zero at 415 min
Pb+Sn/PbO <sub>2</sub> +SnO <sub>2</sub>	96.82	Zero at 430 min	Zero at 470 min
Pb/PbO <sub>2</sub>	95.95	Zero at 460 min	Zero at 490 min

Therefore, the surface area in case of tetrahedral structure is more than orthorhombic one, and hence the  $\beta$ -PbO<sub>2</sub> form will be more effective than  $\alpha$ -PbO<sub>2</sub> form [28]. Because the over potential for oxygen evolution of  $\beta$ -PbO<sub>2</sub> is higher than that of  $\alpha$ -PbO<sub>2</sub> it is expected that the electrocatalytic properties for C/PbO<sub>2</sub> modified electrodes are more efficient than that of Pb/PbO<sub>2</sub> modified electrode [20]. In this work the degradation rate of RR24 was nearly completed and reached 97.66, 95.33 and 94.60 percentage using C/PbO<sub>2</sub>, Pb+Sn/PbO<sub>2</sub>+SnO<sub>2</sub> and Pb/PbO<sub>2</sub> electrodes respectively after 15 min.

### 3.4. Application of the Treatment Process in Real Wastewater Sample

The treatment of RR24 effluents obtained from Hubbub dyeing factory located in the industrial area at Biet Hanon, (PNA) Gaza Strip was carried out by using the prepared (C/PbO<sub>2</sub>, Pb+Sn/PbO<sub>2</sub>+SnO<sub>2</sub> and Pb/PbO<sub>2</sub>) modified electrodes. The treatment was performed, first by collecting actual waste samples (Composite sample) from the wastewater effluents of the RR24 dyeing bath. The chemical characterization of this sample containing the following: (RR24 dye = 175 mg/L, Detergent, Soda ash, Glacial acetic acid, Sodium chloride, pH = 2.23, Temp. = 25 °C).

The dyestuff solutions was treated by the electrocatalytic oxidation technique by the same method as applied to the treatment of RR24 in aqueous solution to investigate the optimum condition for real wastewater containing the dye. After the treatment process, the removal percent of RR24 at 15 min using C/PbO<sub>2</sub>, Pb+Sn/PbO<sub>2</sub>+SnO<sub>2</sub> and Pb/PbO<sub>2</sub> electrodes was (92.30%, 89.90 and 87.30%) respectively, and removal percent of COD showed that (Zero at 415, 470 and 490 min) respectively. These results indicate that the suggested modified electrodes are highly efficient in the treatment of effluents containing RR24 dye with very slight effect of matrix.

## 4. CONCLUSION

The optimum condition for three electrodes in this work are: NaCl (6 g L<sup>-1</sup>), temperature at 25°C, degradation time of 15 min, initial concentration of 100 mg L<sup>-1</sup>, current density equals 25 mA cm<sup>-2</sup> and 1cm distance between the three electrodes of the cell. The three modified electrodes (C/PbO<sub>2</sub>, Pb+Sn/PbO<sub>2</sub>+SnO<sub>2</sub> and Pb/PbO<sub>2</sub>) were prepared by electrodeposition and used as anodes for electrodegradation of RR24 in aqueous solutions. The degradation of RR24 was nearly completed (97.84%, 96.82 and 95.95%) using C/PbO<sub>2</sub>, Pb+Sn/PbO<sub>2</sub>+SnO<sub>2</sub> and Pb/PbO<sub>2</sub> electrodes at pH 2.23, respectively.

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