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Comparative Study of Commercial Oxide Electrodes Performance in Electrochemical Degradation of Reactive Orange 7 Dye in Aqueous Solutions

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The C/PbO_2, $Pb+Sn/PbO_2+SnO_2$ and Pb/PbO_2 electrodes were prepared by electrodeposition and used as anodes for electrochemical degradation of Reactive Orange 7 (RO7) 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. Different operating conditions and factors affecting the treatment process including current density, temperature, initial concentration of RO7, pH, conductive electrolyte and time of electrolysis were studied and optimized. After 15 min, nearly complete degradation of RO7 was achieved (97.66%, 95.33 and 94.60%) using C/PbO_2, $Pb+Sn/PbO_2+SnO_2$ and Pb/PbO_2 electrodes, respectively, at pH 2.54, current density 25 mA cm^{-2} and in the presence of NaCl (4 g L^{-1}) at 25 ^{o}C.

Keywords: Electrochemical degradation; Reactive Orange 7; electrodes; electrodeposition; electrocatalytic oxidation.

1. INTRODUCTION

Advanced oxidation processes (AOPs) are alternative techniques of destruction of dyes and many other organics in wastewater and effluents. These processes generally, involve UV/H_2O_2, UV/O_3 or UV/Fenton's reagent for the oxidative degradation of contaminants. Semiconductor photocatalysis is another developed AOP, which can be conveniently applied to remove of different organic pollutants [1–4]. In Fenton-like reaction $O^{\cdot}$ radicals will be generated by using Fe and UV light, so it can occur without the addition of hydrogen peroxide. Various parameters such as pH, amount of iron powder, initial dye concentration, UV light and contact time were studied [5].

Acid Orange 7 (AO7) commonly used as a textile dye and could be degraded by UV/ZnO, solar photodegradation, UV/H_2O_2 and UV/H_2O_2/Fe (III) processes. In the photocatalytic degradation of dye by UV/ZnO process, effect of some parameters such as UV irradiation time, presence of ZnO and UV irradiation, pH, concentrations of ZnO, dye, H_2O_2 and ethanol was examined [6]. Electrooxidation over anodes made of graphite, Pt, TiO_2, IrO_2, PbO_2, several Ti-based alloys and, more recently, boron-doped diamond electrodes in the presence of a supporting electrolyte (NaCl) has been employed for the decontamination of various industrial effluents [7-9]. Several recent studies report the use of electrooxidation to treat model aqueous solutions containing various dyes. Rajkumar *et al*. [10] studied the electrochemical degradation of Reactive Blue 19 over a titanium-based dimensionally stable anode regarding the effect of operating conditions (current density, salinity, reaction temperature and initial dye concentration) on treatment performance, while they also identified major reaction intermediates. The effect of various operating conditions on Acid Blue and Basic Brown degradation over a lead/lead oxide anode were Studied and optimized [11] while the investigation of various operating conditions on Acid Orange 7 were over a boron-doped diamond anode [12].

The electrochemical oxidation of Acid Orange 7 was performed using $BaPb_{0.9}Sb_{0.1}O_{3-6}$ as anode. Bulk electrolysis was studied using Na_2SO_4 as electrolyte, at a current density 5 $mAcm^{-2}$. UV-Visible absorbance measurements, Chemical Oxygen Demand (COD), Total Organic Carbon (TOC) and High Performance Liquid Chromatography (HPLC) analysis were performed. The obtained results show an almost complete color removal for the solutions containing AO7 after 24 h essay. After 96 h electrodegradation experiment, COD removals between 30 and 70 % and TOC removals ranging from 15 to 40 % [13].

The mechanism of electrochemical degradation of RO7 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 [14, 15].

$$H_2O + M \rightarrow M[OH^{\bullet]} + H^+ + e^- \tag{1}$$

$$R + M[OH^{\bullet}] \rightarrow M + RO + H^+ + e^- \tag{2}$$

In the presence of NaCl, chlorohydroxyl radicals are also formed on the anode surface and then oxidize the organic matter:

$$H_2O + M + Cl^- \rightarrow M[ClOH^{\bullet}] + H^+ + 2e^- \tag{3}$$

$$R + M[ClOH^{\bullet}] \rightarrow M + RO + H^+ + Cl^- \tag{4}$$

Reactions between water and radicals near the anode can yield molecular oxygen, free chlorine and hydrogen peroxide:

$$H_2O + M[OH\bullet] \rightarrow M + O_2 + 3H+ + 3e- \quad (5)$$

$$H_2O + M[ClOH^\bullet] + Cl^- \rightarrow M + O_2 + Cl_2 + 3H^+ + 4e^- \quad (6)$$

$$H_2O + M[OH^\bullet] \rightarrow M + H_2O_2 + H^+ + e^- \quad (7)$$

Furthermore, hypochlorite can be formed as follows:

$$H_2O + Cl^- \rightarrow HOCl + H^+ + 2e^- \quad (8)$$

Therefore, direct anodic oxidation through reactions (2) and (4) results in reduced COD as well as the formation of primary oxidants such as oxygen, chlorine, hypochlorite and hydrogen peroxide. Free chlorine and oxygen can further react on the anode yielding secondary oxidants such as chlorine dioxide and ozone, respectively:

$$H_2O + M[ClOH^\bullet] + Cl_2 \rightarrow M + ClO_2 + 3H^+ + 2Cl^- + e^- \quad (9)$$

$$O_2 + M[OH^\bullet] \rightarrow M + O_3 + H^+ + e^- \quad (10)$$

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 [16].

The purpose of this study, is to remove the Reactive Orange 7 dye electrochemically using C/PbO_2, $Pb+Sn/PbO_2+SnO_2$ and Pb/PbO_2 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 RO7 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 ($K_2Cr_2O_7$), sulfuric acid (H_2SO_4) reagent with silver sulfate (Ag_2SO_4) and potassium hydrogen phthalate (KHP) were prepared to measure the COD. Different standard solutions of RO7 with concentration from 20–200 mg L^{-1} 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 [17].

2.2. Electrodeposition of Doped Lead Dioxide at Different Substrates

2.2.1. Preparation of Pb/PbO_2 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_2 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 g L^{-1}) and sodium carbonate (20 g L^{-1}), to remove any organic materials in the surface, and tri-sodium orthophosphate (20 g L^{-1}) and sulphuric acid (2 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 g L^{-1}) and hydrofluoric acid (5 g L^{-1}) and then chemically polished in boiled oxalic acid solution (100 g L^{-1}) for 5 min [12].

2.2.1.2. Electrochemical deposition of PbO_2

PbO_2 was deposited galvanostatically on the pretreated lead substrate by electrochemical anodization of lead in oxalic acid solution (100 g L^{-1}). This acid solution was electrolyzed galvanostatically for 30 min. at ambient temperature using an anodic current density of 100 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 [12].

2.2.2. Preparation of Pb+Sn/PbO_2+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 [18].

2.2.1.2. Electrochemical deposition of PbO_2+SnO_2

Three electrodes assembly was used for making thin films, in which the working alloy electrodes was of 1 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 g L^{-1}) and sodium carbonate (20 g L^{-1}), to remove any organic materials in the surface, and tri-sodium orthophosphate (20 g L^{-1}), sulphuric acid (2 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 g L^{-1}) and hydrofluoric acid (5 g L^{-1}) and then chemically polished in boiled oxalic acid solution (100 g L^{-1}) for 5 min. Potentiodynamic anodization of Pb-Sn alloy was carried out at 80^{o}C in the potential range from -1.25 V to +2.35 V with a sweep rate 200 mV s^{-1}. After 20 min of continuous anodization, [18] the electrode was taken out of the electrolysis bath and washed thoroughly in doubly distilled water followed by drying in air at 120 ^{o}C for 2 h.

2.2.3. Preparation of modified C/PbO_2 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 [19]. 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 $PbO_{2.}$

2.2.3.2. Electrochemical deposition of PbO_2

The electrodeposition of PbO_2 was performed at constant anodic current of 20 mA cm^{-2} in 12% (w/v) $Pb(NO_3)_2$ solution containing 5% (w/v) $CuSO_4.5H_2O$ 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^{o}C with continuous stirring [19].

2.3. Electrolysis of Reactive Orange 7 Degradation

Galvanostatic electrolyses were carried out at C/$PbO_{2,}$ Pb+Sn/PbO_2+SnO_2 and Pb/PbO_2 electrodes, with current density ranging from 0 to 200 $mAcm^{-2}$ and electrical potential ranging from 1-12 volts. Runs were performed at 10 - 40^{o}C. Solutions of 100 mg L^{-1} of pure RO7 solution were used. The investigations of this study were carried out in the presence of sodium chloride (0.2-20 g L^{-1}) and 2 g L^{-1} of different conductive electrolytes such as; NaCl, $CaCl_2$, KCl, Na_2CO_3, NaF, NaP O_4 and Na_2SO_4 with pH between 1.5 and 12. The electrolysis duration ranges from 0-30 min. The electrochemical degradation of the RO7 solutions was carried out in a 100 mL Pyrex glass cell where the prepared electrodes C/PbO_2, Pb+Sn/PbO_2+SnO_2 and Pb/PbO_2 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 (RO7) concentration was measured with the double-beam UV-visible spectrophotometer from Shimadzu at λ_{max} = 470 nm using calibration curve with standard error ±0.5. The COD was determined using a closed reflux titrimetric method [17].

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 (mg L^{-1}) and COD removal (%) were illustrated in Figs. 1-7.

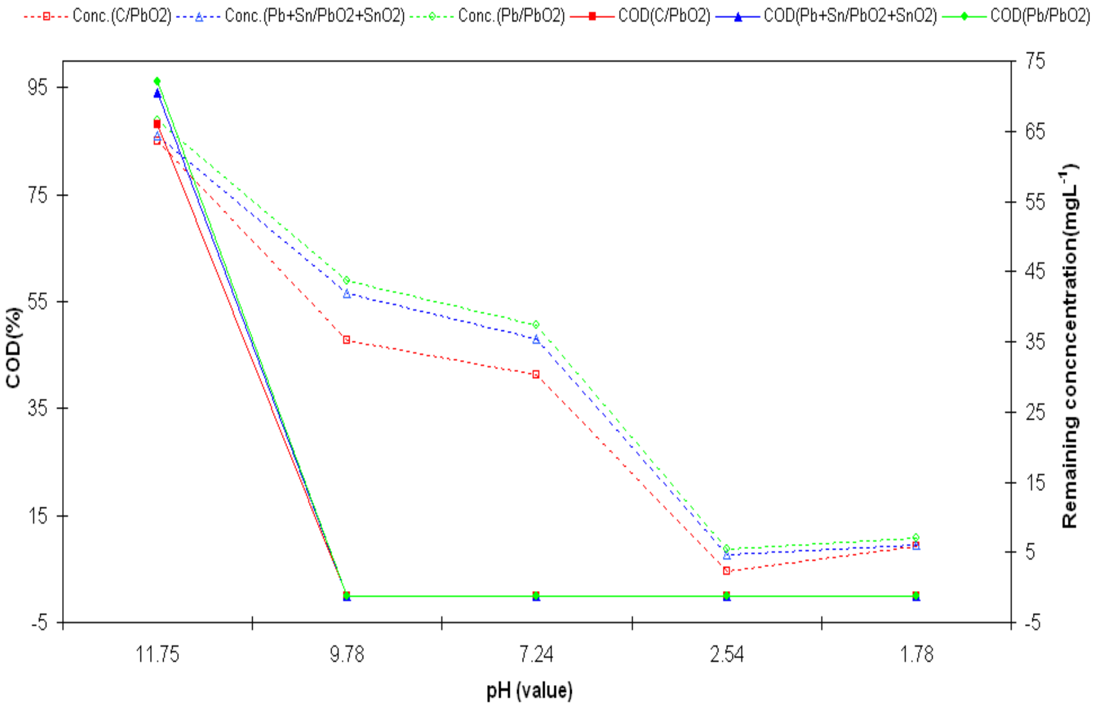

Figure 1. The effect of pH on RO7 and COD removal using C/PbO_2, Pb+Sn/PbO_2+SnO_2 and Pb/PbO_2 electrodes.

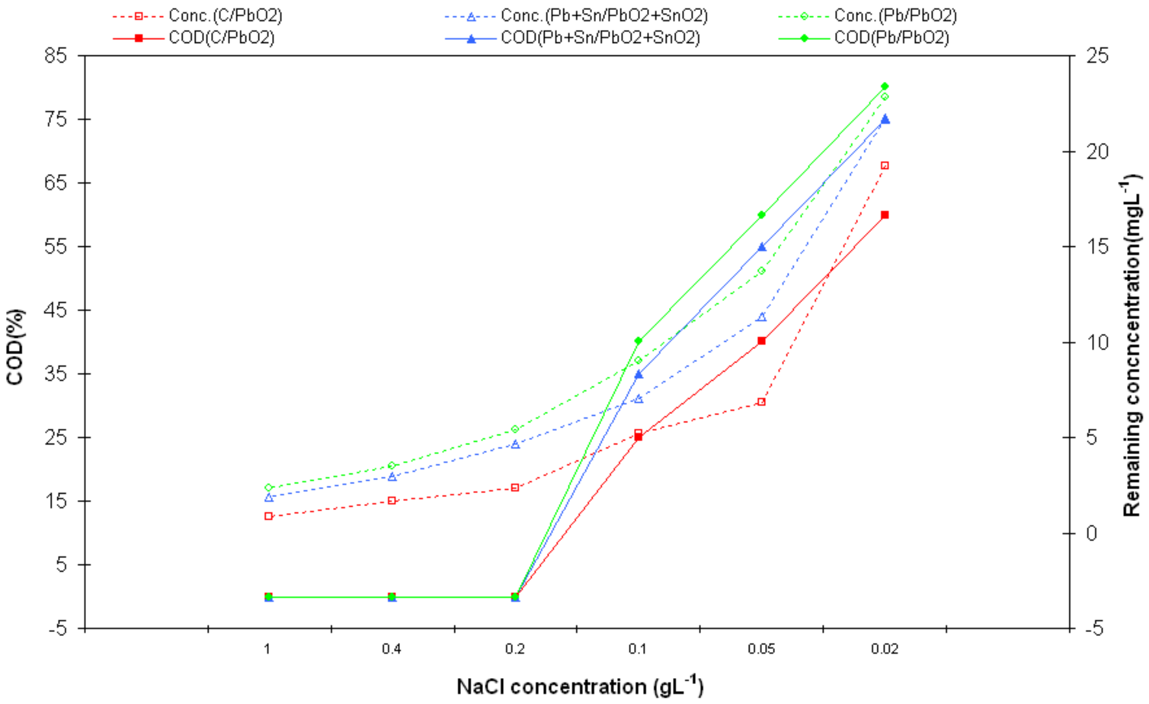

Figure 2. The effect of NaCl concentration on RO7 and COD removal using C/PbO$_2$, Pb+Sn/PbO$_2$+SnO$_2$ and Pb/PbO$_2$ electrodes.

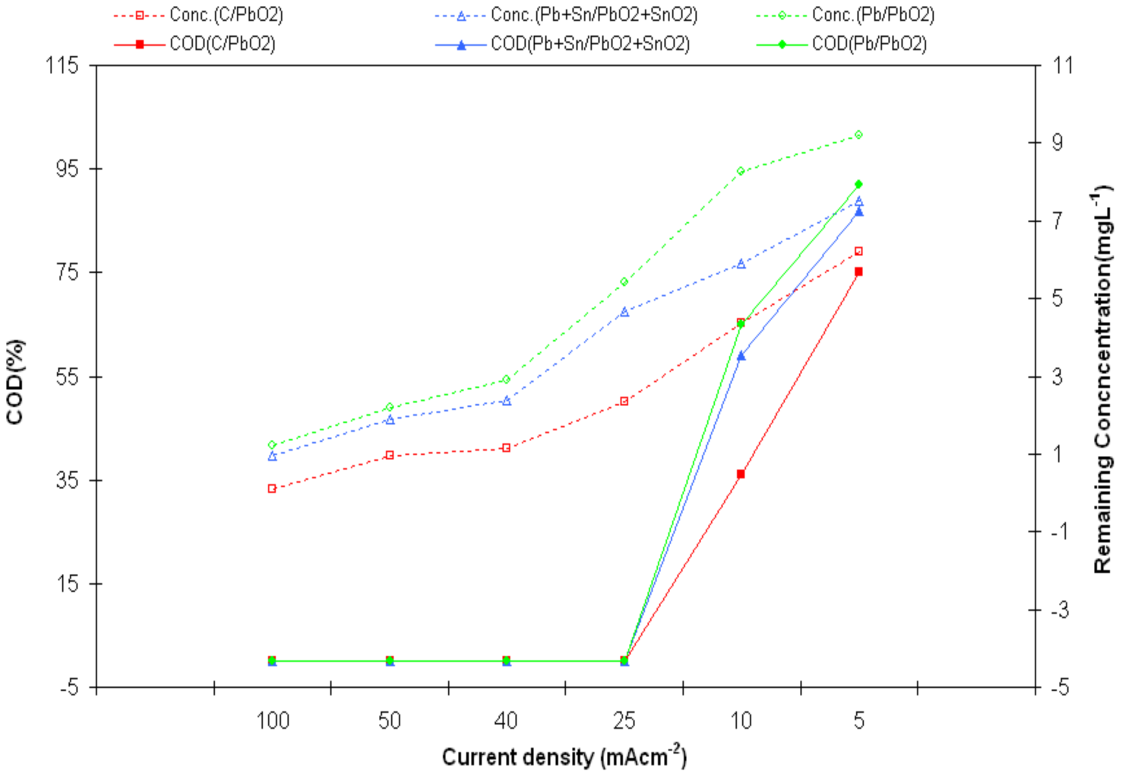

Figure 3. The effect of current density on RO7 and COD removal using C/PbO$_2$, Pb+Sn/PbO$_2$+SnO$_2$ and Pb/PbO$_2$ electrodes.

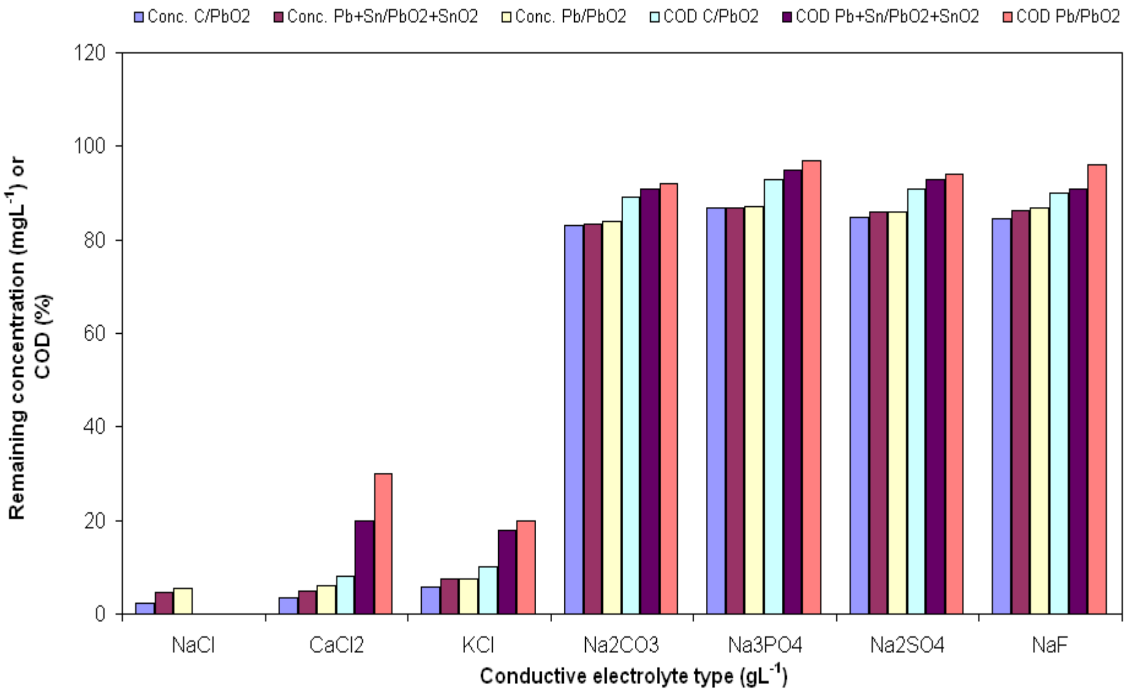

Figure 4. The effect of the conductive electrolyte type on RO7 and COD removal using C/PbO_2, $Pb+Sn/PbO_2+SnO_2$ and Pb/PbO_2 electrodes.

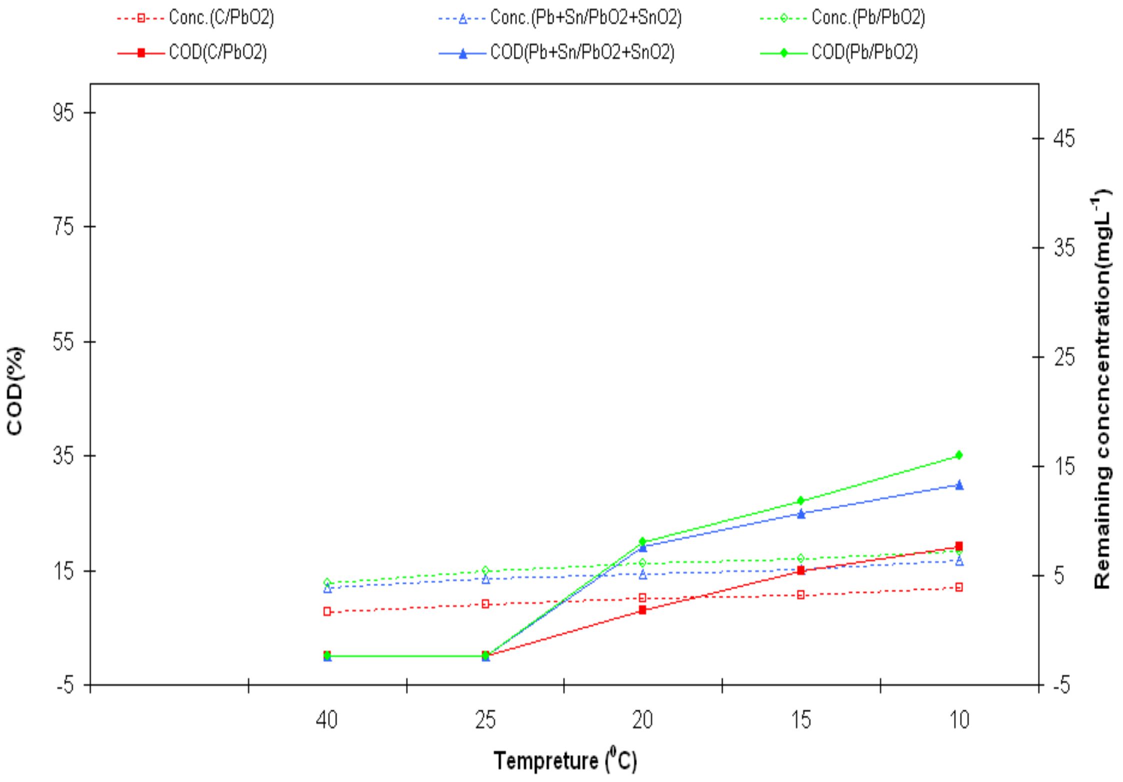

Figure 5. The effect of temperature on RO7 and COD removal using C/PbO_2, $Pb+Sn/PbO_2+SnO_2$ and Pb/PbO_2 electrodes.

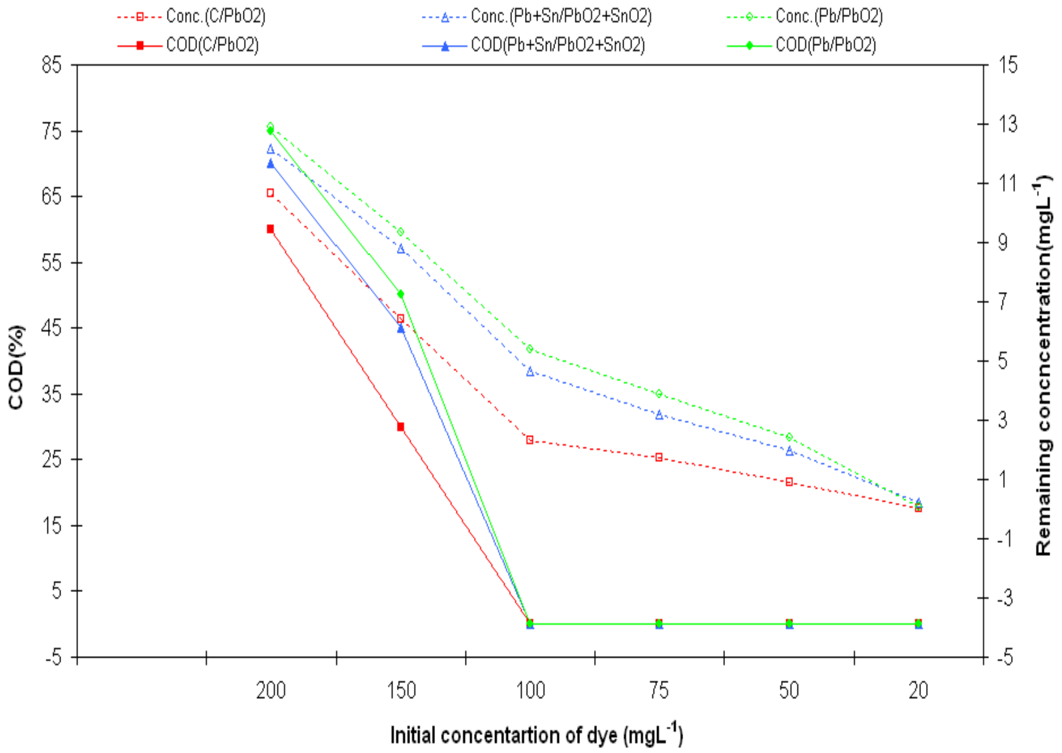

Figure 6. The effect of initial concentration on RO7 and COD removal using C/PbO_2, $Pb+Sn/PbO_2+SnO_2$ and Pb/PbO_2 electrodes.

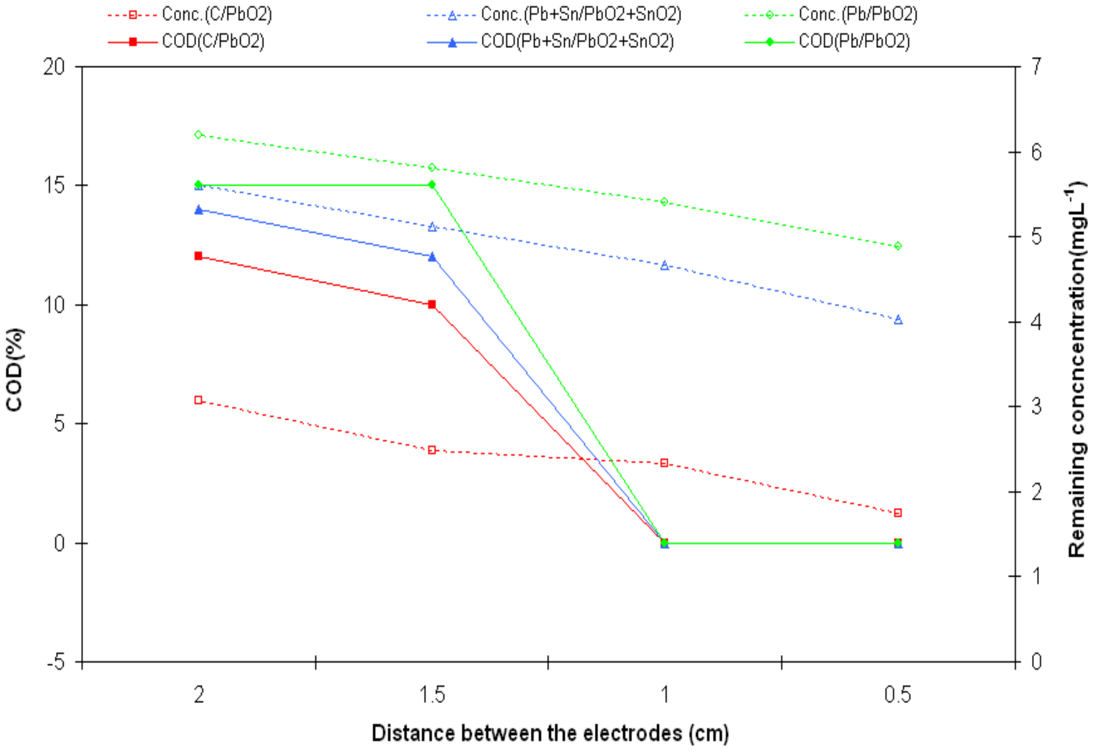

Figure 7. The effect of distance between the cathode and anode on RO7 and COD removal using C/PbO_2, $Pb+Sn/PbO_2+SnO_2$ and Pb/PbO_2 electrodes.

3.1.1. Effect of pH value

The pH of the solution was varied while the other conditions where kept constant. As shown in Fig. 1, maximum removal of RO7 and COD were achieved at pH 2.54 for C/PbO_2, $Pb+Sn/PbO_2+SnO_2$ and Pb/PbO_2, respectively. The pH values of the solutions were adjusted by adding drops of H_2SO_4 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^{-1}, a current density of 25 mA cm^{-2}, a temperature of 25 °C and NaCl concentration of 4 g L^{-1}. The distance between the two electrodes was adjusted to 1cm. It was found that the maximum rate of degradation using C/PbO_2, $Pb+Sn/PbO_2+SnO_2$ and Pb/PbO_2 electrodes was achieved in slightly acidic medium as the optimal medium.

3.1.2. Effect of the NaCl concentration

Different concentrations of NaCl were applied to study their effect on the removal of RO7 and the corresponding COD elimination as indicated in Fig. 2. The results indicate that an increase of the electrolyte concentration up to 4 gL^{-1} lead to increase in the RO7 degradation rate and COD removal for three C/PbO_2, $Pb+Sn/PbO_2+SnO_2$ and Pb/PbO_2 electrodes. The NaCl solution liberates Cl_2 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 RO7 and COD removal.

3.1.3. Effect of current density

As shown in Fig. 3, RO7 degradation and COD removal increase with increasing the applied current density up to 25 mA cm^{-2} by using C/PbO_2, $Pb+Sn/PbO_2+SnO_2$ and Pb/PbO_2 electrodes. Further increase of the current density was followed by gradual decrease in RO7 degradation and COD removal due to increase in temperature. Above a temperature 35^0C, sodium hypochlorite tends to chemically decompose to sodium chlorate (11).

$$3NaClO \rightarrow NaClO_3 + 2NaCl \qquad (11)$$

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.

3.1.4. Effect of type of electrolyte

Electrolytes of 4 g L^{-1} of the following salts; NaCl, $CaCl_2$, KCl, Na_2CO_3, NaF, Na_3PO_4 and Na_2SO_4 were studied by three electrodes. As appears in Fig. 4, The NaCl, KCl and $CaCl_2$ were the most effective conductive electrolytes for the electrocatalytic degradation of the investigated RO7 and COD removal while NaF, Na_2CO_3, Na_3PO_4 and Na_2SO_4 electrolytes show poor results. The Cl^- anion is a powerful oxidizing agent. It enhances the degradation of pollutants. Therefore, addition of NaCl, KCl and $CaCl_2$ provides the effective Cl^- ion. This behavior may be due to the small ionic size of K^+

and Na^+ which increases the ion mobility and the loss ability of Cl^- ion. NaF, Na_2CO_3, Na_3PO_4 and Na_2SO_4 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^-) 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 [10].

3.1.5. 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_2, $Pb+Sn/PbO_2+SnO_2$ and Pb/PbO_2 electrodes. The maximum removal of RO7 was achieved using C/PbO_2, $Pb+Sn/PbO_2+SnO_2$ and Pb/PbO_2 electrodes after at least 15 min. Therefore, this was taken as optimal degradation time for the removal of RO7. The optimal time for COD removal for three electrodes was 300, 360 and 380 min., respectively.

3.1.6. Effect of temperature

It is well known that the rate of diffusion of ions increases with increasing temperature. Fig. 5 represents the correlation between the concentration of the remaining RO7 dye and COD residual as a function of the solution temperature. The rate of the RO7 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.

3.1.7. Effect of initial RO7 concentration

Fig. 6 shows the effect of different initial RO7concentrations on the rate of RO7 degradation and corresponding COD removal. Total removal of the RO7 and COD can be achieved in the presence of initial RO7 load up to 100 mg L^{-1}. However, increasing the RO7 concentration above this level results in a decrease in the electro-catalytic rate of degradation. The removal efficiency of the RO7 by using C/PbO_2, $Pb+Sn/PbO_2+SnO_2$ and Pb/PbO_2 electrodes at 100 mg L^{-1} was the optimum concentration for the initial load concentration of RO7. As the initial RO7 concentration increase, the degradation efficiency decrease. This evidence that the generation of the powerful oxidizing agent Cl^- ions on electrode surface was not increased in constant current density.

3.1.8. 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. 7 that there was an increase of hypochlorite generation by decreasing the distance between the two electrodes up to 1cm for C/PbO_2, $Pb+Sn/PbO_2+SnO_2$ and Pb/PbO_2 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^{-2}, pH of 7.54, temperature of 25 °C and the concentration of NaCl 4 g L^{-1}. 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 [21]. The highest hypochlorite production was achieved with narrow distance between the cell electrodes of 1cm.

3.2. UV-Vis Spectra of Dyes

Fig. 8 shows typical time-dependent UV–Vis spectrum of RO7 dye during electrochemical degradation using C/PbO_2 electrode. The rate of decolorization was recorded with respect to the change in the intensity of absorption peak in visible region. The prominent peak was observed at λ_{max} = 470 nm which decreased gradually and finally disappeared indicating that the dye had been degraded.

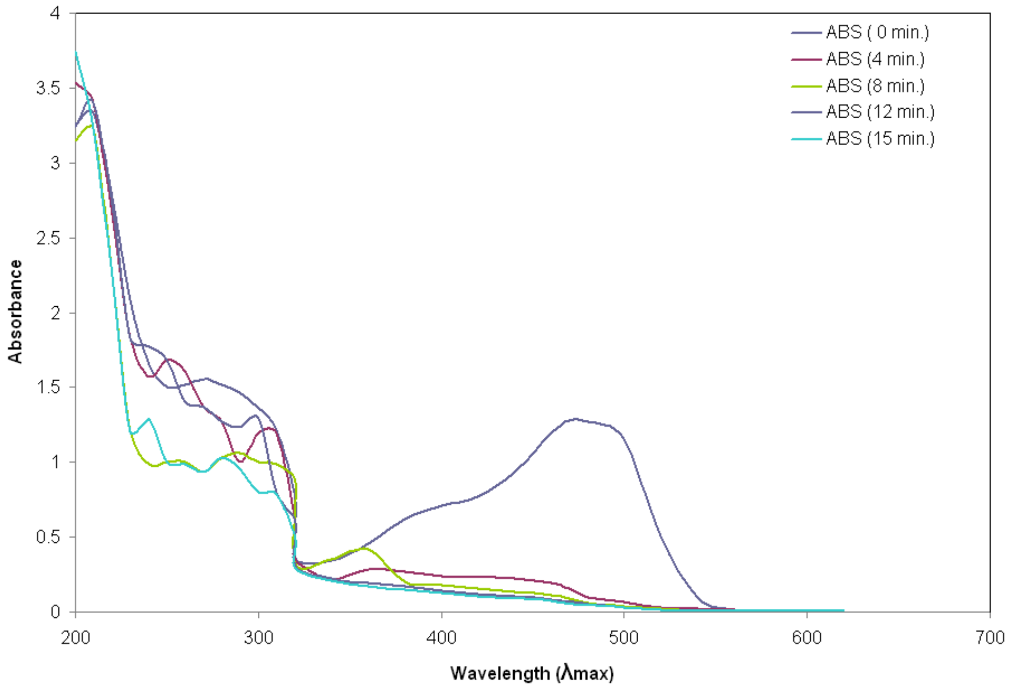

Figure 8. Time-dependent UV-Vis absorption spectra for decolorization of RO7.

3.3. Comparison with other Method of Treatment

The percentages of degradation for each method using in literature and the electrochemical method in this work were represented in table 1. It is clear that the electrochemical degradation is the best.

Table 1. Comparison of proposed electrodes and some decolonization technologies for Reactive Orange 7 (RO7) dye and its derivatives removal.

Method of treatment	Initial dye concentration (mg L−1)	Color removal efficiency (%)	Time (min)	Literature
Fenton_like reaction	50	High removal	120	6
Electrodegradated active chlorine(DSA) electrode	200	Complete color removal	120	9
Electrodegradation (BaPb0.9Sb0.1O3-δ) electrode	350	> 95	24 h	14
UV/ZnO _ Irradiation	20	99.9	60	22
Fenton _ Oxidation	50	> 95	60 min	23
Electrochimical treatment (Ti, Ta, Pt and Ir) elctrode	361 (containing 16 textile dye)	90	180	24
C/PbO2 electrode	100	97.77	15 min	This work
Pb/PbO2 electrode	100	95.33	15 min	
Pb+Sn/PbO2+SnO2 electrode	100	94.60	15 min	

The optimum operating conditions for degradation RO7 dye for each electrode were determined and summarized in Table (2). At optimized conditions, the percentages of RO7 degradation and COD removal for C/PbO$_2$, Pb+Sn/PbO$_2$ +SnO$_2$ and Pb/PbO$_2$ are 97.66%, 95.33 and 94.60% respectively. The results indicate that the C/PbO$_2$ electrode is more adequate than Pb+Sn/PbO$_2$+SnO$_2$ and than Pb/PbO$_2$ modified electrode for the degradation of RO7. These behaviors may be attributed to the color and structure of tested electrodes. C/PbO$_2$ modified electrodes have a black color, while Pb+Sn/PbO$_2$+SnO$_2$ and Pb/PbO$_2$ modified electrodes has a brown color.

Table 2. Percentage of COD and concentration removal of RO7 on C/PbO$_2$, Pb+Sn/PbO$_2$+SnO$_2$ and Pb/PbO$_2$ electrodes.

Type of electrode	Removal percent of RO7 at 15 min	Removal percent of COD	Removal percent of COD for real samples
C/PbO2	97.66	Zero at 300 min	Zero at 350 min
Pb+Sn/PbO2+SnO2	95.33	Zero at 360 min	Zero at 390 min
Pb/PbO2	94.60	Zero at 380 min	Zero at 410 min

It was reported that PbO$_2$ film has two structures, α-structure (brown color) and β-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 α-form (orthorhombic). Therefore, the surface area in case of tetrahedral structure is more than orthorhombic one, and hence the β-PbO$_2$ form will be more effective than α-PbO$_2$ form. Because the over potential for oxygen evolution of β-PbO$_2$ is higher than that of α-PbO$_2$ it is expected that the electrocatalytic properties for

C/PbO_2 modified electrodes are more efficient than that of Pb/PbO_2 modified electrode [20]. In this work the degradation rate of RO7 was nearly completed and reached 97.66 , 95.33 and 94.60 percentage using C/PbO_2, $Pb+Sn/PbO_2+SnO_2$ and Pb/PbO_2 electrodes respectively after 15 min.

3.4. Application of the Treatment Process in Real Wastewater Sample

The treatment of RO7effluents obtained from dyeing factories was carried out by using the prepared C/PbO_2, $Pb+Sn/PbO_2+SnO_2$ and Pb/PbO_2 modified electrodes. The treatment was performed, first by collecting actual waste samples from the wastewater effluents of the RO7 dyeing bath. The initial dye load concentration of these samples were 180 mg/L taken from Hubbub dyeing factory located in the industrial area at Biet Hanon, Gaza Strip, PNA. The dyestuff solutions were treated by the electrocatalytic oxidation technique by the same method as applied to the treatment of RO7 in aqueous solution to investigate the optimum condition for real wastewater containing the dye. After the treatment process, the removal percent of RO7 at 15 min using C/PbO_2, $Pb+Sn/PbO_2+SnO_2$ and Pb/PbO_2 electrodes was (93.40%, 90.92 and 89.88%) respectively, and removal percent of COD showed that (Zero at 350, 390 and 410 min) respectively. These results indicate that the suggested modified electrodes are highly efficient in the treatment of effluents containing RO7 dye with very slight effect of matrix.

4. CONCLUSION

In this work three modified electrodes (C/PbO_2, $Pb+Sn/PbO_2+SnO_2$ and Pb/PbO_2) were prepared by elecrodeposition and used as anodes for electrodegradation of RO7 in aqueous solutions. The optimum condition for three electrodes are: NaCl (4 g L^{-1}), temperature at 25°C, degradation time of 15 min, initial concentration of 100 mg L^{-1}, current density equals 25 mA cm^{-2} and 1cm distance between the three electrodes of the cell. The degradation of RO7 was nearly completed (97.66%, 95.33 and 94.60%) using C/PbO_2, $Pb+Sn/PbO_2+SnO_2$ and Pb/PbO_2 electrodes at pH 2.54, respectively.

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