



Electrochemical degradation of some organic dyes by electrochemical oxidation on a Pb/PbO₂ electrode

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Received 7 February 2010; Accepted 20 October 2010

ABSTRACT

This work investigated the electrocatalytic degradation of three types of textile dyes by electrochemical oxidation on lead dioxide anode. The influence of pH, current density, time of electrolysis, temperature, the conductive salt concentration and the initial dye concentrations were critically examined. The results of these influences are expressed in terms of the remaining organic compounds concentrations (color removal) and Chemical Oxygen Demand (COD removal). Also, both of the current efficiency and power consumption values are calculated. In this manuscript we report that, the highest electrocatalytic activity was achieved in the presence of NaCl (3 g/l), 30 mA/cm², pH of 3 and temperature of 30 °C. The highest electroactivity could be attributed to indirect oxidation of the investigated dyes by the electrogenerated hypochlorite ions formed from the chloride oxidation. In addition, contribution from direct oxidation could also be possible via reaction of these dyes with the electrogenerated hydroxyl radicals adsorbed on the lead dioxide surface.

Keywords: Electrochemical degradation; Reactive dye; Direct dye; Disperse dye; PbO₂ electrode

1. Introduction

The textile industry is one of the most polluting industries in term of discharge volume and effluent composition. The 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 pose greatest problems in textile industry [1,2].

Conventionally effluents containing organics are treated with adsorption, biological oxidation, coagulation, etc. Though the conventional methods have individual advantages, they are lacking in effectiveness, if applied individually. For example, biological treatment is the most efficient and economic way of reducing

the environmental impact of the industrial effluents containing organic pollutants, but this technique is time consuming and cannot be employed for textile effluent, as textile effluent is recalcitrant to biodegradation. On the other hand, the physical adsorption is expensive for adsorbent regeneration difficult. Furthermore, biological and chemical methods generate considerable quantity of sludge, which itself requires treatment. Due to the large variability of the composition of textile wastewater, most of the traditional methods are becoming inadequate [3–5]. For these reasons, researchers are trying various alternative processes, such as electrochemical techniques, wet oxidation, ozonization and photocatalytic methods for the degradation of organic compounds. Among these advanced oxidation processes, the electrochemical treatment has been receiving greater attention in recent years due to

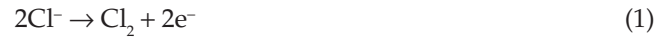
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its unique features, such as versatility, energy efficiency, automation and cost effectiveness [6,7].

In electrochemical techniques, the main reagent is the electron, called the “Clean Reagent,” which degrades all the organics present in the effluent without generating any secondary pollutant or by-product/sludge. The electrochemical technique offers high removal efficiencies and has lower temperature requirements compared to non-electrochemical treatment. In addition to the operating parameters, the rate of pollutant degradation depends of the anode material effective and economic electrochemical treatment of organic pollutants requires the choice of appropriate catalytic electrode material as well as appropriate electrolysis conditions. 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 (Vitt and Johnson, 1992; Gattrel and Kirk, 1993). Oxygen transfer is usually favored on an anode material with high oxygen evolution overpotential. Lead dioxide, is characterized by high oxygen overpotential, therefore it is one of the most commonly used anodes for electrochemical degradation for many pollutants (Polcaro et al., 1999; Iniesta et al., 2001; Panizza and Cerisola, 2003; [18]) particularly when it is doped with metallic cations whose oxides have low oxygen evolution overvoltage which improve the transfer rate of oxygen atom. It was reported that (Johnson and Chang, 1990; Kawagoe and Johnson, 1994; Borrás et al., 2003) doping PbO_2 with bismuth improved the oxidation kinetics of several organic compounds, due to the formations of a low surface density at the bismuth oxide (Bi_2O_3) sites [8].

2. Theory

The mechanism of electrochemical oxidation of wastewater is a complex phenomenon involving coupling of the electron transfer reaction with a dissociative chemisorptions step. Basically two different processes occur at the anode; on anode having high electrocatalytic activity, oxidation occurs at the electrode surface (direct electrolysis); on the metal oxide electrode, oxidation occurs via surface mediator on the anodic surface, where products are generated continuously [indirect electrolysis]. In direct electrolysis, the rate of oxidation is depends on electrode activity, pollutant diffusion rate and current density. On the otherhand, temperature, pH and diffusion rate of generated oxidants determine the rate of oxidation in indirect electrolysis. In indirect electro-oxidation, chloride salts of sodium or potassium are added to the wastewater for better conductivity and generation of hypochlorite ions [9]. The reaction of anodic oxidation of chloride ions to form chlorine is given as:



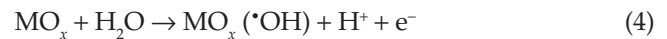
The liberated chlorine form hypochlorous acid



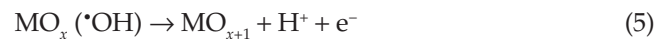
and further dissociates to give hypochlorite ion.



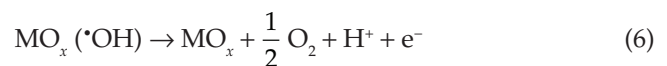
The generated hypochlorite ions act as main oxidizing agent in the pollutant degradation. The direct electro-oxidation rate of organic pollutants depends on the catalytic activity of the anode, on the diffusion rate of the organic compounds in the active points of anode and applied current density. A generalized scheme of the electro-chemical conversion/combustion of organics of pollutant [10] on noble oxide coated catalytic anode (MO_x) is given below. In the first step, H_2O is discharged at the anode to produce adsorbed hydroxyl radicals according to the reaction.



In the second step, generally the adsorbed hydroxyl radicals may interact with the oxygen already present in the oxide anode with possible transition of oxygen from the adsorbed hydroxyl radical to the oxide forming the higher oxide MO_{x+1} .



At the anode surface, the “active oxygen” can be present in two states. Either as physisorbed (adsorbed hydroxyl radicals $\cdot\text{OH}$) or/and as chemisorbed (oxygen in the lattice, MO_{x+1}). In the absence of any oxidizable organics, the “active oxygen” produces dioxygen according to the following reactions:

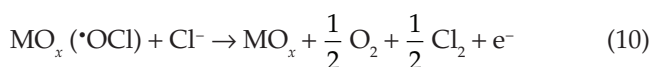
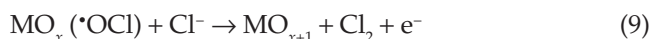


When NaCl is used as supporting electrolyte, the Cl ion may react with $\text{MO}_x(\cdot\text{OH})$ to form adsorbed OCl radicals according to the following [11]:

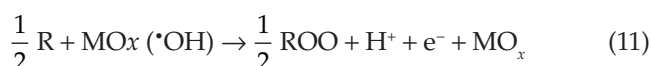


Further, in presence of Cl ion, the adsorbed hypochlorite radicals may interact with the oxygen already present in the oxide anode with possible transition of oxygen from the adsorbed hypochlorite radical to the oxide forming the higher oxide MO_{x+1} according to the following reaction and also $\text{MO}_x(\cdot\text{OCl})$ simultaneously react

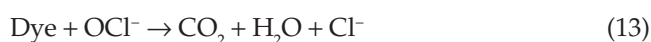
with chloride ion to generate active oxygen (dioxxygen) and chlorine according to the following reactions:



In the presence of oxidizable organics the physisorbed “active oxygen” ($\cdot\text{OH}$) should cause predominantly the complete combustion of organics and chemisorbed will participate in the formation of selective oxidation products [12] according to the following reactions:



The physisorbed route is preferable for waste treatment. It is probable that dioxxygen participates also in the combustion of organics according to the reactions, such as formation of organic radicals by a hydrogen abstraction mechanism: $\text{RH} + \cdot\text{OH} \rightarrow \text{R} + \text{H}_2\text{O}$; reaction of organic radical with dioxxygen formed at the anode: $\text{R}^{\cdot} + \text{O}_2 \rightarrow \text{ROO}^{\cdot}$ and further abstraction of a hydrogen atom with formation of an organic hydrogen peroxide (ROOH) and another radical; $\text{ROO}^{\cdot} + \text{R}'\text{H} \rightarrow \text{ROOH} + \text{R}'$. Since the organic hydrogen peroxides formed are relatively unstable, decomposition of such intermediates leads to molecular breakdown and formation of subsequent intermediates with lower carbon numbers. These sequential reactions continue until the formation of carbon dioxide and water. In this case the diffusion rate of organics on the anode area controls the combustion rate [13,14]. In the same way, the indirect electrochemical oxidation mechanism has been proposed for metal oxide catalysis with chloride as supporting electrolyte for wastewater treatment [15,16]. The role of hypochlorite in electrochemical treatment of dye effluent via chlorine generation is:



The aim of the present study is to investigate the electrocatalytic degradation of some organic pollutants (Reactive dye, Direct dye, and commercial of disperse dye) from a simulated wastewater by direct and indirect electrochemical oxidation. The effect of different operating factors, such as type and concentration of conductive (supporting) electrolyte, applied current density, initial pollutant load, solution pH and others, on the pollutant removal efficiency and COD depletion was

analyzed to optimize the conditions of electrochemical treatment of wastewater in real situation. Lead dioxide electrode (Pb/PbO_2) is selected for the electrode in this investigation.

3. Experimental

3.1. Preparation of the lead/lead dioxide (Pb/PbO_2) electrode

3.1.1. Lead surface treatment

3.1.1.1. Mechanical polishing: Mechanical polishing of lead substrate was carried out using different sand papers of different grades, down to 4/0 and subdivided into small pieces of dimension $2 \times 6 \text{ cm}^2$.

3.1.1.2. Degreasing: Degreasing in the present work was carried out by using either solvent cleaners or alkali soaking cleaners. Degreasing accomplished by solvent degreasing process was used with all metals. The solvent used here was acetone, which possesses the all requirements necessary to for degreasing particles because of its ease of application and its great penetrating power.

The alkali soaking cleaner contains sodium hydroxide (50 g), sodium carbonate (20 g), trisodium phosphate (20 g) and sulphonic acid (2 g), dissolved in bidistilled water, transferred to a measuring flask (1 l) and the volume of solution is completed to 1 l.

The best temperature used in our experiments was about 50°C and degreasing was ensured by washing the metal with water, the presence of a continuous unbroken film of water over the lead substrate indicates the complete removal of greases.

3.1.1.3. Pickling: The complete removal of scales is very important to ensure uniform deposition and good adhesion of the deposit with no peeling or blistering. Pickles are mineral acid solutions, which will generally remove oxides and scales without difficulty, will render the metal active and will not pit or excessively roughen the basis metal. The composition of the pickling solution consists of nitric acid (400 g/l) and hydrofluoric acid (5 g/l). This mixture was found to be a good pickle [17].

3.1.2. Electrochemical deposition of PbO_2 (Anodizing)

PbO_2 was deposited galvanostatically on the pre-treated lead substrate by electrochemical anodization of lead at a current density of $10 \text{ mA}/\text{cm}^2$, in 10% sulfuric acid solution and at 25°C , during 90 min [18]. The cathode was stainless steel (austenitic type), the two electrodes were concentric with the lead electrode is axial as shown in Fig. 1. This process was accomplished for the aim of activation of lead electrode surface by the formation of a thin layer of lead-oxide.

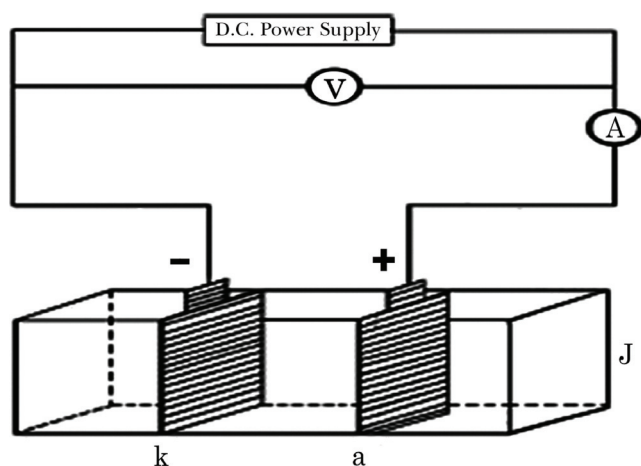
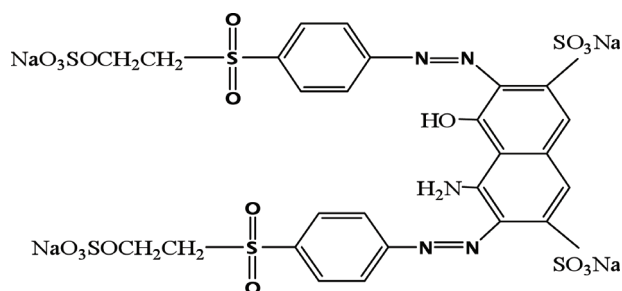


Fig. 1. Circuit diagram for anodization process of Pb substrate.

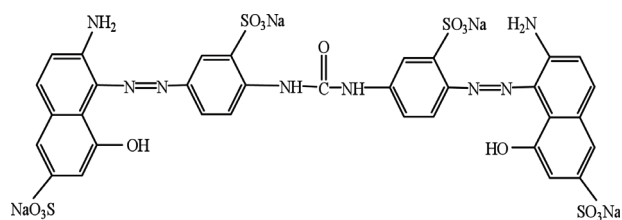
3.2. Chemicals

Chemicals tested for degradation are different types of dyes; reactive dyes, direct dyes and synthetic dispersed dyes. All these types are soluble in water.

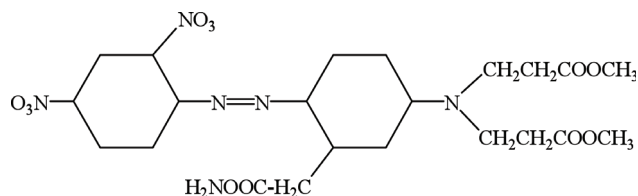
a) Reactive Black 5 (*Hoechst, Germany*) (FW 991.82) ($\lambda_{\max} = 597 \text{ nm}$).



b) Direct Red 75 (*Aldrich*) (FW 990.8) (C.I. 25380) ($\lambda_{\max} = 522 \text{ nm}$).



c) Disperse dark red [P-R], (*China*) (FW 576.55) ($\lambda_{\max} = 556 \text{ nm}$).



3.3. Electrolysis

The electrolysis of the aqueous solutions (250 ml) containing the dyes and the electrolyte solution to be treated electrochemically was carried out in a one-compartment Pyrex glass cell of 250 ml volume with three plates electrodes of 12 cm², which consists of the prepared Pb/PbO₂ electrode as anode and two austenitic stainless steel cathodes. DC power supply GW (model: GPR-1810HD, Taiwan) was used. The current and potential measurements were carried out using two digital multimeters (BK Mini-Pro Multimeter, model: 2405A, Taiwan). All experiments were carried out with magnetic stirring as in Fig. 2.

3.4. Analysis

Analytical parameters were measured to evaluate the electrocatalytic oxidation efficiency of above-mentioned organic compounds dyes, these parameters were:

A. Chemical Oxygen Demand COD (mg O₂/l) is a measure of the oxygen equivalent to the organic matter content of a sample that is susceptible to the oxidation by strong chemical oxidant. COD can be related empirically to organic matter. COD during the electrolysis was determined by an open reflux (COD reactor, ECO 6, VELD SCIENTIFICA, Italy), dichromate titrimetric method as described in standard methods [19]. This method for the determination of COD may be used where sample chloride concentration is known to be less than 2000 mg/l. This means that, in the present investigations, interferences from Cl⁻¹ ions present in the solution and the electrogenerated species may occur.

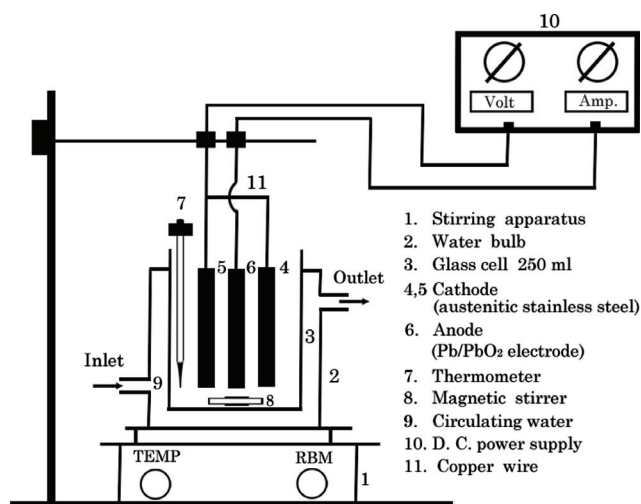


Fig. 2. Schematic diagram of the electrolysis cell used for the electrocatalytic degradation of different investigated dyes from simulated wastewaters.

To eliminate the effect of these interferences, two different methods were taken into considerations [20]. The **first** was carried out by adding sodium bisulphate ($\text{Na}_2\text{S}_2\text{O}_5$) to the organic compound (dye) solutions and heating before measurements of COD. The added of sodium bisulphate destroys the hypochlorite with evolution of chlorine gas. The **second** includes the measurements of COD for blank solutions, which are free from the under test organic compound. These blank solutions were treated under the same operating conditions used in the electrocatalytic oxidation of organic (dyes) compound solutions. From the measurements of COD values of blank and organic (dyes) compound solutions after treatment, the value of COD is corresponding to the organic compound present in solution that could be evaluated. The COD values obtained from the two methods were matched with each other. The equation used to calculate the COD removal efficiency in the experiments is:

$$\text{COD Removal \%} = [\text{COD}_0 - \text{COD}_{\text{final}} / \text{COD}_0] \times 100 \quad (14)$$

where, COD_0 (initial) and $\text{COD}_{\text{final}}$ of the dye solutions are calculated in mg/l.

B. The remaining dye concentrations, using a UV-Vis Spectrophotometer, (OPTIMA, PHOTOMECH 301-D*, Japan). The equation used to calculate the color removal efficiency in the treatment experiments is:

$$\text{Color Removal \%} = [C_0 - C / C_0] \times 100 \quad (15)$$

where C_0 and C were initial and present concentrations of the dye in solution (mg/l), respectively.

4. Results

A series of experiments was carried out in NaCl electrolyte to investigate the effect of different operating factors on the rate of the electrochemical degradation of the investigated dyes (a–c).

4.1. Effect of applied current density

Different current densities of values 10, 15, 20 and 25 mA/cm^2 were applied to investigate the electrocatalytic degradation of the dyes (a–c) in 3 g/l NaCl solution at the following operating conditions: 200 mg/l initial dye concentration, pH of 3 and temperature of 30°C. Fig. 3 shows the 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:

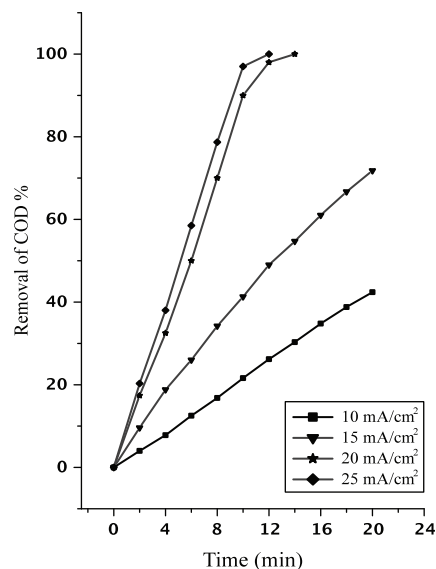


Fig. 3. Removal of COD with electrolysis time for 200 mg/l of dye (b), supporting electrolyte 3 g/l NaCl, pH 3, temperature of 30°C and Pb/PbO₂ electrode.

1. At a given current densities, the COD removal % increases with increase of electrolysis time reaching a limiting value.
2. At a given time of electrolysis, the COD removals % increased with increase of the applied current density up to 20 mA/cm^2 and further increase in the current density did not bring any further effect. For this reason, the current density of value 20 mA/cm^2 was taken as optimum. The values of COD removals % at this optimum current density were; 93, 100, and 100% for the dyes (a–c) respectively.

4.2. Effect of pH of solution

Fig. 4 shows the variation of the COD removal percentage as a function of electrolysis time at pH values of 2, 3, 7 and 10 for the investigated dye (b). The electrocatalytic degradation experiments on Pb/PbO₂ electrode were carried in 3 g/l NaCl solution at the following operating conditions: current density of 20 mA/cm^2 , 200 mg/l of initial dye concentration and temperature of 30°C. As shown from the plots of Fig. 4 that, at a given pH values, the COD removals % increased with increase of electrolysis time reaching limiting values. At a given electrolysis time, the maximum values of COD removal percentage were obtained at pH values of 2 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.

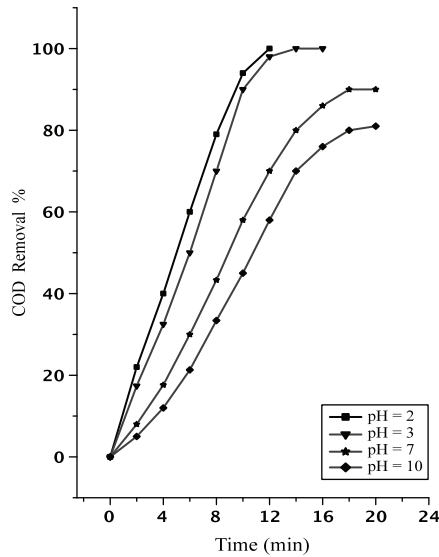


Fig. 4. Removal of COD with electrolysis time for 200 mg/l of dye (b), supporting electrolyte 3 g/l NaCl, pH (2,3,7,10), temperature of 30°C and Pb/PbO₂ electrode.

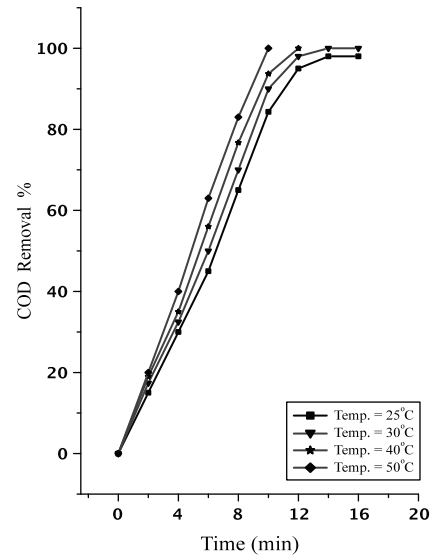


Fig. 5. Effect of temperature on COD removal for solution of 200 mg/l of dye(b), supporting electrolyte 3 gm/l NaCl, pH (3) and Pb/PbO₂ electrode.

4.3. Effect of temperature

This investigation was carried out in 3 g/l NaCl solution at the following operating conditions: current density of 20 mA/cm², 200 mg/l of initial dye concentration and about 30 min of electrolysis time for electrochemical degradation of the investigated dyes (a–c). It is to be noted that, there are some conditions which ensure more or less complete electrocatalytic degradation of the treated dyes (a–c) as indicated from the results which so far. Fig. 5 shows the variation of the COD removals percentage as a function of temperature (25–50°C) for the investigated dye (b), at the above mentioned operating conditions. It is clear from the plots of the Fig. 5, that the change of temperature from 25–50°C had a slight effect on the efficiency of the degradation process. For this reason, the temperature of 30°C was taken as optimum.

4.4. Effect conductive electrolyte concentration

In this investigation, the concentration of NaCl was 1, 3 and 5 g/l and the electrocatalytic degradation of the treated dyes was carried under the following operating conditions: current density of 30°C, pH of 3 and the initial concentration of each dye was 200 mg/l. Fig. 6 shows the variation of COD removal % as a function of electrolysis time at NaCl concentration of 1, 3 and 5 gm/l for the electrocatalytic degradation of the investigated dye (b) on Pb/PbO₂ electrode at the above mention operating conditions. Inspection of the plots of Fig. 6, revealed that:

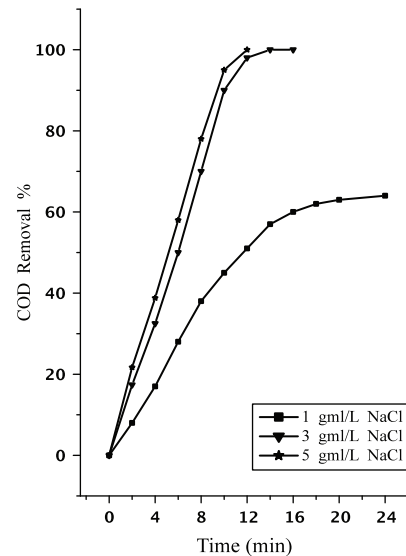


Fig. 6. Removal of COD with electrolysis time for 200 mg/l dye of (b) in different supporting electrolyte (1,3,5) g/l NaCl, pH (3), temperature of 30°C and Pb/PbO₂ electrode.

1. At a given NaCl concentrations, the COD removal percentage increased with increase of electrolysis time reaching a limiting value.
2. At a given electrolysis time, the COD removal percentage of dyes are greatly increased with the increase of NaCl concentrations to 3 and 5 g/l.
3. At a given electrolysis time, the COD removal percentage of dyes in 3 and 5 g/l NaCl are almost equal to each other. So, the concentration of 3 g/l was taken as the optimum.

4.5. Effect of initial dye dosage

The results so far indicated that the optimum electrochemical degradation of the investigated dyes was attained at 20 mA/cm² current density in 3 g/l NaCl solution of pH 3 and temperature of 30°C. Fig. 7 shows the effect of the investigated dye (b) of concentrations 100, 200 and 500 mg/l on the variation of COD removal percentage as a function of electrolysis time under the optimum operating conditions mentioned above. Inspection of the plots of Fig. 7, reveals that:

1. At a given time of electrolysis, the COD removal percentage decreased with increasing initial concentration from 100–500 mg/l respectively.
2. COD removal percentage can be achieved in the presence both of 100 and 200 mg/l as initial concentrations.
3. At a given initial loaded concentrations, the COD removal percentage increases with increase of the electrolysis time with a rate depending on both of nature of the dye and its initial concentration. However, increasing the dye concentration resulted in a decrease in its electrochemical degradation rate. This might be explained that the ratio of hydroxyl radical concentration is decreased with increase in initial concentration. Although, the degradation rate of the investigated dyes (a–c) 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. 7 as an example represent the dyes (a–c). It is found that, the COD removal percentage at initial concentration of 500 mg/l were: 63, 74 and 78.5%, respectively for the dyes (a–c).

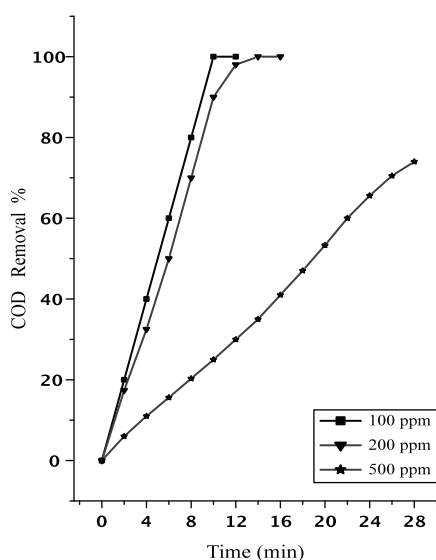


Fig. 7. Removal of COD with electrolysis time for 100, 200 and 500 mg/l of dye (b), supporting electrolyte of 3 g/l NaCl, pH (3), temperature of 30°C and Pb/PbO₂ electrode.

4.6. Color removal

This investigation was carried out in the presence of 200 mg/l as initial concentration of each dye in 3 g/l NaCl solution under the following operating conditions: 20 mA/cm² of current density, temperature of 30°C and pH of 3. Fig. 8 shows the variation of color removal percentage as a function of time of electrolysis. Inspection of Fig. 8, indicates that the color removal percentage increases with increase of electrolysis time, with different rates depending on the nature of the dye, till reaching a limiting value and the maximum values achieved for the color removal were: 100, 100 and 100% for the investigated dyes (a–c), respectively. These values are relatively comparable and in agreement with those previously deduced from COD removal percentage, but complete removal of color was achieved within a short period of time and as discussed before the COD removals percentage were: 93, 100 and 100% for the investigated dyes (a–c), respectively at long period times. It is well known that the removal of color is due to the cleavage of Chromospheres bond in the dye molecule. On the other hand, the oxidation of an aromatic ring compounds takes a long time and hence the removal of COD is less due to the formation of lower molecular weight aliphatic compounds, which in turn were resistant to chlorine/hypochlorite attack [21].

The results of these investigations indicated that the operating parameters play a fundamental role in the electrochemical degradation of organic pollutants and controlling these parameters leads to an efficient treatment.

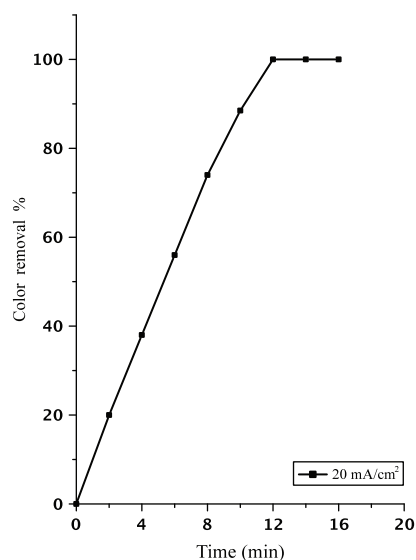


Fig. 8. Removal of color with electrolysis time for 200 mg/l of dye (b), Supporting electrolyte of 3 g/l NaCl, pH (3), temperature of 30°C and Pb/PbO₂ electrode.

4.7. Electrical yield (current efficiency)

The current efficiency is defined as the ratio between the electrical charge that actually used to oxidize the organic compounds and the total consumed electrical charge [22].

At a given time of electrolysis t , the average current efficiency (ACE) can be calculated as [23]:

$$\text{ACE \%} = [(\text{COD}_0 - \text{COD}_t) FV / 8 It] \times 100 \quad (16)$$

where COD_0 and COD_t are the chemical oxygen demand at initial time and at the given time t (g O_2/l), respectively, I the current (A), F the Faraday constant (96487 C/mol), t the treatment time (h), V is the volume of solution (l) and 8 is the oxygen equivalent mass (g/eq). Table 1 represents the current efficiency values of the Pb/PbO₂ anodic electrodes used for the electrolysis degradation of the dyes (a–c) at the optimum operating conditions.

It was found that, the current efficiencies could exceed 100%. The high current efficiency values could be attributed to the indirect electrochemical and chemical reactions, in addition to the high conductivity and catalytic activity of the electrode which used as anode and/or cathode [22].

4.8. Energy consumption (EC)

The energy consumption (kWh/kg COD) is calculated by the following equation [23]:

$$\text{EC}_{(\text{kWh}/\text{kg COD})} = UIt / 3.6(\text{COD}_0 - \text{COD}_t) V \quad (17)$$

where COD_0 and COD_t are the chemical oxygen demand at initial time and the given time t (g O_2/l), respectively, U is the voltage applied, I the current (A), t the treatment time (hr) and V is the volume of solution (L). Table 2 represents the energy consumption values of the undertest anodic electrodes used for the electrolysis degradation of the dyes (a–c) at the optimum operating conditions.

Use of a modified electrode may enhance the cathodic reactions and increase the current efficiency of the electrocatalytic oxidation process. In the present investigation, it could be concluded that, the use of the undertest modified electrodes (Pb/PbO₂) in the electrocatalytic degradation of some organic compounds (Dyes) lead to low energy consumption and low cost of the process, so Pb/PbO₂ electrode could be applied in

Table 1

Dye	a	b	c
ACE %	88.3	100	100.5

Table 2

Dye	a	b	c
EC	4.74	3.73	4.44

industrial fields for treatment of industrial wastewaters containing organic compounds such as dyes.

4. Conclusions

The electrochemical treatment of simulated wastewater containing the investigated dyes (a–c) has been investigated in NaCl conductive electrolyte and under several operating conditions using of Pb/PbO₂ electrode. The results of these studies revealed the following:

1. The optimal electrocatalytic activity was achieved in the presence of NaCl (3g/l) for Pb/PbO₂ electrode in which the degradation of the investigated dyes occurs by both direct as well as indirect oxidation.
2. The optimal electrocatalytic activity was achieved at applied current density of 30 mA/cm² for Pb/PbO₂ electrode.
3. The optimal electrocatalytic activity was achieved at pH of 3 and temperature of 30°C for Pb/PbO₂ electrode.
4. Both of the color and COD removal are increased with treatment time and high current efficiency was achieved.

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