



Evaluation of electrochemical oxidation techniques for degradation of dye effluents—A comparative approach

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ABSTRACT

The high energy cost of an electrochemical method is the fatal drawback that hinders its large scale application in wastewater treatment. The traditional single-chamber electrochemical method used in the waste water treatment mainly focused on anodic oxidation, but hydrogen produced on the cathode and indirect electrochemical treatment involves application of an electrical current to the wastewater containing chloride to convert into chlorine/hypochlorite. The two-compartment electrolytic cell, separated by an anion exchange membrane, has been developed in this work. In the new reactor, indirect oxidation at anode, indirect oxidation by hydrogen peroxide and ultraviolet/hydrogen peroxide (UV/H₂O₂) at cathode can occur simultaneously. The electrochemically produced hydrogen peroxide at the cathode by reduction of oxygen is affected by passing atmospheric air. Therefore “dual electrochemical oxidation” in one electrochemical reactor was achieved successfully. Compared to a traditional one-cell reactor, this reactor reduces the energy cost approximately by 25–40%, and thus the present work becomes significant in wastewater treatment. Experiments were carried out at different current densities using Ti/RuO₂/IrO₂ as anode and carbon felt gas diffusion electrode used as a cathode fed with oxygen containing gases to produce hydrogen peroxide. During the various stages of electrolysis, the parameters such as, effect of pH, chemical oxygen demand (COD), colour, energy consumption were monitored. UV–vis spectrometry, Fourier transform infrared spectroscopy (FTIR), high-performance liquid chromatography (HPLC) studies were carried out to assess efficiencies of dye degradation.

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1. Introduction

Textile wastewaters from dyeing and finishing processes in the textile industry have been a serious environmental problem for years. Carcinogenic products such as aromatic amines due to the large consumption of azo dyes in the dyeing processes contain considerably strong colour, a broad range of pH varying from 2 to 12, high chemical oxygen demand (COD) concentration and suspended particles, and low biodegradability [1–4]. These are usually treated by conventional methods such as biological oxidation, chemical coagulation and activated carbon adsorption [5,6].

Biological methods cannot be applied to most textile wastewaters due to the toxicity of most commercial dyes to the organisms used in the process [7]. Chemical coagulation is not effective for

the removal of dissolved reactive dyestuffs [8]. Activated carbon adsorption has the associated cost and difficulty of the regeneration process and a high waste disposal cost. Advanced oxidation processes such as ozonation, UV and ozone/UV combined oxidation, photocatalysis (UV/TiO₂), Fenton reactive and ultrasonic oxidation are not economically feasible [9,10].

Many investigators are studying alternative oxidation methods like ozonation, photo catalytic oxidation, electrochemical oxidation, etc. The photo catalytic oxidation experiments were conducted for Acid Blue 80 [11], Acid Orange 7 [12], Brilliant Orange K–R [13] and Reactive Orange 16 [14]. The electrochemically assisted photochemical degradation was also conducted to improve the degradation efficiency of the dye [15]. Ozonation process was studied for the removal of colour and COD [16], however; this process showed less COD removal [17]. Researchers also investigated electro-coagulation methods for textile dye removal using aluminum [18] or iron [19,20] electrodes.

Several researchers have studied the feasibility of electrochemical degradation of textile dyes using various electrode materials for wastewater treatment. Electrochemical degradation of different dye compounds was studied using titanium based DSA electrodes

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Table 1
Characterization of the industrial dye effluent.

Particulars	Dye effluent	Undivided cell	Anode compartment	Cathode compartment Without O ₂ flow	Cathode compartment Without UV	Cathode compartment with UV
pH	13	14	12.8	2.6	2.6	2.6
COD (mg/L)	1320	80	160	720	380	80
T.S.S (mg/L)	420	210	180	320	260	160
T.D.S (mg/L)	8600	7820	7940	8592	8580	8560
Chloride (mg/L)	5380	4560	4890	4336	4320	4340

[16], platinum electrodes [21], diamond and metal alloy electrodes, [22] and boron doped diamond electrodes [23,24].

The exact mechanisms of electrochemical oxidation are complicated and not yet entirely clear, but it is postulated that organic pollutants could be oxidized directly or indirectly by O₃, H₂O₂, O₂, •OH, and other oxidants [25–32]. The traditional single-chamber electrochemical method used in the wastewater treatment mainly focuses on anodic oxidation, but hydrogen is produced on the cathode, which also consumes much energy, is often ignored. The simultaneous production of evolved hydrogen at a cathode as a byproduct, along with high power requirements [33], is the main disadvantage for electro-oxidation of organics.

In this work, an innovative two-chamber electrolytic cell, connected with an anion exchange membrane, was developed. In this new reactor, indirect oxidation at anode, indirect oxidation by hydrogen peroxide and UV/H₂O₂ at cathode can occur simultaneously. Therefore “dual electrodes oxidation” in one electrochemical reactor was achieved successfully. Compared to a traditional one-cell reactor, this reactor considerably reduces the energy cost by 25–40%, and thus the present work becomes significant in wastewater treatment for dye effluents.

2. Materials and methods

2.1. Experimental section

All the reagents used were of analytical reagent grade. Industrial dye effluent collected from a textile industry (Kongoor textile processing, Tirupur, Tamilnadu, India). Anion exchange membrane

(0.4 mm in thickness and 1.8 mol/kg in exchange capacity) based on polystyrene divinyl benzene was used in the experiment. All the solutions were prepared with double distilled water. The characteristics of the dye effluents are shown in Table 1.

2.2. Instruments and analysis procedure

The COD of all samples were determined by the dichromate reflux method. The chloride ions cause interference, as they can be oxidized to Cl₂ by dichromate during the analysis. To avoid the interference the samples were treated with Ag₂SO₄ to form a precipitate of AgCl, and then separated by centrifugation. The concentration of H₂O₂ solution was determined by titration with standard KMnO₄ solution. The oxidized products and the reduction in dye concentration were measured using UV–vis spectrophotometer (Systronics 118). The percentage of colour removal was calculated by the following formula:

$$\% \text{Color removal} = 100 \left(\frac{\text{ABS}_0^{\text{M}} - \text{ABS}^{\text{M}}}{\text{ABS}_0^{\text{M}}} \right) \quad (1)$$

where ABS₀^M is the maximum absorbance value before electrolysis, ABS^M is the maximum absorbance value after electrolysis. The Fourier transform infrared spectroscopy (FTIR) study was made by PerkinElmer-Paragon 500. Dye effluent and its degradation product analysis was also carried out on a high-performance liquid chromatograph (HPLC), consisting of a Waters model 501 pump (flow rate 0.5–1.0 mL/min), Rheodyne injector containing a 20 μL sample loop, and Waters model 440UV absorbance detector oper-

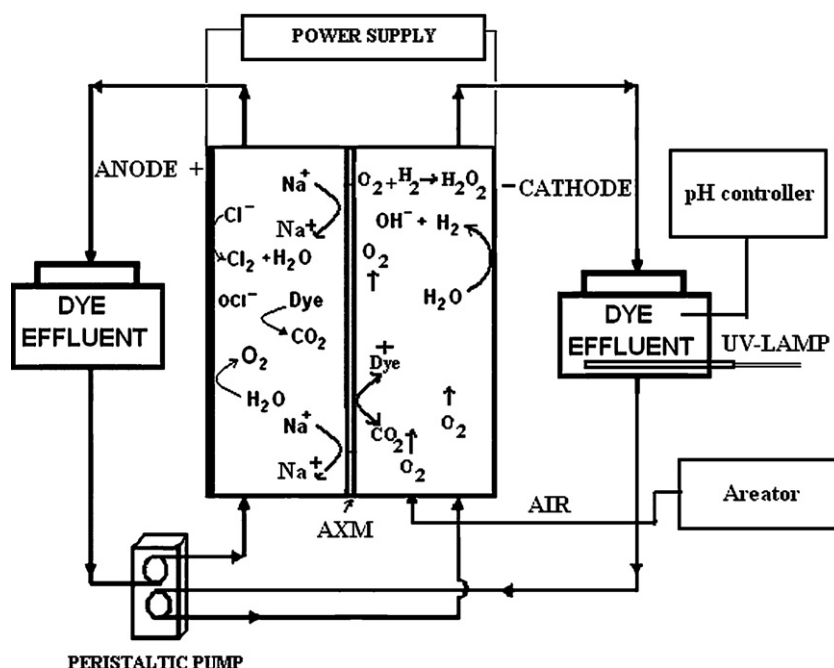


Fig. 1. Diagram of experimental setup.

ated at 254 nm. The detector output was processed with peak simple software. Separation was achieved on a reverse phase C18 (25 cm × 4.6 mm) stainless steel column, using 40:60–70:30 (v/v) methanol: sodium phosphate buffer (pH 2) as the mobile phase. All solvents used were of Fisher Scientific HPLC grade.

2.3. Electrochemical membrane cell

The electrochemical membrane cell set up is shown in Fig. 1. The electrochemical membrane cell was separated into two compartments with an anion selective membrane using commercially available Ti/RuO₂/IrO₂ as anode and carbon felt as cathode. The dimension of the anode and cathode was 7 cm × 7 cm. The thickness of the carbon felt was 0.8 cm. The distances between electrodes were 1 cm. They were connected to 2 A and 15 V DC regulated power supply. Both the anode and cathode electrolytic cell volume was 36 mL each. The anolyte and catholyte compartments were connected separately to two different effluent reservoirs of 1 L capacity each. The dye effluent was passed through each compartment using double head peristaltic pump under batch recirculation process. The UV lamp held axially in the center of the catholyte reservoir. In cathode compartment, atmospheric oxygen was passed using aerator and the pH was measured using pH meter. Both compartment reservoirs were connected to the peristaltic pump using silicone rubber tubes. The electrochemical cell that is discussed above is plate and frame model cell. Also the undivided cell having without membrane and volume of the reservoir is 1 L. The experiment with cathode compartment was carried out in presence and absence of aeration, with and without UV treatments. During the electrolysis at various current densities, pH, colour, COD reduction, and energy consumption were monitored. UV-vis spectrometry, FTIR and HPLC studies were also made. In the case of undivided cell system, the experiment was performed taking only 1 L of wastewater.

3. Results and discussion

3.1. Dual electro-oxidation mechanism of dye degradation

The traditional single-chamber electrochemical method used in the wastewater treatment mainly focused anodic oxidation, but hydrogen gas is produced at the cathode. However, this hydrogen gas is not involved in the oxidation of organics. Hence we developed dual electro oxidation system; it involves anodic and cathodic indirect oxidation of organics.

In anodic compartment, the colour removal and COD reduction occurred only in the presence of chloride. Thus, the de-colourisation is effected in the dye effluent due to the reaction between the generated chlorine/hypochlorite and the dye molecule. The indirect electrochemical treatment involves the application of an electrical current to the wastewater containing chloride to convert into chlorine/hypochlorite. The chlorine/hypochlorite oxidizes the pollutants and is then reduced to chloride ion.

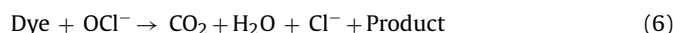
On the other hand, in cathodic compartment a small amount of hydrogen peroxide is produced at the cathode by reduction of oxygen (atmospheric oxygen). The colour removal and COD reduction depend upon the generation of H₂O₂, pH, presence of UV lamp and if any catalyst. Also the degradation of dyes depends upon the formation of OH• radical and the dye molecule. Hence the following reactions assume to take place:

In anodic reaction

Main reaction



Side reaction



At cathodic reaction



The hydrogen per oxide can be electrochemically produced by reducing oxygen at cathode. The formal half-cell reaction in acidic medium is given by



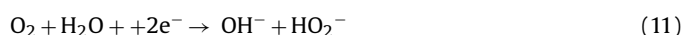
This shows hydrogen peroxide to be the product of a two-electron transfer to oxygen. However, if oxygen is reduced by a four-electron process, water is formed as the end product



Hydrogen peroxide can reduce further to water



In alkaline media, the reaction stoichiometry is given by



The per hydroxyl ion (HO₂⁻), is formed by hydrogen peroxide dissociation in base



In presence of UV lamp



The hydroxyl radical is a powerful oxidizing agent and attacks organic pollutants. There is also the photocatalytic degradation of dye effluent in acidic solutions, which is probably due to the formation of OH• [34].

3.2. Effect of COD reduction, colour removal, and pH

3.2.1. Undivided cell system

Fig. 2 shows the effect of current density on various treatments. It is evident from Fig. 2 that the extent of degradation of dye effluent

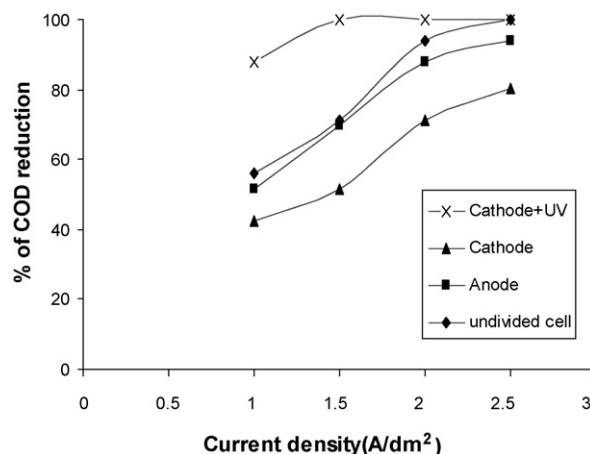


Fig. 2. The effect of current density on COD reduction under different treatment techniques.

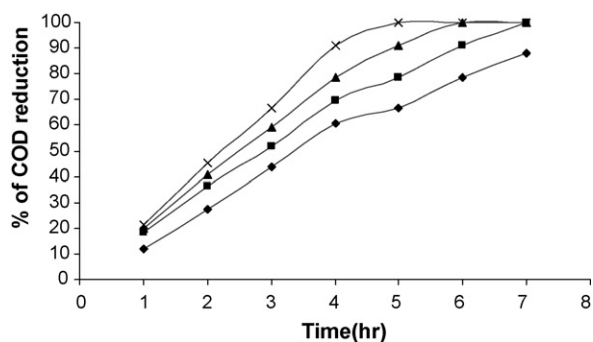


Fig. 3. The effect of current density on COD removal efficiency in relation to time in cathode compartment with UV treatment technique (—◆—) 1 A/dm², (—■—) 1.5 A/dm², (—▲—) 2 A/dm², and (—×—) 2.5 A/dm².

increases with increase in applied current density. With increase in the applied current density, the catalytic anodes produce OCl⁻ that mineralizes the dye. Figs. 3 and 4a shows the colour removal of undivided cell system. The COD reduction efficiency showed an increase with increasing current density. At 1 A/dm², about 56% COD reduction was obtained and it increased to 93.94% at 2 A/dm². However approximately 100% COD reduction could be achieved at the maximum current density of 2.5 A/dm² in 7 h (data not shown). The decrease in the absorbance of residual dye was measured spectroscopically at the peak of maximum visible wavelength (622 nm) and expressed in terms of percentage. The maximum colour removal of about 99.48% was obtained at all the current densities studied (1–2.5 A/dm²) within 2–4 h.

3.2.2. Dual electrode system

3.2.2.1. Indirect oxidation of anode compartment. The COD reduction and colour removal efficiencies during a preliminary electrolysis, carried out in anode compartment, were studied (the anode and cathode compartment separated by anion exchange membrane). Fig. 4b shows the efficiency of colour removal in the anode compartment. The COD reduction efficiency showed an increase (51.51–93.94%), with increasing current density (1–2.5 A/dm²). However, the environmental permissible COD limit of 250 ppm could be achieved even at 2 A/dm². Hence at optimum current density of 2 A/dm², the COD reduction and colour removal were found to be 87.89% and approximately 100% respectively, in anode compartment.

3.2.2.2. Indirect oxidation of cathode compartment. In presence of aeration treatment (the blank experiment in cathode compartment), the formation of hydrogen peroxide is 0.23 M for 2 h electrolysis at pH 2. In this process, formation of hydrogen peroxide and degradation of dye effluent were studied. The atmospheric oxygen passed through the catholyte compartment was reduced by carbon felt cathode leading to formation of hydrogen peroxide. As the hydrogen peroxide is a strong oxidizing agent, the effects of oxidation of the dye by the electrochemically generated hydrogen peroxide were studied. The reactivity of hydrogen peroxide depends on the pH of the medium. Hence, the effect of pH on the COD reduction has been studied in the pH ranges of acidic, neutral and alkaline. The results are shown in Fig. 5. Decrease in pH from 13 to 7 increases the COD reduction from 48% to 59% and colour removal 94.8–96.6%. Further decrease in pH from 7 to 2 increases the decolourisation from 96.6% to 99.3% and COD reduction from 59% to 71.2% at current density 2 A/dm² for 7 h.

In the case with no oxygen flow, the COD reduction and colour removal were 46% and 94% respectively (2 A/dm²). Here dye contained chromogen (N=N) compounds are reduced. Hence colour

removal reached up to 94% but COD reduction was not completely removed.

From the results, it is clear that the process is more efficient in acid medium (pH 2). The lowering of dye removal rate in alkaline pH range is due to reduction of hydroxyl radical concentration. Under this condition H₂O₂ undergoes decomposition to form water and oxygen rather than hydroxyl radical. In alkaline medium the oxidizing species hydroperoxy anion (HO₂⁻) is also formed which is the conjugated base of H₂O₂. This HO₂⁻ anion reacts with OH[•] radical and residual H₂O₂ consequently lowering the removal rate. It is well documented that pH has a significant effect on the electrochemical cathodic degradation (H₂O₂ and H₂O₂/UV) of organics over carbon felt cathode in the range of 2–13. It has been reported that decrease in the pH leads to more efficient oxidation of organics [35,36]. The percentage reduction of COD and colour removal efficiencies of dye effluent observed at optimum pH 2 at various current densities are shown in Fig 4c. As high as 80.3% COD reduction was observed at 2.5 A/dm² with a maximum colour removal efficiency of 99.4%.

3.2.2.3. Indirect oxidation of cathode compartment with UV. An attempt was made in the present study in order to investigate further the effects of oxidation of the dye in presence of UV lamp (6 W). For UV/H₂O₂ process, irradiation was performed in a re-circulating photo reservoir of 1 L capacity, by a pencil type, 6 W lamp covered by a quartz sleeve positioned inside the reservoir. The lamp mainly provides ultra visible light in the range of 254 nm. The electrolysis of dye on carbon felt cathode was performed at different current densities of 1 A/dm², 1.5 A/dm², 2 A/dm² and 2.5 A/dm² under controlled pH 2. As can be seen from Figs. 3 and 4b, that the reduction of COD and colour removal was strongly influenced by the photo electric conditions and, in particular, the complete decolourisation and degradation was effected even at low current density (1 A/dm²), which is due to the formation of more OH[•] radical during the oxidation of dye in presence of UV. Similar results were also obtained by Muruganatham and Swami Nathan [35] during the oxidation of azoic dye with UV/H₂O₂ process.

3.3. Energy consumption

The energy consumption of the three processes is shown in Fig. 6. The energy consumption showed increasing trend with increasing applied current density. Hence the optimum current density (2 A/dm²) was taken in all the process. In anodic compartment, the maximum COD reduction of 87.8% with 10.36 kWh/kg of COD was obtained. At indirect oxidation of cathode compartment with UV process approximately 100% COD removal was achieved within 7 h with a maximum energy consumption of 11.58 kWh/kg of COD; while at cathodic compartment without UV process, relatively low COD reduction of 71.2% with high energy consumption of 16.8 kWh/kg of COD was evident.

However, 93.9% of the maximum COD removal, at 2 A/dm², was achieved with energy consumption of about 18.05 kWh/kg of COD in undivided cell system.

Therefore an optimum point must be carefully determined giving a faster removal rate and quite low energy consumption.

Hence, the optimal energy consumption process was chosen (2 A/dm²) for industrial wastewater treatment process. In the present study the observed total energy consumption for electrochemical oxidation-undivided cell, dual electro oxidation without UV and dual electro oxidation with UV are 18.05 kWh/kg of COD, 10.36 kWh/kg of COD + 16.8 kWh/kg of COD = 13.58 kWh/kg of COD and 10.36 kWh/kg of COD + 11.58 kWh/kg of COD = 10.97 kWh/kg of COD respectively. From the results, it is understood that the process involving dual electro oxidation with and without UV process, completely removes the dye with low electrical energy consump-

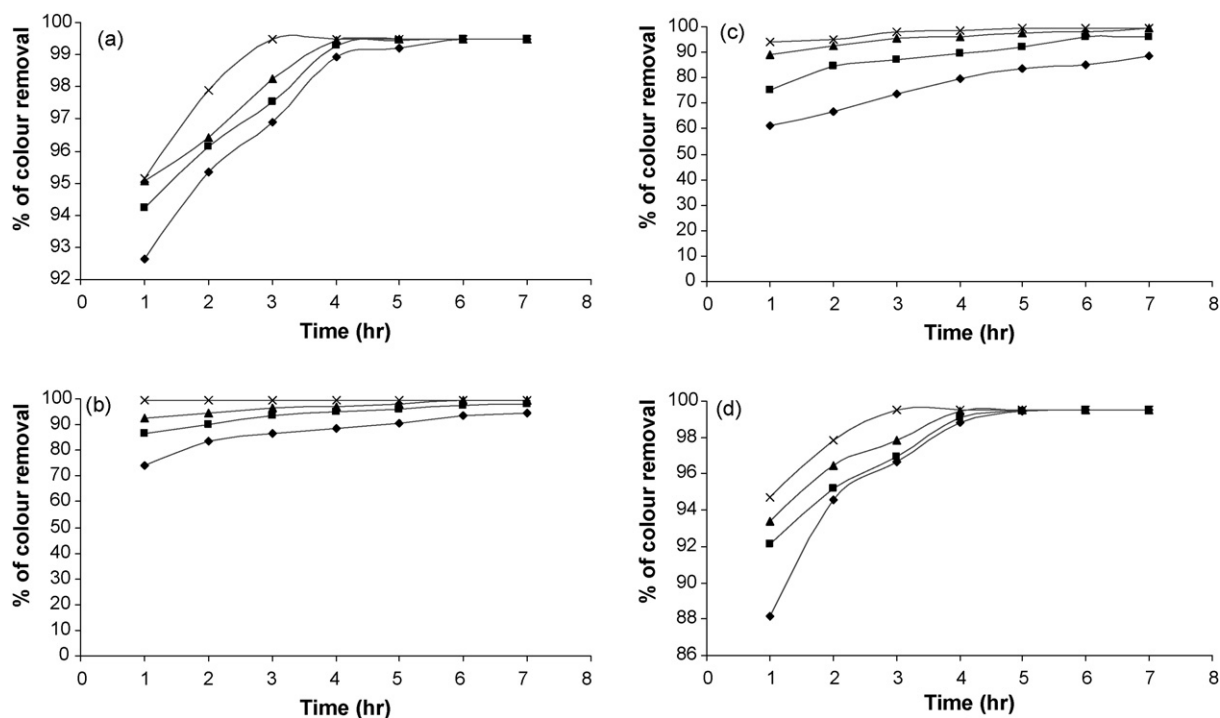


Fig. 4. The effect of current density on colour removal efficiency in relation to time under different treatment techniques (a) undivided cell, (b) anode compartment, (c) cathode compartment and (d) cathode compartment with UV. (—◆—) 1 A/dm², (—■—) 1.5 A/dm², (—▲—) 2 A/dm², and (—×—) 2.5 A/dm².

tion (the average energy consumption of 13.58 kWh/kg of COD and 10.97 kWh/kg of COD) in a short time and thus this process reduces the energy consumption by 25% and 40% respectively when compared to that of the undivided cell system.

3.4. UV-vis spectrum

The changes in absorbance characteristics of dye effluent were investigated over a large wavelength interval during the electrochemical decolourisation process and the results are shown in Fig. 7. The spectra showed that there was a maximum absorbance at 622 nm in the visible region. This peak disappeared gradually during the electrolysis. There was also another peak observed at 667 nm in the visible region. These two peaks were completely disappeared in all the three processes. This result indicated the cleavage of azoic group and total decolouration of the solution. The disappearance of all the peaks at the end of the electrolysis shows that the mineralization of the dye effluent is completely achieved. It is clear from Fig. 7 that the electrochemical oxidation, dual electro-oxidation and dual electro-oxidation with UV have effectively removed completely the colour of the dye.

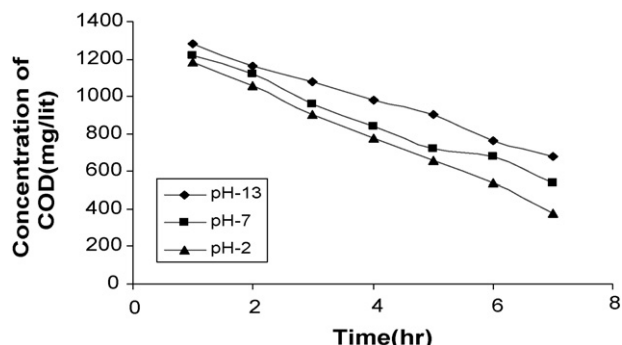


Fig. 5. Influence of pH on the COD removal efficiency at 2 A/dm².

3.5. HPLC study

HPLC and FTIR studies were carried out only for the system which gave better performance in terms of low energy consumption and maximum dye degradation in short period of time. Hence the electrolyzed effluents from dual electro-oxidation with UV at 2 A/dm² for 7 h were used for both HPLC and FTIR studies.

The dye effluents were extracted before and after electrolysis using ether and allowed to complete dryness at room temperature. Then the residues were dissolved in small volume of HPLC-grade methanol for HPLC analysis. Fig. 8 shows, the characteristics of initial dye effluent, and after electrochemical treatment of anode compartment, cathode compartment and cathode compartment with UV treatment. Fig. 8a, shows two peaks of initial dye at 4 and 3.5 min with 4.3 V and 0.8 V respectively. Fig. 8b also shows two peaks for the electrolyzed dye from cathode compartment, at 2 A/dm² after 7 h. Both the peak areas were reduced to 0.7 V and 0.2 V respectively. It indicates the existence of very small amount of parent dye even after 7 h. But in the case of anodic compartment

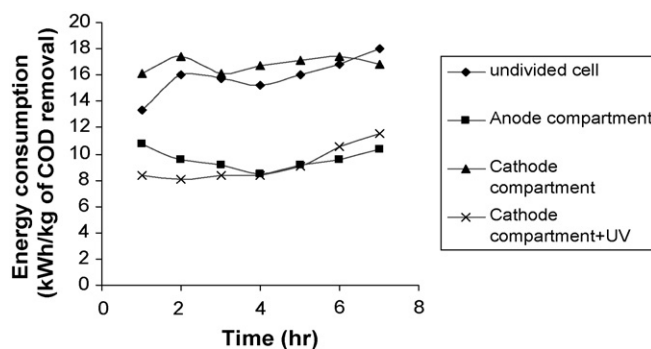


Fig. 6. Energy consumption for COD removal in relation to time under different treatment techniques at 2 A/dm². (—◆—) Undivided cell, (—■—) anode compartment, (—▲—) cathode compartment, (—×—) cathode compartment with UV.

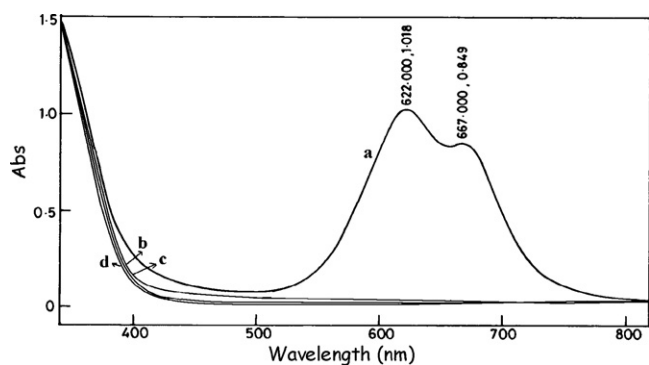


Fig. 7. The characteristic of UV-vis Spectra for untreated dye effluent (a) and treated effluents of anode compartment (b), cathode compartment (c) and cathode compartment with UV (d) at operating current density 2 A/dm^2 .

and cathodic compartment with UV treatment complete degradation of dye was observed (Fig. 8c and d). The HPLC data reveal that cathodic compartment with UV treatment process is efficient than that of other methods.

3.6. FTIR study

Fig. 9 shows the IR spectra of the dried solution residue before and after the electrochemical treatment. It can be seen that some structural changes might have occurred during the electrochemical process. In Fig. 9c, the appearance of peak at 1579 cm^{-1} , 1492 cm^{-1} and 1410.5 cm^{-1} indicates the presence of azo group, the presence of secondary and primary amine respectively. Other peaks were also noticed at $1250\text{--}1000 \text{ cm}^{-1}$ (S–O stretching and aromatic C-H bending), and at 1036.7 cm^{-1} (C–O–H stretching). The other peaks at 625.2 cm^{-1} , 679.8 cm^{-1} , 734.9 cm^{-1} and 550.8 cm^{-1} indicate the aromaticity or benzene ring. In anode compartment, after electrolysis (Fig. 9b), there were two peaks appeared at 1629.5 cm^{-1} and 1440.1 cm^{-1} . These suggest formation of aliphatic amines, while peaks at 1579 cm^{-1} , 1492 cm^{-1} , 1410.5 cm^{-1} and 1129 cm^{-1} are completely disappeared and the peak 1036.7 cm^{-1} shifted to 983 cm^{-1} . The appearance of peaks at around 983 cm^{-1} and 811 cm^{-1} suggests the formation of ClO_3^- and OCl^- , which may generally be present in the hypochlorite solution. Presence of peak at about 662.4 cm^{-1} is thought to belong to aromaticity

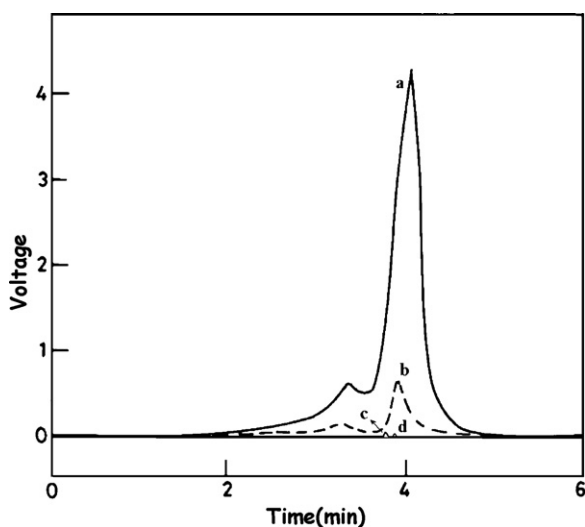


Fig. 8. The characteristic of HPLC analysis for initial dye effluent (a) electrochemically treated dye effluents of anode compartment (b), cathode compartment (c) and cathode compartment with UV treatment (d).

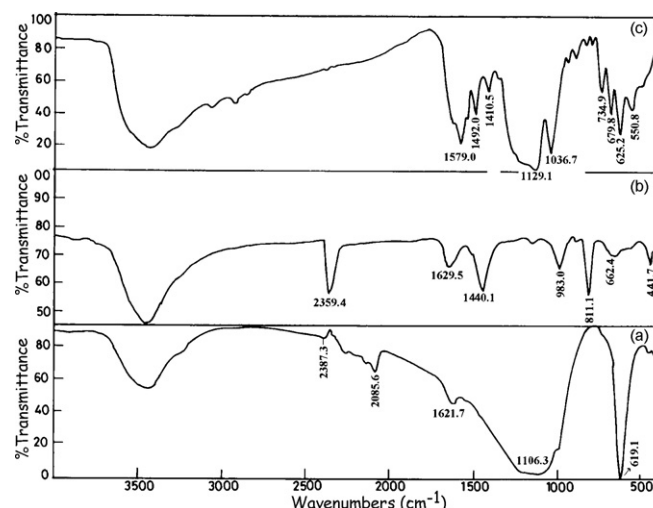


Fig. 9. Changes of infrared absorption bands of untreated (a), electrochemically treated dye effluents of anode compartment (b) and cathode compartment with UV treatment (c).

or benzene ring. In cathode compartment with UV, after electrolysis (Fig. 9a), the formation of peaks at 1621.7 cm^{-1} , 1106.3 cm^{-1} and 619.1 cm^{-1} indicates the aliphatic secondary amine, C–O–H stretching and OH^* . The peak 619.1 cm^{-1} suggests the OH, which may generally be present in the hydrogen peroxide. This variation in the FTIR spectra can be explained by the complete degradation of organic compound and formation of other intermediate organic compounds.

4. Conclusions

- (1). From over all results for a typical undivided electrochemical wastewater treatment reactor for the effluent containing COD 1320 ppm, the energy consumption is found to be at 18.05 kWh/kg of COD.
- (2). But in the dual electrochemical oxidation with and without UV treatment the energy consumption is markedly decreased by 25% (13.58 kWh/kg of COD) and 40% (10.97 kWh/kg of COD) respectively.
- (3). Three systems were studied, and the dual electro-oxidation with UV treatment is proven to be an efficient method for the degradation of dye effluents.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2009.06.063.

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