Electrochemical Decolorization of Different Dyes on Carbon Electrodes

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ABSTRACT

Electrochemical decolorization of some acid and reactive dyes has been investigated using carbon electrodes. The decolorization rate significantly depends on current density, concentration of a conductive electrolyte, pH of solution as well as the initial dye concentration. Increasing the conductive electrolyte concentration and the current density enhances the decolorization rate, while increasing the pH of dye solution and initial dye concentration result in decrease in the rate of decolorization. The decolorization rate of a mixture of the used acid and reactive is lower than the individual dye. The Experimental results revealed the suitability of the electrochemical method to effectively decolorize wastewaters from dyeing processes.

Keywords: Decolorization, Dyes; Electrochemical Oxidation, Carbon electrode.

1. Introduction:

In recent years, there is an increasing interest in the development of innovative treatment of industrial wastewaters particularly those containing toxic and non-biodegradable organic pollutants that traditional processes cannot completely oxidize them. Carcinogenic products such as aromatic amines due to the large consumption of azo dyes in the dying processes contain a considerable strong color, a broad range of pH varying from 2 to 12, high COD concentration and suspended particles, and low biodegradability [1-4]

There are different techniques to achieve color removal, among them the most used are: activated carbon adsorption,[5] membrane filtration,[6-7] coagulation-flocculation processes,[8-9] treatment with ozone and biological treatment[10-11].
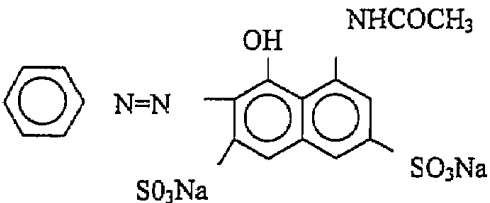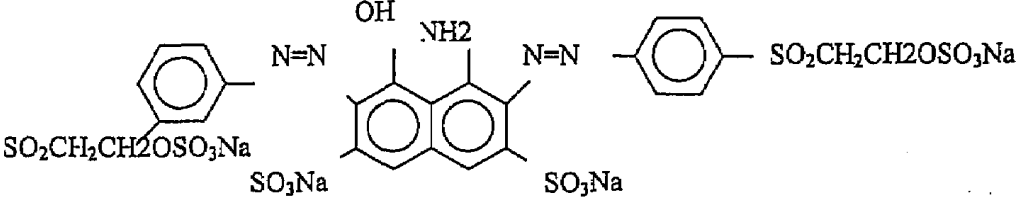
Biological methods cannot be applied to most textile wastewater due to the toxicity of most commercial dyes to the organisms used in the process[12]. Chemical coagulation is not effective for the removal of dissolved reactive dyestuffs[13]. Activated carbon adsorption has the associated cost and difficulty of the regeneration process and a high wastewater disposal cost. Advanced oxidation processes such as ozonation, UV and ozone/UV combined oxidation, photocatalysis (UV/TiO$_2$), and Fenton reactive and ultrasonic oxidations are not

economically feasible[10, 13-16]. These offer the possibility of in site destruction or modification of various pollutants to less deleterious structures by anodic oxidation on high surface electrodes[17, 18,19,20,16]. There is little work done on application of the electrochemical techniques for decolorization of different azo dyes[21-22]. The electrochemical techniques are considered as an attractive methodology and powerful means of pollution control. The aim of the present work is to apply the electrochemical techniques for degradation of dyes in order to minimize the water pollution under different controlling parameters such as electrolyte concentration, current density, and initial concentration of dyes and pH of solution. Thus, it is intended to apply the obtained proper standard condition for applications in the industrial sector to remove toxic matters, detergents, and suspended solids as well as to recycle free-toxic textile wastewaters.

2. Experimental Work:

2.1 Materials

Chemicals used in this study were Acid Red 1 (CI 18050) and Remazole Black T, the structural formulas of which are shown in table blew. Sodium chloride was employed as conductive electrolytes.

Acid Red 1 (Acid dye)	
Remazole Black T (Reactive dye)	

2.2 Electrolysis and electrode material

The electrolysis of the aqueous solutions containing the commercial dyes to be treated electrochemically was carried out in a one-compartment Pyrex glass cell of 150 ml volume. Two identical carbon electrodes (area = $1 cm^2$) were used as cathode and anode and placed with 1cm apart. DC power supply (WP-704-AX) was used for controlling the applied constant current.

23. Experimental procedure

An aqueous solution of tested dyes was prepared and an aliquot was taken from the dye solution to determine the initial concentration prior to reaction. The reaction started with the application of specified current. Samples were taken from the reactor at appropriate time intervals and analyzed.

2.4 Experimental conditions

Dyes aqueous solution, with an initial concentration of 0.1 g/l was used in most runs. For the investigation of the effects of initial dyes concentration, the runs were carried out in the range 10-100 mg/l with an electrolyte concentration of 15g/l NaCl and different current density of 10-100 mAcm^{-2}. The effect of electrolyte concentration was tested in the range of 10-50 g/l NaCl.

2.5 Analytical measurements

Decolorization was calculated from the initial dye concentrations (C_i) and final dye concentrations (C_f) by measuring their absorbance at the maximum dye absorbance. % D was calculated as:

$$D\% = 100 \ (C_i - C_f) \ / \ C_i$$

% D is an extent decolorization   (1)

Absorbance measurements were carried out with a UV – visible spectrophotometer (V-530 Jasco).

3. Result and discussion

Batch reactor experiments were carried out for the determination of the effects of electrolyte concentration, current density, pH of the solution and initial dyes concentration on the rate of decolorization. The first task of this study was to select suitable current densities in which the highest extent of decolorization of the treated dyes solutions.

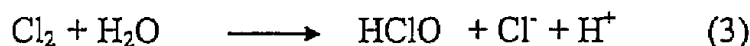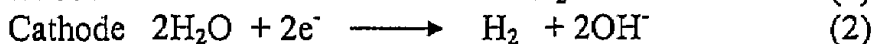### 3.1 Effect of current density

Different current densities (10-100 mA/cm^2) were applied to investigate the rate of decolorization of dyes in NaCl solution (15g/l) at a 100mg/l initial dye concentration. The results clearly showed that an increase in the current density decreases the decolorization time and yields an increase in the efficiency of color removal as shown in Figures 1(a) and (b) for Acid and Reactive dye, respectively. The results can be explained on the basis that as the current density increases, the efficiency of chloride and hypochlorite ion production increases, which in turn enhances the color decolorization. Therefore, there is an increase in oxidation of dyes and hence an improvement in the efficiency of color removal. This was carried out within a period of 120 minutes electrolysis. The time to reach a complete decolorization decreases with an increase in

current density and depends on the type of dye as revealed from the data quoted in Table (1). The rate of dye oxidation increases with an increase in the current density and hence, the rate of decolorization due to an increase in the charge required for color removal. It can be seen from Table (1) that a complete decolorization occurs within 120 minutes of electrolysis except at 10 mA/ cm^2, no complete decolorization occurs within this period for all different types of dyes. The results may be attributed to a decrease in the charge required for complete decolorization and the slow rate of dye oxidation within 120 minutes. The faster rate of decolorization in acid dye can be accounted to the highest production of chloride and hypochlorite ions along with the lowest charge required for decolorization.

3.2 The effect of electrolyte concentration

The effect of NaCl (10-50) g/l on the removal rate of acid and reactive dye is shown in Figs 2(a) & 2(b). The operating conditions for both dyes are similar and carried out at T=25 °C and 120 min. electrolysis time, except for the current density, which was different, being 20mA/cm^2 for acid dye and 30mA/cm^2 for reactive dye. The effect of NaCl concentration on % decolorization for both acid and reactive dyes is presented in Table (2). |
A general trend was observed for both dyes, an increase in color removal with increasing the electrolyte concentration. It is obvious that the presence of chloride ions improved the yield of decolorization, which can be attributed to the action of oxidizing species generated on the anode by chloride oxidation. The mechanism of its electro- generation from a solution containing chloride ions involves the primary oxidation of chloride ions to the chlorine at the anode surface according to [31]

Anode $2Cl^-$ $\longrightarrow$ $Cl_2 + 2e^-$ (1)

Cathode $2H_2O + 2e^-$ $\longrightarrow$ $H_2 + 2OH^-$ (2)

   $Cl_2 + H_2O$ $\longrightarrow$ $HClO + Cl^- + H^+$ (3) |

This stimulatory effect could be explained by the transformation, at the anode surface of the electrolyte in a strong oxidizing agent, which can then attack the dye in solution. In this case, chloride ions are oxidized to Cl_2 at the anode, whereas on the cathode, the electrolysis of water yields OH $^-$ and hydrogen ions. The oxidation of the dye by hypochlorite as a final product often implies the regeneration of the chloride ion that can be recycled back at the anode surface for further production of Cl_2. In this regard, the overall process is cyclical although the anode reaction is irreversible in the electrochemical sense. These results confirm that the electrochemical process is a valid method to degrade acid and reactive dyes in liquid medium. Moreover, the addition of an electrolyte clearly increases the degradation rate.

3.3 Effect of pH

The influence of initial pH (5-9) on the decolorization of reactive dye with initial concentration 100 mg/l and 15g/l NaCl concentration at current density 30mA/cm^2 during the electrochemical degradation is presented in Fig. 3. It is apparent from the figure that extent of decolorization decreases with increase in pH. The results in Fig. 3 indicated that the electrocatalytic degradation rate of this dye increased with decreasing the solution pH. The highest electrocatalytic activity was attained under acidic conditions. The complete oxidation of the dye and total removal of the color was achieved in acidic solution (pH 5) than that observed at pH 7 and 9. The results may be accounted to the decreased production of chlorine/hypochlorite at higher pH solution, because of the formation of chlorate or perchlorate. In addition, at acidic pH, the chlorine is present in the solution in the form of hypochlorous acid, which has higher oxidation potential (1.49 V) than that of hypochlorite (0.94 V), which is prevalent in alkaline condition. In addition, at high pH 9, hypochlorite is present as hypochlorite form and with very low concentration of HOCl. Hence, the reaction was very slow suggesting the rate of reaction between OCl− and the dye is small, and decreases percentage decolorization. At pH 7 the concentrations of hypochlorite and hypochlorous acid will be equal. With further increase in acid concentration (pH=4), the HOCl concentration increases and at pH 5, the percentage of hypochlorous acid in the mixture increases, suggesting the major pathway for the reaction is through oxidation of dye by HOCl leading to high percentage decolorization.

3.4 Effect of initial dye concentration:

Effect of initial dye concentrations ranging from (10-100) mg/l on the decolorization rate in a solution containing 15 g/l NaCl using a current density of 20 mA/cm^2 at 25 °C was shown in Fig. 4a and 4b for acid and reactive dye respectively. An increase in dye concentration causes a decrease in the decolorization rate due to lower diffusion rates of chloride ion. The faster the rate of chloride ion diffusion, the higher the percentage decolorization. Moreover, the charges required for complete de-colorization of initial dye concentration increased with an increase in initial dye concentration under a constant DC current condition. It can be concluded that a mass transfer of chloride ion kinetically controls the production rate of chlorine/hypochlorite and decreased with an increase in initial dye concentration, which causes a color removal. On the other hand, at high concentration the dye radical screened the mass transfer of chloride ion, which makes the oxidation of dye, is more difficult than the diluted one, which facilitates the access of chloride ion to oxidize the dye and causes color removal. This can be postulated by considering that, an

increase in dye concentration induces an inner filter effect and hence the solution becomes more and more impermeable to chloride ion diffusion. Thus, reducing the decolorization efficiency, namely, the dye has a chloride -screening effect. Hence, this effect thus reduces the color removal of dye.

Generally, when the concentration of the dye increases, the charge required for achieving a desired percentage of color removal increased.

Therefore, the electrochemical process was more effective in decolorizing the dye solution when the concentration of the dye was dilute.

3.5. Optimization of the operational conditions and application to simulated mixture of different dyes

The main objective of this research is to determine the experimental conditions required to remove dye color and application of the methodology for experimental design and determination of the range of parameters required to obtain optimum conditions. Real effluents often include more than one component and the study of the possible interactions between different dyes will be very useful for the treatment of real effluents. Once the electrochemical treatment has been tested on monocomponent solutions, an attempt was made to determine the efficiency of decolorization of different mixtures of two kinds of dyes. Simulated dye bath effluent was prepared from two dyes (acid and reactive dyes).

The percentage decolorization of any mixture is lower than that observed for a monocomponent as shown in Fig. 5. This result can be explained on the basis of interaction between both dyes, leading to a formation of stronger intermediate (The dye tends to bind co-operatively) to be oxidized by chloride ion. The amount of this intermediate decreases when the ratio of the mixture increases toward the monocomponent purity (100%). The time required for complete removal of the color for one and the same mixture is longer than in mixture with high percentage of pure dye.

3.6. COD removal

The chemical oxygen demand (COD) of dye solutions was measured using dichromate method [32] for pure acid dye, reactive dye and different mixture of both dyes using the optimal conditions (current density, 30mA/cm2, concentration of electrolyte 15g/l., 1g/l dye concentration and time of electrolysis 2 h) and presented in Table (3). It is evident that the percentage of COD removal was less than 50% for all dyes in spite of the complete color removal in these solutions. The results can be explained on the basis that the removal of color is due to the cleavage of chemical bond in the dye molecule, but the oxidation of aromatic ring compounds

takes long time and hence the removal of COD is much less. It seems that the current density applied for COD removal is not enough for complete COD removal, which increased with increasing current density.

Conclusions

The electrochemical treatment of acid, reactive and simulated wastewater containing both dyes has been investigated in different conductive electrolytes and under several operating conditions using carbon electrodes. The following conclusions can be drawn from this work:

1- The electrochemical technique can be considered as very clean and suitable for treating industrial wastewaters containing acid and reactive dyes.

2- The decolorization rate largely increases with an increase in conductive electrolyte concentration and current density.

3- The rate of color removal decreases with increasing in pH of electrolytic solution and initial dye concentration.

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Table 1: Dependence of time required for a complete decolorization on type of dye.

Current density (mA/cm^2)	Time to a complete decolorization (Acid dye)	Time to a complete decolorization (Reactive dye)
10		
20	100 min	120 min
30	50 min	100 min
50	20 min	40 min
100	20 min	20 min

Table (2): Effect NaCl concentration on percentage decolorization of acid and reactive dyes.

NaCl concentrations (g/l)	% Decolorization (Acid dye)	% Decolorization (Reactive dye)
10	96 at 120 min	95.79 at 120 min.
15	96.8 at 80 min.	96.4 at 80 min
30	99.7 at 60 min	98 at 60 min

Table (3): Dependence of percentage COD on type of dyes

Type of Dye	% COD
100% Acid dye	28.27
100% Reactive dye	33.42
75% Acid + 25% Reactive dye	22.59
25% Acid + 755 Reactive dye	22.92
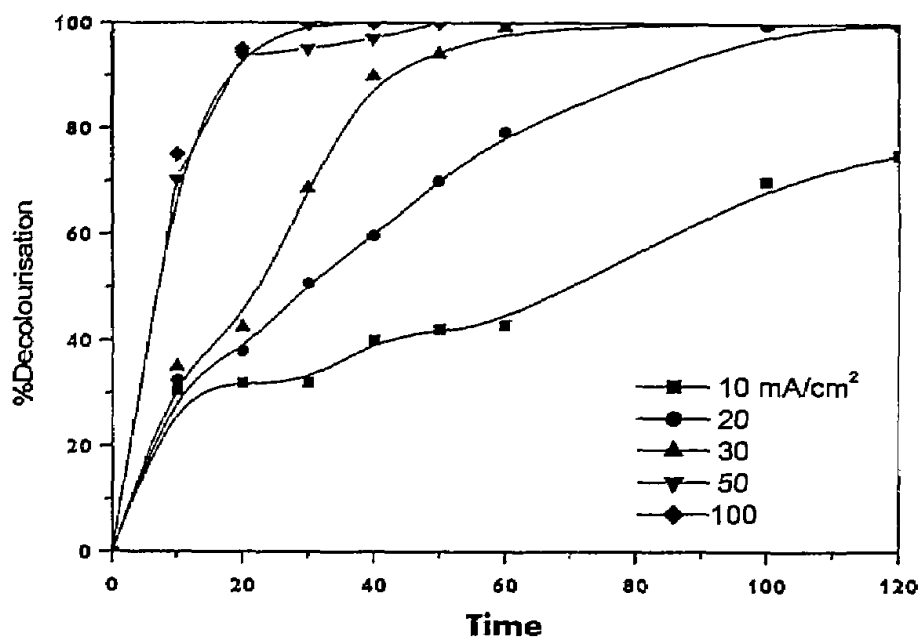
Fig.1 (a): The change of % decolorization with time at different current densities (initial concentration of dye 0.1g/l, electrolyte concentration 15 g/l, 1g/l Hostapal).
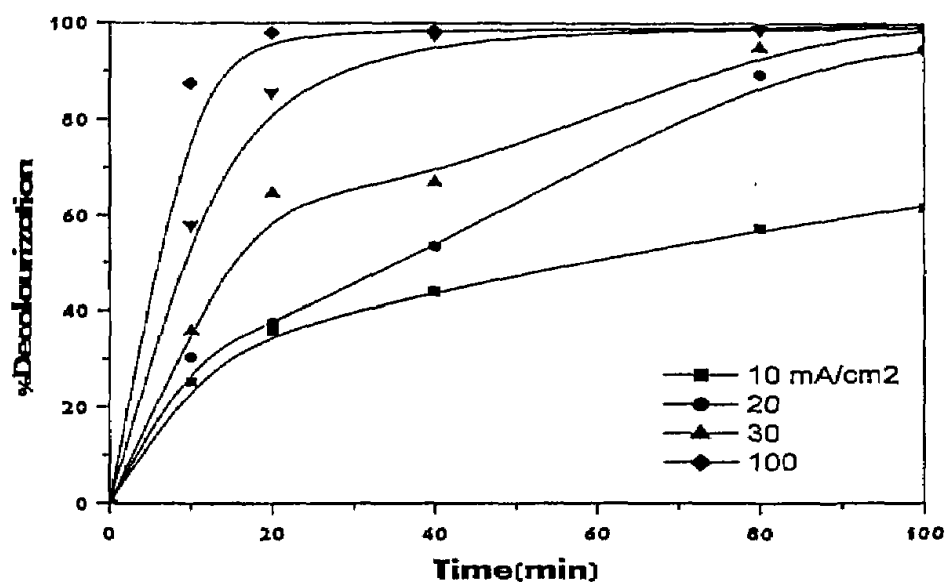
Fig. 1(b): The change of % decolorization with time at different current densities (initial concentration of dye 0.1g/l, electrolyte concentration. 15g/l, 1g/l of Hostapal)
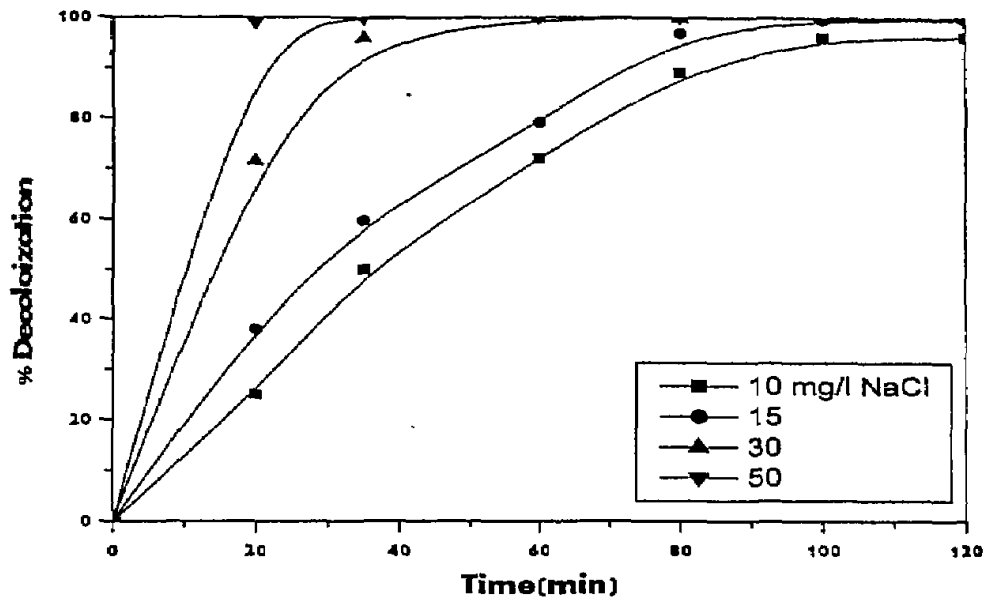
Fig. 2(a): Variation of % decolorization with time at different electrolyte: concentrations initial concentration o.1g/l, current density 20 mA/cm^2,1g/l Hostapal) with no NaCl there is no current &no decolourisation.
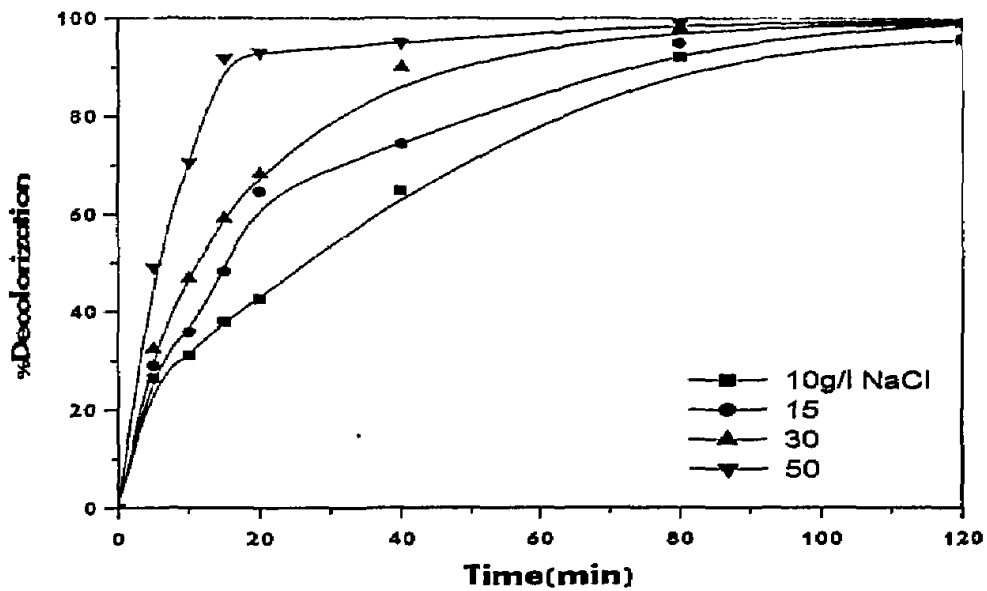
Fig. 2(b): The change of %decolorization with time with(10-50)g/l electrolyte conc.(initial dyes concentration 0.1g/l, Current density 30 mA/cm^2,1g/l Hostapal)
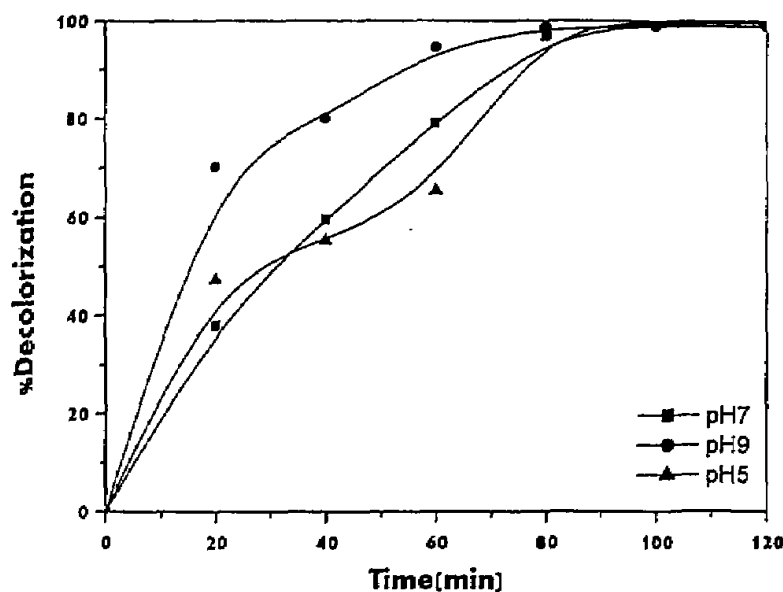
Fig. 3(a): The change of decolorization with time at different pH (initial concentration 0.1g/l,electrolyte concentration 15g/l ,current density 20 mA/cm2, 1g/l Hostapal.
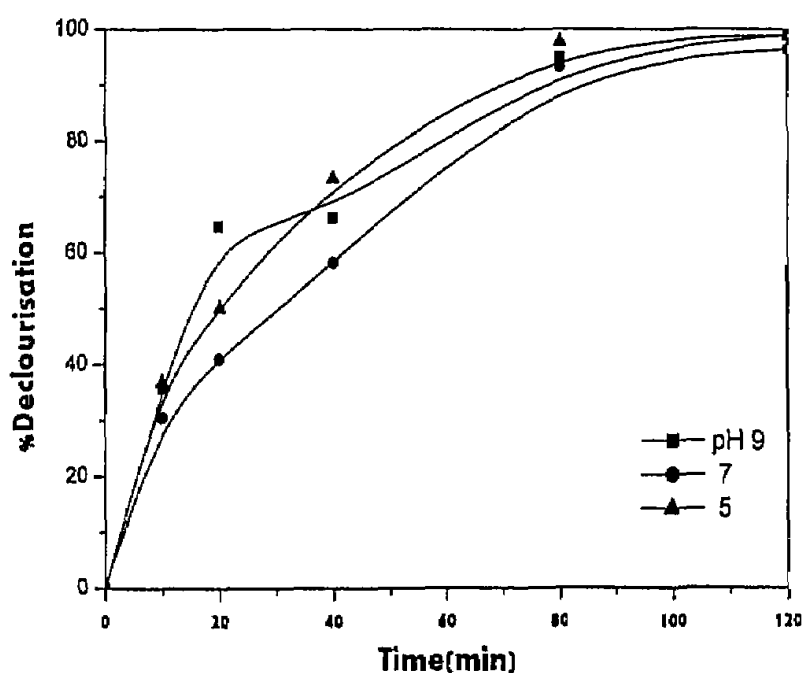
Fig 3(b) The change of decolorization with time at different pH (initial concentration of dye 100mg/l ,electrolyte conc. 15g/l ,current density 30mA/cm^2 ,1g/l Hostapal
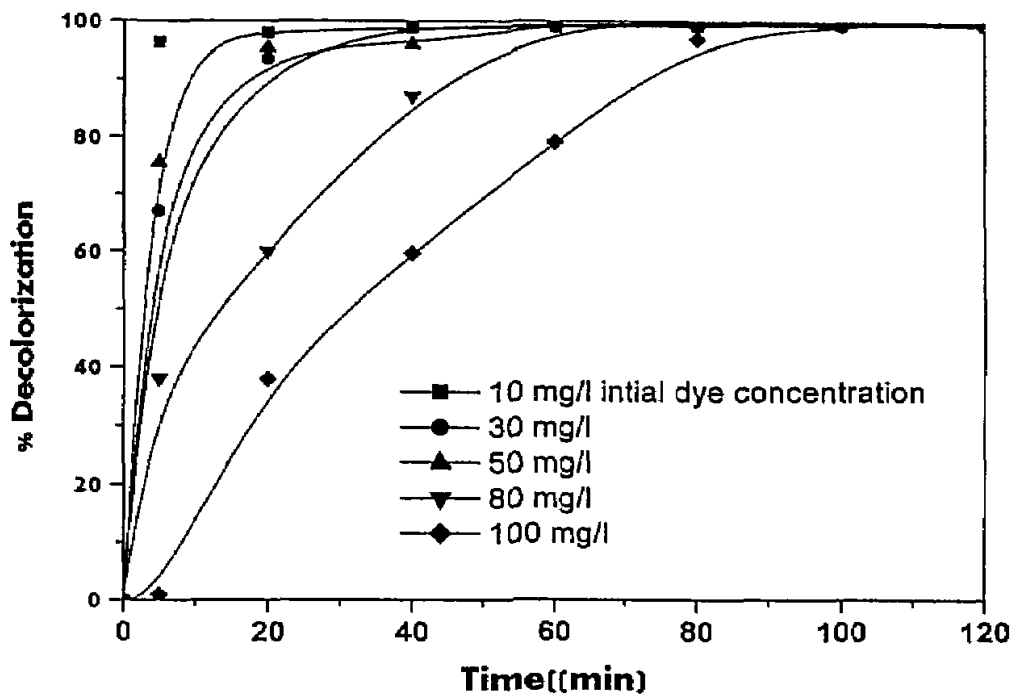
Fig. 4(a): Dependence of % decolorization on initial dye concentration range from (10 to 100) of initial concentration, current density 20 mA /cm^2
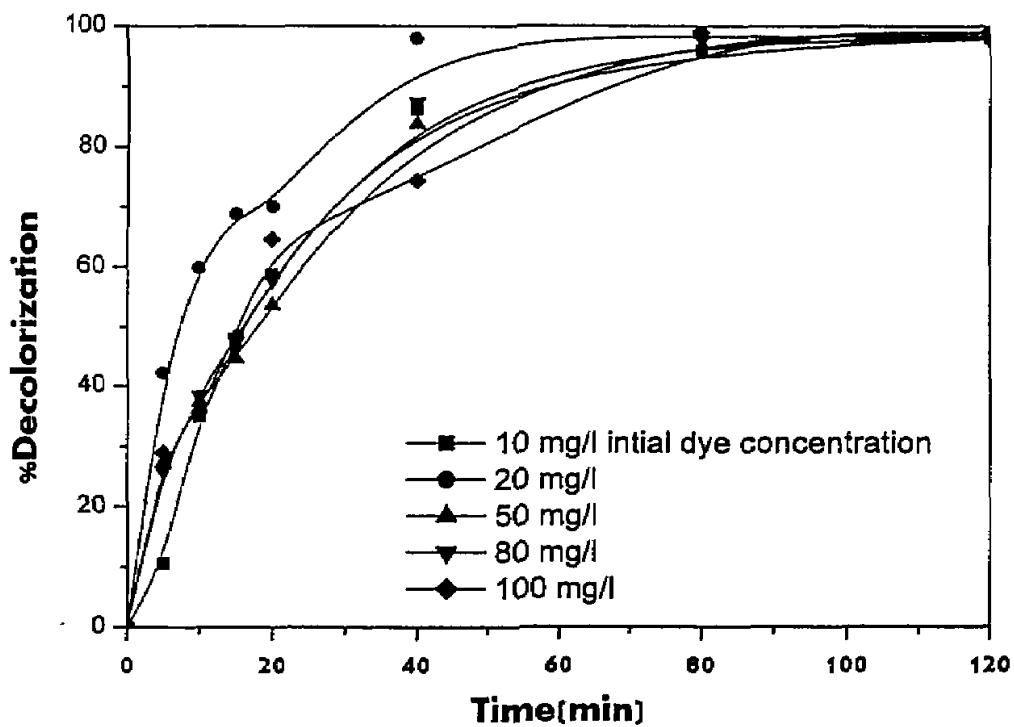

Fig. 4(b): The change of decolorization with time at different initial conc. of dye10-100 mg/l(electrolyte concentration. 15g/l, current density 30mA /cm^2, 1g/l Hostapal.)
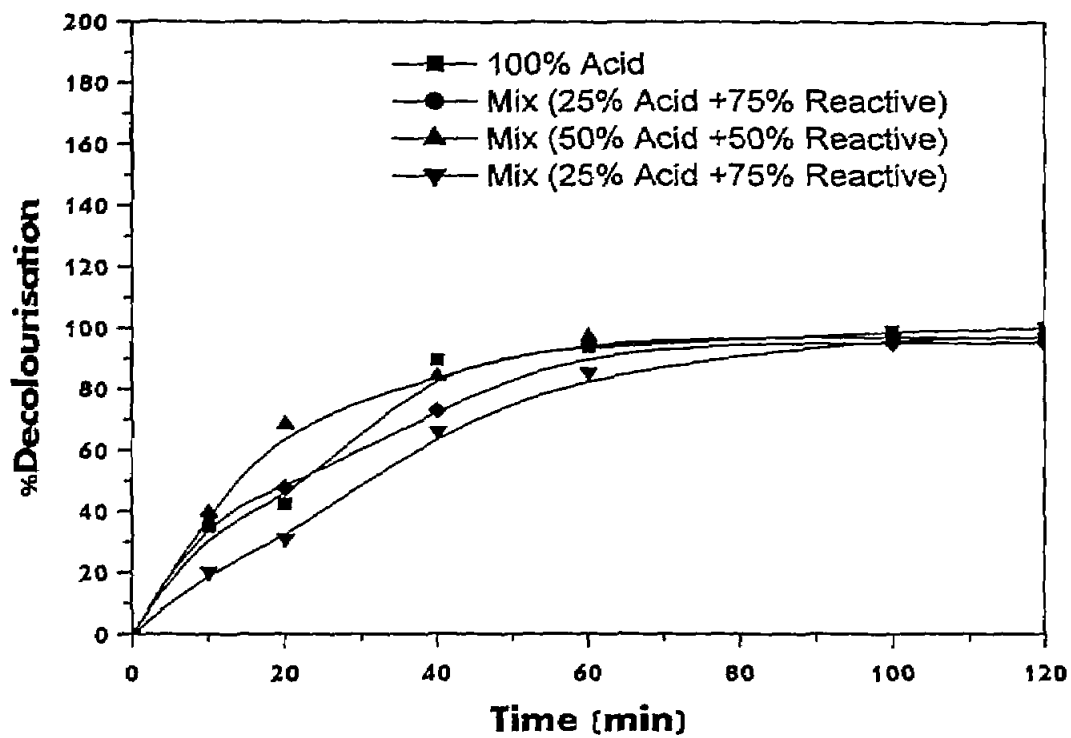
Fig. (5): The change of %decolorization with time at optimal condition (Current density 30 mA/cm2, concentration of electrolyte 15g/1.1g/1 Hostapal).