

Oxidation of various reactive dyes with in situ electro-generated active chlorine for textile dyeing industry wastewater treatment

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Abstract

The present investigation revealed that all the reactive dyes were degraded in chlorine mediated electrochemical oxidation. Titanium based dimensionally stable anode (DSA) was used for in situ generation of chlorine in the dye solution. All classes of reactive dyes (100 mg/L) showed a complete color removal at a supporting electrolyte concentration of 1.5 g/L NaCl and 36.1 mA/cm² current density. The chemical oxygen demand (COD) and total organic carbon (TOC) removals were from 39.5 to 82.8% and from 11.3 to 44.7%, respectively, for different reactive dyes. It can be concluded in general that the triazine containing higher molecular weight diazo compounds takes more time for complete de-colorization than the mono azo or anthraquinone containing dye compounds. The degradation rate of mixed dye compounds was affected by reaction temperature, current density, NaCl concentration and initial dye concentration. However, the initial pH of the dye solution ranging from 4.3 to 9.4 did not show significant effect on de-colorization. A complete color removal with 73.5% COD and 32.8% TOC removals were obtained for mixed reactive dyes (200 mg/L) at the end of 120 min of electrolysis under the optimum operating conditions of 4 g/L NaCl concentration and 72.2 mA/cm² current density.

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Keywords: Reactive dyes; Electrochemical oxidation; DSA; Active chlorine; COD; TOC; UV-vis spectra; Wastewater treatment

1. Introduction

Textile processing industries nowadays are widespread sectors in developing countries. Among the various processes in the textile industry, dyeing process uses large volume of water for dyeing, fixing and washing process. Thus, the wastewater generated from the textile processing industries contains, suspended solids, high amount of dissolved solids, un-reacted dyestuffs (color) and other auxiliary chemicals that are used in the various stages of dyeing and other processing. The presence of even small amount of dye in water (example 10–20 mg/L) is highly visible and affects the water transparency and the gas solubility of water bodies [1]. Among several classes of textile dyestuffs, the reactive dyes contribute about 50% [2] of the total market share and the most common group used as chromophore is the azo (70%), followed by anthraquinone [3].

Several wastewater treatment technologies have been applied for color removal, including physical, chemical and biological

process. All of them have advantages and drawbacks and a combination of different technologies are generally required. The biological treatment of textile wastewater showed low degradation efficiency because of the presence of biologically inert high molecular weight dyestuffs [4,5]. The conventional method of textile wastewater treatment consists of chemical coagulation (using ferrous, lime and polyelectrolytes), biological treatment followed by activated carbon adsorption. The conventional coagulation process generates huge volume of hazardous sludge and poses a problem of sludge disposal. In order to meet the legal requirements for the discharge of textile wastewater, researchers are attempting a combination of two or more treatment methods for the complete and successful removal. Combination of electrochemical treatment and chemical coagulation [6], combined chemical coagulation, electrochemical oxidation, and activated sludge process [7], and combination of electrochemical method, chemical coagulation, and ion exchange [8] were reported for textile effluent treatment to comply with the legal requirements or for reuse standards. However the previous investigators demonstrated combined process successfully, the generation of iron sludge due to the usage of sacrificial iron electrodes is another problem.

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Hence, many investigators are studying alternative oxidation methods like ozonation, photocatalytic oxidation, electrochemical oxidation, etc. The photocatalytic oxidation experiments were conducted for acid blue 80 [9], acid orange 7 [10], brilliant orange K-R [11], and reactive orange 16 [12]. However, this process may not have practical feasibility for real textile industry wastewater treatment due to the inhibition of photocatalytic activity at low pH. Because, the isoelectric point of TiO₂ is around 6.3, so the TiO₂ particles carry positive charges when the solution pH is lower than 6.3. Thus, chloride ions can be adsorbed to the positively charged TiO₂ particle surface at low pH due to ionic force. Similarly, surficial holes of TiO₂ will be blacked by chloride ions will lead to decrease the formation of hydroxyl radicals, resulting in the low photocatalytic efficiency since the dyeing industry wastewater contains large amount of chloride in the effluent. The electrochemically assisted photochemical degradation was also conducted to improve the degradation efficiency of the dye [13]. Ozonation process was studied for the removal of color and chemical oxygen demand (COD) [14]; however, this process showed a less COD removal [15].

Electrochemical treatment is an emerging technology used for the removal of organic and inorganic impurities from water and wastewater. Hence, many researchers are attempting to use electrochemical methods for the treatment of wastewater. In the electrochemical process, the pollutants are destroyed by either the direct or indirect oxidation process. In a direct anodic oxidation process, the pollutants are first adsorbed on the anode surface and then destroyed by the anodic electron transfer reaction. In an indirect oxidation process, strong oxidants such as hypochlorite/chlorine, ozone, and hydrogen peroxide are electrochemically generated. The pollutants are then destroyed in the bulk solution by oxidation reaction of the generated oxidant. All the oxidants are generated in situ and are utilized immediately [16]. Among the oxidants, generation of hypochlorite is cheaper and most of the effluents have a certain amount of chloride. Though direct electrolysis of organic compounds at the anode surface is also possible, a major portion of oxidation is mediated by active chloro species when conducting electrochemical oxidation in the presence of chloride using an undivided cell.

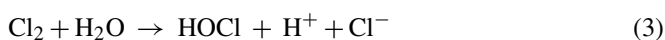
Anode:



Cathode:



Bulk solution:



The application of indirect electrochemical oxidation mediated by chlorine/hypochlorite was studied for textile industry effluents by several investigators. Vlyssides and Israilides [17] studied the electrochemical degradation of textile dye and finishing wastewater using Ti/Pt anode. At the end of 40 min of elec-

trolysis, there was 92% COD, 92.2% BOD and 94% color reduction with energy consumption of 44 kWh/kg of COD removal. Szyrkowicz et al. [18] conducted experiments using seven different electrode materials for the degradation of disperse dyes. The best results were obtained in a chloride rich medium under acidic pH using Ti/Pt–Ir anode. Muthukumar et al. [19] studied the textile wastewater treatment using Ti/RuO₂ anode and reported that a maximum COD reduction was observed at an optimum operating conditions of 80 dm³/h flow rate and 5 A/dm² current density. Recently, boron doped diamond (BDD) anode was studied for dye degradation using sodium sulfate as supporting electrolyte. Degradation of acid orange 7 by electrochemical method using BDD anode showed a complete color removal with more than 90% COD reduction [20]. Similarly, Chen et al. [21] reported a very high COD removal for various dye compounds with high current efficiency using the BDD electrode.

Since the real textile dyeing industry is using different kinds of dyestuffs with varying concentrations, nine dye compounds containing azo, anthraquinone and triazine groups were selected for chlorine mediated electrochemical degradation. Though, sodium sulfate or sodium chloride is the common salts used for the dyeing process, most of the textile processing industries are using sodium chloride due to less cost. Hence, it was decided to study with sodium chloride as supporting electrolyte using a titanium based dimensionally stable anode (DSA).

2. Materials and methods

Bulk oxidation of reactive dyes was carried out using an undivided electrochemical cell in a galvanostatic condition. The anode was a titanium mesh coated with oxides of titanium, ruthenium and iridium available in the commercial market. The cathode was stainless plate. The effective surface area of anode and cathode were 27.7 and 50 cm², respectively. The electrodes were positioned vertically and parallel to each other with an inter-electrode gap of 10 mm in a 1 L reactive dye solution. A dc power supply was used as the source of constant electric current for the experiments (UP-3010S model, Unicorn Co. Limited, South Korea). To enhance the mass transport and to maintain a uniform concentration of the electrolyte, the reactor solution was constantly stirred at 300 rpm using a magnetic stirrer. The temperature of the reactor was maintained constantly using an external water re-circulation system. A schematic illustration of the experimental setup is shown in Fig. 1.

The temperature and pH values were measured using Hanna Instruments pH meter equipped with a temperature sensor. The initial pH of the dye solution was set appropriately using dilute solutions of either sodium hydroxide or sulfuric acid. UV–visible spectra during the degradation of dyes were recorded between 200 and 800 nm using a scanning UV–visible spectrophotometer (Jasco model V-530, Japan). The visible color removals for the mixed reactive dyes were measured at optimum absorption wavelength of 516 nm in order to study the effects of various operating parameters. The color removals during the experiments with individual dye compound were measured at their optimum visible absorption wavelength. Samples

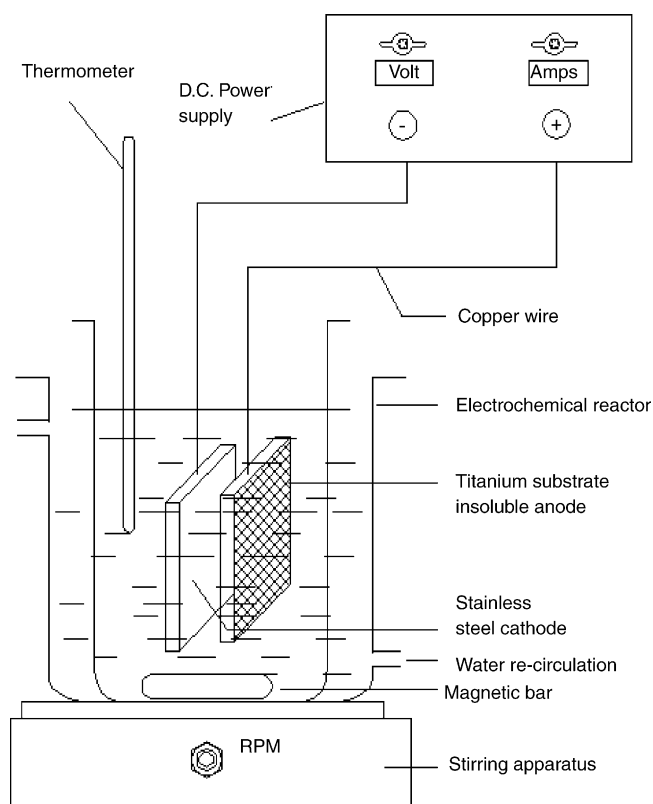


Fig. 1. Experimental setup of electrochemical reactor.

were diluted using distilled water if the absorbance exceeded the range of calibration curve. The total organic carbon (TOC) of the initial and the electrolyzed solution was determined using TOC analyzer (Shimadzu, model TOC 5000A, Japan). The instrument was operated at 680 °C furnace temperature and 50 μ L sample injection. The chemical oxygen demand during the electrolysis was determined by an open reflux, dichromate titrimetric method [22]. All the reactive dyes were obtained from a commercial manufacturing company (Rifa Co. Limited, South Korea). The detailed chemical structure and other related information of dyes were presented in Fig. 2(a–i). The dyes were used for experiments as such without any purification.

The individual dye compounds (100 mg/L) were studied for complete color removal with a supporting electrolyte concentration of 1.5 g/L sodium chloride and a current density of 36.1 mA/cm², which was equal to 1 A current input. Samples were drawn at convenient time intervals during the course of electrolysis and the COD determinations were done up to 120 min of electrolysis. The TOC values were determined for the samples of initial and also at the end of 120 min of electrolysis. The energy required to remove color (>95%) and COD (up to 120 min of electrolysis) was calculated and expressed as kWh. The average cell voltage during the course of electrolysis was taken for the calculation of energy consumption. A detailed investigation was conducted for the mixture of reactive dye compounds to study the effect of various operating variables. The mixed dye solution 200 mg/L containing the following composition: reactive red 120 = 25 mg, reactive red 141 = 20 mg, reactive red 198 = 20 mg, reactive blue 49 = 25 mg,

reactive blue 19 = 20 mg, reactive orange 16 = 20 mg, reactive black 5 = 25 mg, reactive yellow 84 = 20 mg, reactive yellow 15 = 25 mg.

3. Results and discussion

Since the textile industry uses different dyes to obtain a desired color, we have studied various classes of reactive dyes for degradation studies. The details of various reactive dyes used in the present investigation are summarized in Fig. 2(a–i) with chemical structure along with the UV–vis spectra recorded during the various stages of electrolysis. It is evident from the spectra that all classes of dye compounds undergo de-colorization by chlorine-mediated electrochemical oxidation. In the indirect electrochemical oxidation process, the color or COD removal rate is proportional to the concentration of the dye compound and to the chlorine/hypochlorite concentration because the indirect oxidation is mediated by chlorine/hypochlorite. Therefore, the kinetics for color or COD removal is:

$$\frac{-d[\text{color}]}{dt} = k[\text{color}][\text{Cl}_2] \quad \text{or} \quad \frac{-d[\text{COD}]}{dt} = k[\text{COD}][\text{Cl}_2] \quad (5)$$

The electrochemical oxidation involves the application of an electrical current to the dye wastewater containing chloride to convert into chlorine/hypochlorite. The chlorine/hypochlorite oxidizes the dye compound in the bulk solution and then get reduced to chloride ion. The process is then repeated in a catalytic fashion. Therefore, the concentration of chlorine/hypochlorite during the electrolysis is assumed to be a constant, and so Eq. (5) can be written as a pseudo-first-order kinetic equation:

$$\frac{-d[\text{color}]}{dt} = k'[\text{color}] \quad \text{or} \quad \frac{-d[\text{COD}]}{dt} = k'[\text{COD}] \quad (6)$$

The log plots of the color or COD concentration show the plot of rate expression:

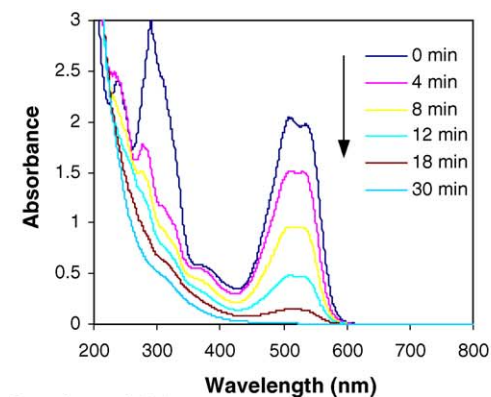
$$\log \left(\frac{[\text{color}]_t}{[\text{color}]_0} \right) = -k't \quad \text{or} \quad \log \left(\frac{[\text{COD}]_t}{[\text{COD}]_0} \right) = -k't \quad (7)$$

The slope of the plot of $\log(C_t/C_0)$ versus time gives the value of rate constant k' (reciprocal min). The rate constant values obtained for the various reactive dyes were presented in Table 1.

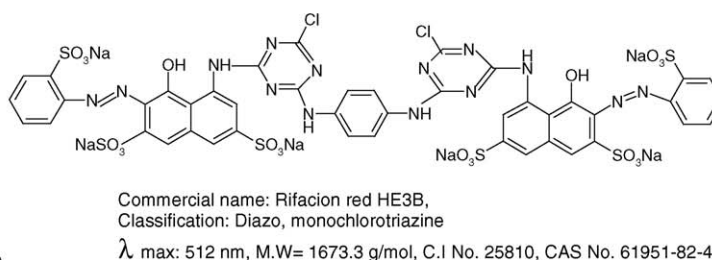
Among the nine dye compounds studied, reactive blue 49 and reactive blue 19 showed shorter electrolysis time for complete color removal with rate constant values of 28.48×10^{-2} and $28.01 \times 10^{-2} \text{ min}^{-1}$, respectively. However, reactive black 5, reactive yellow 15, reactive orange 16 and reactive red 198 dyes showed little longer time for complete de-colorization with a rate constant values of 27.71×10^{-2} , 21.86×10^{-2} , 19.07×10^{-2} and $18.02 \times 10^{-2} \text{ min}^{-1}$, respectively. However, the reactive yellow 84, reactive red 120 and reactive red 141 showed much longer time for de-colorization when compare to all other dyes with rate constant values of 14.26×10^{-2} , 6.32×10^{-2} and $5.92 \times 10^{-2} \text{ min}^{-1}$, respectively. From this study it can be said in general that anthraquinone (RB49, RB19) dyes under goes rapid de-colorization followed by diazo (RB5), monoazo (RY15,

RO16), mono azo triazine (RR198) and diazo triazine (RY84, RR120, RR141). At the same time, the percentage removal of COD and the rate of COD removal do not follow the above order. Hence, it is clear from Table 1 that there is no correlation among the color removal, percentage COD removal, the COD removal rate and the degree of TOC removal. Here, the degree of COD removal is more or less optimum at 120 min of electrolysis for all dye compounds, beyond that the degree of COD removal is less. The reactive red 141 showed the highest degree of COD removal (82.8%) among the other dye compounds though the color removal rate was very less. On the other hand, reactive red

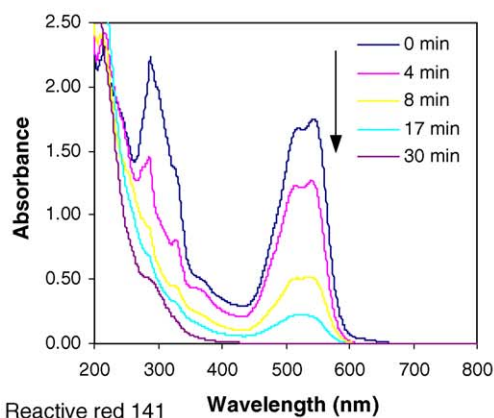
198 showed a lowest degree of COD removal (39.5%) though the color removal rate is comparatively high. The pseudo-first-order rate constant values for COD removals for various dye compounds were between 71×10^{-4} and $19 \times 10^{-4} \text{ min}^{-1}$. Reactive red 141 and reactive yellow 15, respectively, showed the highest (44.7%) and the lowest (11.3%) degree of TOC removals at the end of 120 min of electrolysis among the dyes studied. The energy consumption for color and COD removal is presented (Table 1) for one who is interested in the cost effectiveness of the treatment. The energy consumption is largely depends on the cell voltage during the electrochemical treatment. It is well



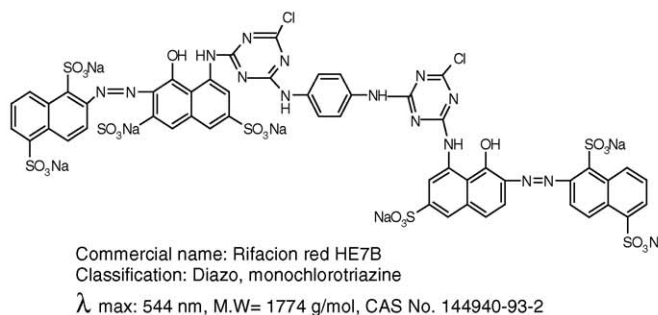
Reactive red 120



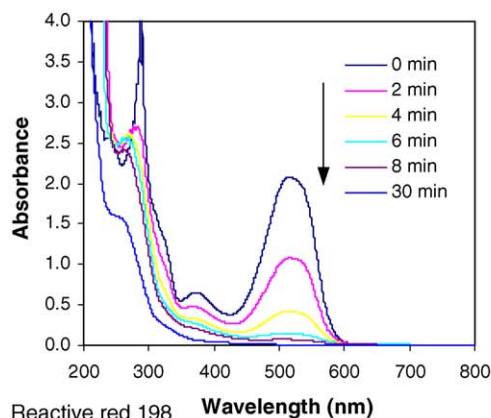
(a)



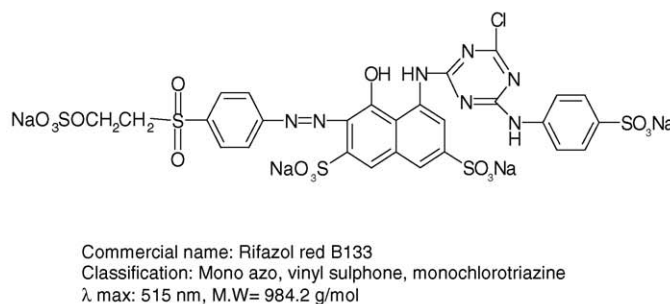
Reactive red 141



(b)

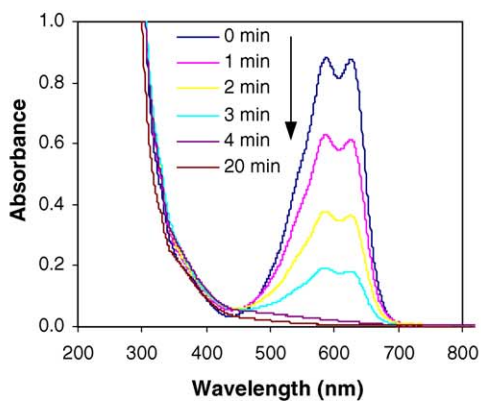


Reactive red 198

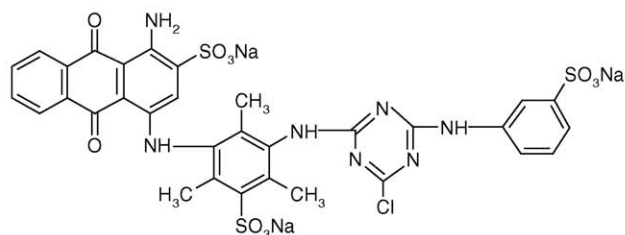


(c)

Fig. 2. (a–i) UV–visible spectra during the electrochemical degradation of various reactive dyes, the chemical structure and other details of dyes.

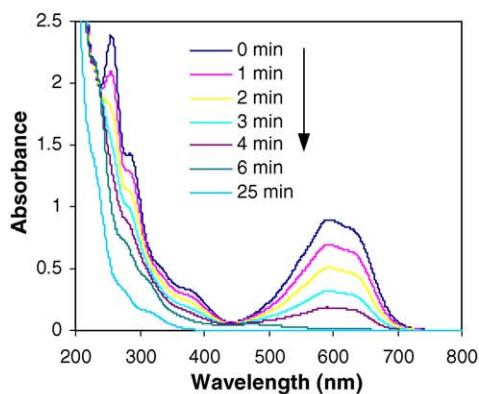


Reactive blue 49

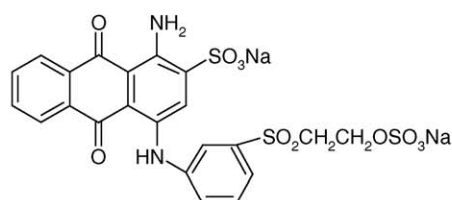


Commercial name: Rifacion blue P-3R
 Classification: Anthraquinone, monochlorotriazine
 λ max: 587 nm, M.W.=882.2 g/mol

(d)

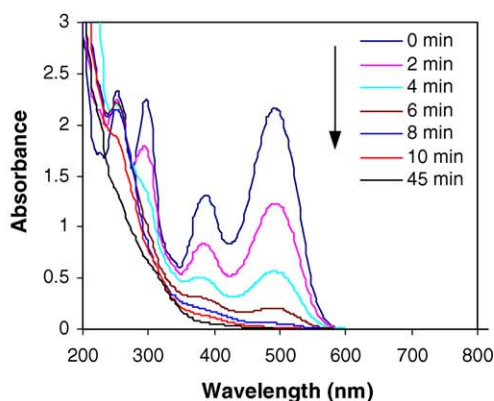


Reactive blue 19

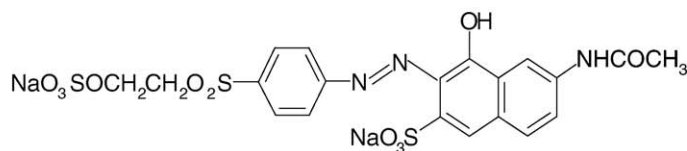


Commercial name: Rifazol Brill. Blue R special
 Classification: Anthraquinone, vinylsulphone
 λ max: 594 nm, M.W.= 626.6 g/mol, C.I No.61200, CAS No. 2580-78-1

(e)



Reactive orange 16



Commercial name: Rifazol Brill. Orange 3R
 Classification: Mono azo, vinyl sulphone
 λ max: 492 nm, M.W.= 617.5 g/mol, C.I No. 17757, CAS No. 12225-83-1

(f)

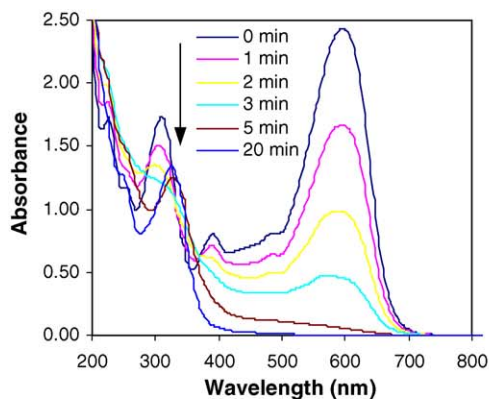
Fig. 2. (Continued)

known that the cell voltage is ultimately depending on the conductivity of the electrolytic solution, which in turn related to the chloride concentration. In the present study, it was considered only very low electrolyte concentration of 1.5 g/L NaCl. However, the real textile industry wastewater contains high concentration of NaCl between 5 and 12 g/L for combined effluent and about 15–40 g/L for the segregated reactive dye bath wastewater. Hence the energy values presented here is at the higher side.

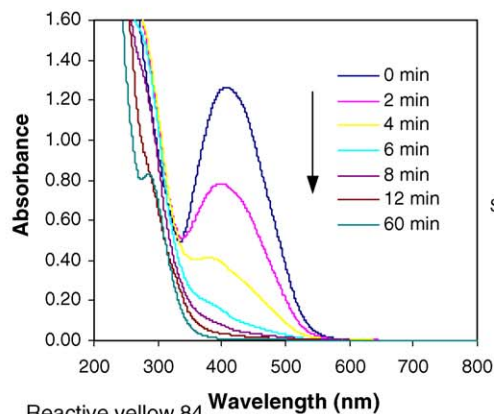
The effect of various operating variables of electrochemical oxidation was studied with mixture of dye solution. The effect of initial pH on the color removal was presented in Fig. 3. It is

clear that varying the initial pH from 4.3 to 9.4 does not have significant influence on the color removal. Many investigators explained this fact that the generation of chlorine/hypochlorite is not depending on the initial pH conditions. The generation of chlorine is more or less same under the fixed current density, irrespective of the initial pH values. This observation is similar to that of electrochemical treatment of land fill leachate [23], tannery wastewater [24], textile wastewater [25], cresols [26] and phenol [27].

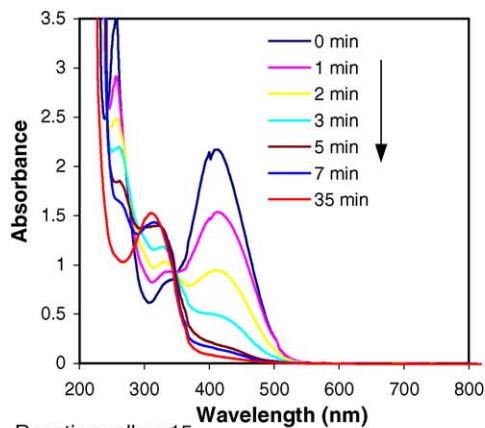
Fig. 4 presents the color removal at different operating temperatures. It is clear that increasing the reaction temperature



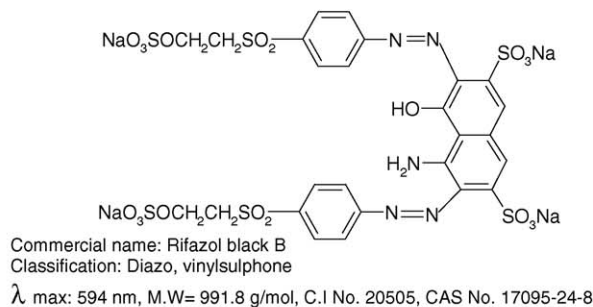
Reactive black 5



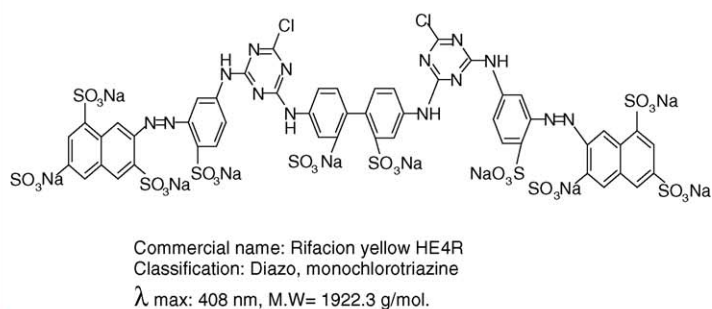
Reactive yellow 84



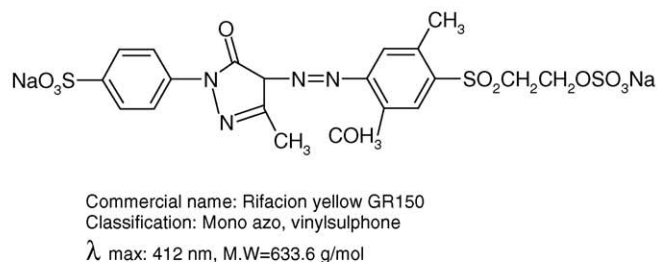
Reactive yellow 15



(g)



(h)

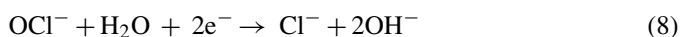


(i)

Fig. 2. (Continued).

decreases the color removal. Under fixed operating conditions, with an initial concentration of 200 mg/L, the final color concentrations were 2.4, 2.4, 4.6, 12.6 and 50.2 mg/L, respectively, for 20, 25, 32, 46 and 60 °C reaction temperatures at the end of 20 min of electrolysis. It is clear that the rate of removal of color is less significant between 20 and 32 °C, however the reaction temperature above 30 °C showed a marked decrease in the rate of color removal. At high temperatures, the mass transport controlled reduction of hypochlorite may be the reason for a decreased de-colorization according to the following cathodic

loss reaction [28]:



Another reason may be the less solubility of Cl_2 gas while increasing the temperature of the solution.

Fig. 5(a and b) presents the color removal during the electrochemical oxidation at different current densities. It is clear and well known that increasing current density increases the rate of color removal due to increased generation of

Table 1
Summary of electrochemical degradation of reactive dyes (conditions: initial pH 6.2–6.5, reaction temperature = 25 °C, NaCl = 1.5 g/L, current input = 1 A, dye concentration = 100 mg/L)

C.I. name of the dye	Color removal (>95%)		COD removal (time of electrolysis = 120 min)					TOC removal (time of electrolysis = 120 min)					
	Time of electrolysis (min)	Rate constant, k (10^{-2} min^{-1})	r^2	Energy consumption (kWh/m ³)	Final COD (mg/L)	Initial COD (mg/L)	COD removal (%)	Rate constant k (10^{-4} min^{-1})	r^2	Energy consumption (kWh/kg of COD)	Initial TOC (mg/L)	Final TOC (mg/L)	TOC removal (%)
Reactive red 120	21	6.32	0.93	2.695	23	72	68.1	45	0.92	316	23.6	15.0	36.4
Reactive red 141	28	5.92	0.99	3.453	16	93	82.8	71	0.91	192	19.0	10.5	44.7
Reactive red 198	8	18.02	0.99	0.973	46	76	39.5	19	0.95	487	24.6	21.5	12.6
Reactive blue 49	4	28.48	0.86	0.500	48	100	52.0	30	0.81	288	33.8	27.8	17.8
Reactive blue 19	5	28.01	0.93	0.633	36	77	53.3	31	0.95	366	24.7	19.2	22.2
Reactive orange 16	7	19.07	0.96	0.863	24	88	72.7	42	0.95	231	26.7	21.5	19.5
Reactive black 5	5	27.71	0.96	0.600	28	60	53.3	26	0.92	450	21.9	16.2	26.0
Reactive yellow 84	12	14.26	0.97	1.480	21	58	63.8	43	0.84	400	14.4	11.0	23.6
Reactive yellow 15	6	21.86	0.98	0.740	62	116	46.6	24	0.89	274	29.1	25.8	11.3

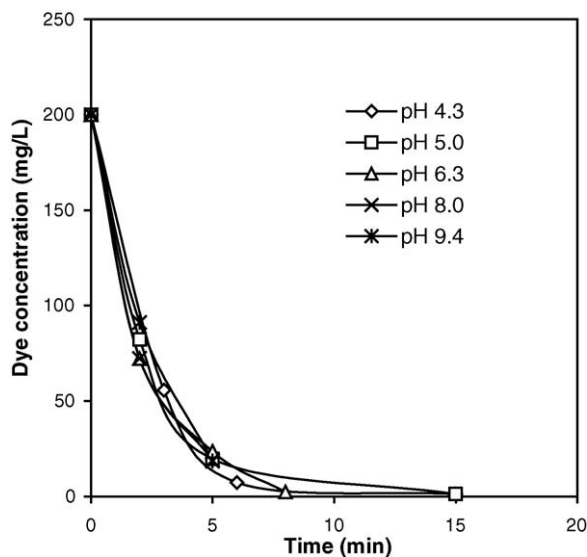


Fig. 3. Effect of initial pH on the degradation of mixed reactive dyes (conditions: reaction temperature = 30 °C, NaCl = 4 g/L, current input = 2 A, dye concentration = 200 mg/L).

chlorine/hypochlorite under galvanostatic conditions. However, under well mass transport conditions and chloride rich medium (here we have used 4 g/L NaCl), there is not much significant variation in the color removal when a same amount of charge passed (Fig. 5(b)). Because, the reactor performance depends on mass, charge or mixed control. Though the current density showed an insignificant variation, the energy consumption at higher current density may be higher because of increase of cell voltage at higher current densities. But, operating at lower current density requires more electrolysis time. In the present study, the time required for the de-colorization of mixed dye under various current densities were 50, 20, 15, 8, 7 and 6 min, respectively, for 18.1 (0.5 A), 36.1 (1.0 A), 54.2 (1.5 A), 72.2 (2.0

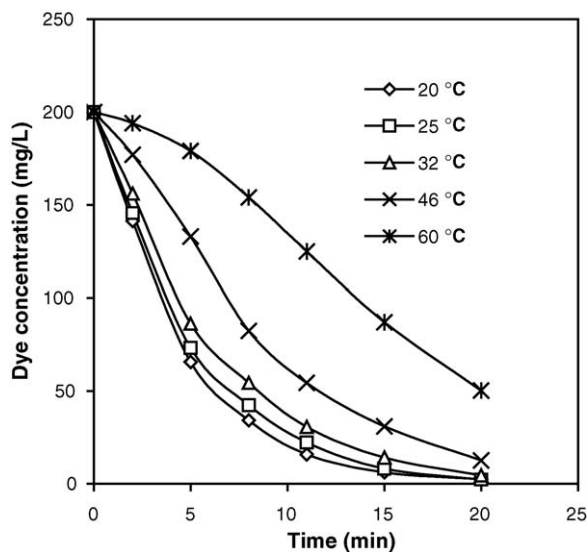


Fig. 4. Effect of reaction temperature on the degradation of mixed reactive dyes (conditions: initial pH 6.5, NaCl = 4 g/L, current input = 1 A, dye concentration = 200 mg/L).

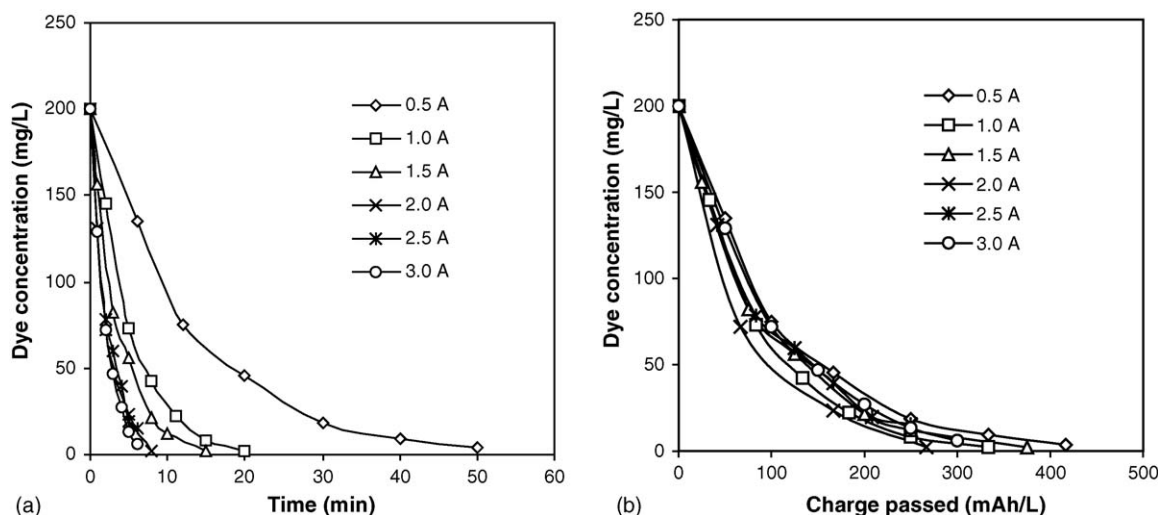


Fig. 5. (a and b) Effect of current density on the degradation of mixed reactive dyes (conditions: initial pH 6.5, reaction temperature = 25 °C, NaCl = 4 g/L, concentration = 200 mg/L).

A), 90.3 (2.5 A), 108.3 (3.0 A) mA/cm². Therefore, choosing an optimum current density by considering a shorter reaction time with a maximum pollutant removal is essential for the scaling up of the electrochemical process in order to reduce the operating costs [19,26].

Fig. 6 presents the effect of NaCl concentration under fixed current density and dye concentration. It is clear that increasing chloride concentration decreases the reaction time for the de-colorization. The time required for the de-colorization is 27, 15, 11, and 8, 8 min, respectively, for 1, 2, 3, 4 and 5 g/L NaCl concentrations. Hence, the optimum sodium chloride concentration for the present experimental condition is 4 g/L. The reason is that more amount of chlorine/hypochlorite will be generated while increasing the chloride concentration due to increased mass transport of chloride ions to the anode surface. Fig. 7 presents the effect of dye concentration on the electrochemical degradation.

The time required for the de-colorization is proportionally reduced if the concentration of dye is proportionally increased. For example, time required for the de-colorization of 100 mg/L dye is 6 min, at the same time; it is 18 min for 500 mg/L dye concentration. Hence, operating at higher concentration of dyes may reduce the energetic cost of the treatment process. Fig. 8 presents the UV–visible spectra during the electrochemical degradation of mixed dye compounds. A broad visible color absorption spectra between 380 and 700 nm was completely removed at the end of 8 min of electrolysis, however, the absorption in the UV region was not removed which indicates the presence of intermediate compounds after the color removal. Fig. 9 presents the electrochemical degradation of 200 mg/L dye under optimum operating conditions. A complete de-colorization with 73.5% COD and 32.8% TOC removals were obtained at the end of 120 min of electrolysis. The energy consumption for color and COD

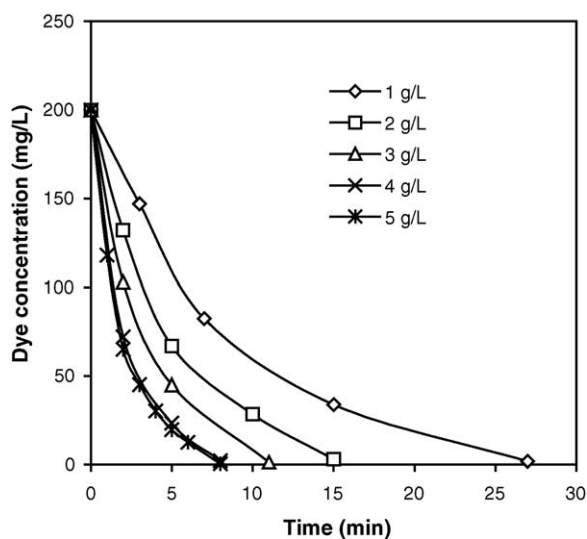


Fig. 6. Effect of NaCl concentration on the degradation of mixed reactive dyes (conditions: initial pH 6.5, reaction temperature = 25 °C, current input = 2 A, dye concentration = 200 mg/L).

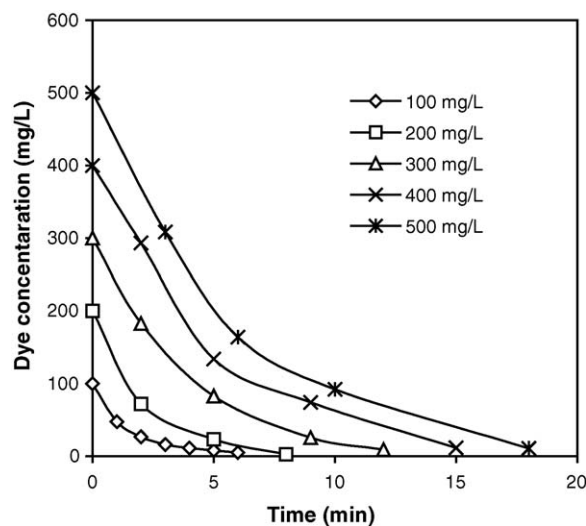


Fig. 7. Effect of initial concentration on the degradation of mixed reactive dyes (conditions: initial pH 6.5, reaction temperature = 25 °C, NaCl = 4 g/L, current input = 2 A).

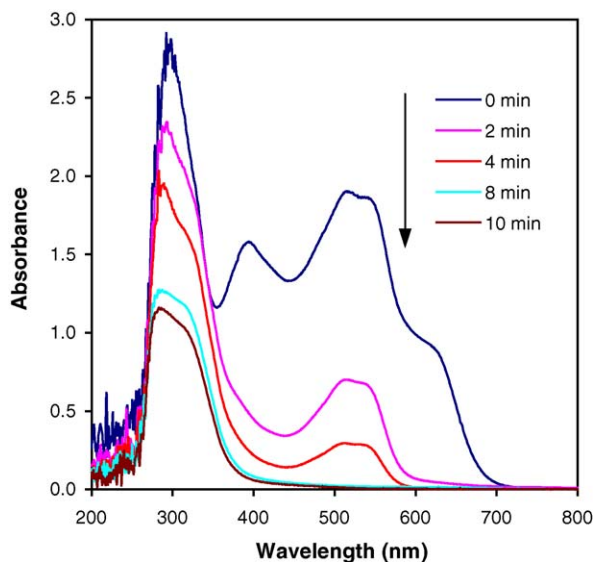


Fig. 8. UV-vis spectra during the electrochemical oxidation of mixed reactive dyes (conditions: initial pH 6.5, reaction temperature = 25 °C, NaCl = 4 g/L, current input = 2 A, dye concentration = 200 mg/L).

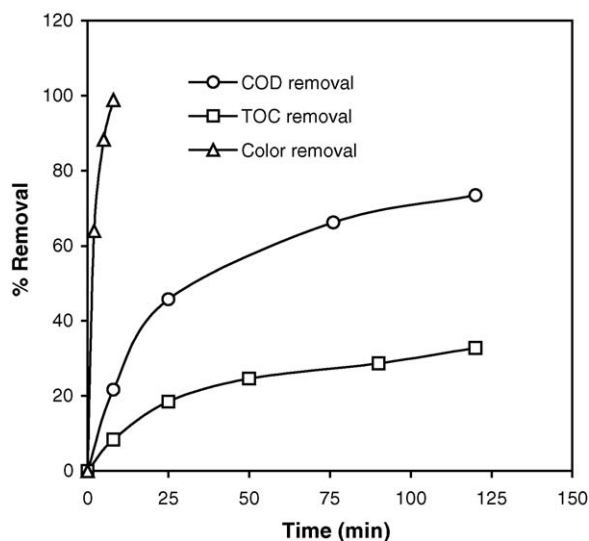


Fig. 9. Color, COD and TOC removal during the electrochemical degradation of mixed reactive dyes (conditions: initial pH 6.5, reaction temperature = 25 °C, NaCl = 4 g/L, current input = 2 A, dye concentration = 200 mg/L).

removals were 1.65 kWh/m³ and 184 kWh/kg, respectively, for 200 mg/L of mixed dye compounds. The pseudo-first-order rate constant for color and COD removals were 27.7×10^{-2} and $54 \times 10^{-4} \text{ min}^{-1}$, respectively.

4. Conclusion

Based on the present investigation, it can be concluded that all classes of reactive dyes are degraded by chlorine mediated electrochemical oxidation. Pseudo-first-order rates constant were presented for color and COD removal for various reactive dyes. The energy values given in this paper is only to get some basic idea. Since, the real textile dyeing wastewater contains higher concentrations of chloride than the present study, the energetic

costs will be definitely be lowered when apply to highly concentrated segregated dye bath during the large-scale operations. The important limitation of the process is the formation of chlorinated organic compounds since the electrochemical oxidation is mediated by active chlorine. Further investigation is required to identify the final compounds present in the solution after the electrochemical oxidation and their toxicity level to the living organisms. Hence it is recommended the activated carbon polishing treatment for the removal of chlorinated organic compounds before the discharge of treated water.

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