

## Photocatalytic and electrochemical combined treatment of textile wash water

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### Abstract

Various chemical and physical processes for treatment of textile effluent are not destructive but they only transfer the contaminants from one form to another. The presence of high concentration of organic dye and total dissolved solids (TDS) in the effluent that are not removed by biological treatment must be eliminated by an alternative method to the conventional ones is the advanced oxidation process (AOP). A procion blue dye effluent was treated by photo and electrochemical oxidation process as well as by combining photocatalytic degradation using TiO<sub>2</sub> suspensions. Chemical oxygen demand (COD) and colour removal can be used to follow the degradation of the organic pollutant. The effects of pH, current density, flow rate of effluent that passes into the reactor and supporting electrolyte were studied. Comparative studies were carried out on photocatalytic and electrochemical process to degrade the procion blue. The maximum COD reduction and colour removal were 96 and 100%, respectively. Photodegradation efficiency of dye was high when photolysis was carried out in the presence of 40 mg/l of TiO<sub>2</sub>. © 2007 Elsevier B.V. All rights reserved.

*Keywords:* Electrooxidation; Photocatalytic; Degradation; Titanium oxide; Dye

### 1. Introduction

Textile industry can be classified into three categories, viz. cotton, wool and synthetic fibers depending upon the raw material used. Generation of wastewater from a textile dye industry is due to the processing operations employed during the conversion of fiber to textile fabric. It was estimated that 1–15% of dye was lost during dyeing process hence these textile industries produce large quantities of highly coloured effluents, which are generally toxic and resistant to destructive action by normal treatment methods. With the new and more stringent environmental policies, the textile industry is bound to face the daunting challenges of improving its conventional system of management and control of its effluent discharge.

The carcinogenic nature of these dyes and their precursors pose an environmental threat [1–3]. In the process industries, the cotton yarns are dyed using procion blue reactive dyes. In textile industry this particular dye is obtained from the combination of four different dyes such as reactive black, reactive green,

reactive navy blue and reactive yellow. About 60% of reactive dyes applied on to the cotton fabrics and yarn is hydrolyzed and discharged as the effluent. The dye house releases two types of wastewater, viz., dye bath water and rinse water. The rinse water mainly consists of complex dyestuff and various intermediate complexes. It was noticed that in a typical factory the effluent from the dye bath had the COD 5000–6000, TDS 52,000, SS 2000 mg/l and pH 9. After dyeing, the fabrics are washed with water to remove the excess dye present in the fabrics by rinsing. The wastewater generated due to this operation is commonly called as ‘wash water’ having the value of COD 400–860, TS 4000, TDS 3200 mg/l and pH 8. The environmental pollution due to dye bath water is very high. The treatment of dye bath water is also very tedious when compared to wash water.

Various chemical and physical processes such as chemical precipitation methods and separation of pollutants, coagulation, electro coagulation and elimination by adsorption on activated carbon, etc., are not destructive but they only transfer the contaminants from one form to another, therefore, a new and different kind of pollution problem is being faced which in turn calls for further treatment [4–6]. In the recent years, an alternative method to the conventional ones is the advanced oxidation pro-

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cess (AOP) based on the generation of very reactive species such as hydroxyl radicals that oxidize a broad range of organic pollutants non-selectively and quickly [7,8].

The photocatalytic oxidation of organic pollutants (advanced oxidation process) has recently received much attention. This is an attractive method to destroy a variety of toxic, recalcitrant organic pollutants, both aliphatic and aromatic compounds in wastewater. A particular attention has been directed towards heterogeneous photocatalytic degradation technique, which makes use of suitable semiconductor, irradiated by a light source whose energy is higher than or at least equal to their band gap. Titanium dioxide has been the most extensively utilized as photocatalyst, due to its high activity together with its chemically non-photo corrosives and inert nature.

Advanced oxidation process like photocatalysis system which includes a combination of semiconductor (e.g.,  $\text{TiO}_2$ , ZnO, CdS,  $\text{Fe}_2\text{O}_3$  and ZnS) and UV light [9]. Due to a faster electro less transfer to molecular oxygen,  $\text{TiO}_2$  is found to be more efficient for photocatalytic degradation of pollutants [10]. However, widespread use of  $\text{TiO}_2$  and platinum catalyst is uneconomic for large-scale water treatment operation.

Photocatalytic reaction occurs when charge separation is induced in a large band gap semiconductor by excitation with ultraviolet radiation [9–12]. The appeal of this technology is the prospect of complete mineralization of the pollutants into pollution free compounds to environment in addition to the abundance and relatively low cost, chemically stable and non-toxic nature of the catalyst. However, the practical application of this technology has been limited due to its low photocatalytic efficiency [11].

In this paper, to augment the overall efficiency of the process, a study of photocatalytic phenomena in combination with potentiality of  $\text{Ti/TiO}_2/\text{RuO}_2$ -coated anode in the electrolysis process is investigated. Efficiencies of photocatalysis, electrochemical and photo and electrochemical treatments were compared for procion blue abatement and COD reduction. The effect of various experimental parameters such as pH, concentration of supporting electrolyte, current densities and photocatalyst concentration on the degradation efficiency of the effluent has also been studied. The result showed that combined photocatalytic and electrochemical process could be efficiently used to degrade the procion blue up to 98 and 100% removal of colour. The degradation efficiency was also increased with increase of current density and concentration of NaCl. Photodegradation efficiency of dye was small when photolysis was carried out in the absence of  $\text{TiO}_2$ .

## 2. Materials and methods

### 2.1. Materials

Procion blue dye,  $\text{TiO}_2$  (Anatase form),  $\text{H}_2\text{SO}_4$ , NaOH, NaCl and  $\text{Na}_2\text{CO}_3$  were of laboratory reagent grade and used without further purification. Synthetic effluent was prepared from procion blue (a commercially available Reactive Blue dye). The colour index of the dye was 61211 CI Reactive Blue. It con-

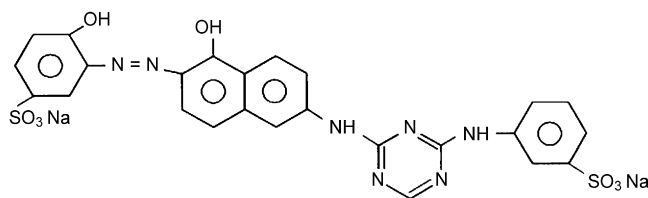


Fig. 1. Structure of procion blue.

tains one chromogenic system. The structure of dye is shown in Fig. 1.

### 2.2. Apparatus

The schematic diagram of experimental setup is shown in Fig. 2, which consists of the following four parts.

#### 2.2.1. Solution flow part

The effluent flow part consists of a reservoir (1), double head peristaltic pump (2), thin film photo reactor (3), electrochemical flow reactor (4) and for flow of the effluent 4 mm silicone tubes were used to interconnect them. The effluent flow was effected by means of a batch recirculation system. The effluent from the reservoir is passed at required flow rate to photo reactor on adjusting the rpm of peristaltic pump, the effluent flows down as thin film on the wall of the photo reactor and reaches the electrolytic cell and from the cell, the effluent is pumped using the second head of the peristaltic pump back to the reservoir.

#### 2.2.2. The current flow part

It consists of a multi-output dc regulated power supply (5) together with an ammeter and voltmeter connected to electrolytic flow cell (4). The main component of the experimental setup is electrochemical flow cell, whose design is based on plate and frame, filter press type arrangement. The electrochemical

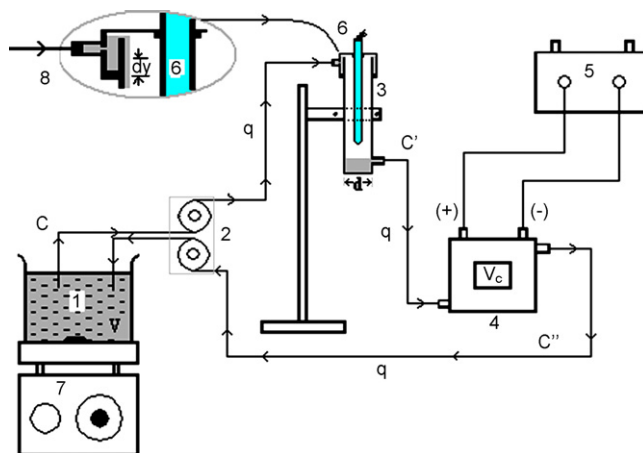


Fig. 2. Experimental setup of photo-electrochemical treatment process: (1) reservoir containing synthetic effluent, (2) peristaltic pump, (3) photocatalytic reactor, (4) electrochemical flow cell with  $\text{Ti/RuO}_2$ -coated expanded mesh anode and stainless steel cathode, (5) dc regulated power supply (0–2 A, 0–30 V), (6) UV lamp (6 W), (7) magnetic stirrer and (8) enlarged view for depicting falling thin film.

reactor consists of titanium expanded mesh anode coated with  $\text{TiO}_2/\text{RuO}_2$  and has an area of  $0.4 \text{ dm}^2$  and the stainless steel cathode of size  $70 \text{ mm} \times 70 \text{ mm} \times 1 \text{ mm}$  is fixed in a PVC frame with gaskets. The reactor holdup is 130 ml. Necessary provisions are made for inlet of the effluent into the reactor as well as for discharge of the effluent from the outlet of reactor.

### 2.2.3. UV irradiation part

The light flow part consists of UV lamp (6 W), the light sources with a photo reactor (3). The thin film photo reactor comprises a titanium cylindrical container of diameter 50 mm and height of 270 mm. The inside wall of the reactor is coated with  $\text{RuO}_2/\text{TiO}_2$  catalytically active immobilized layer of about  $10 \mu$  thickness by thermal decomposition technique [12] which consisted of the following steps: dissolution in isopropanol of  $\text{RuCl}_3$ ; varnish application on the pre-treated titanium base; drying at  $80^\circ\text{C}$ ; thermal decomposition at  $500^\circ\text{C}$ ; cooling and repeating the above operation till we get the required layer thickness, finally post-heat treat for 2 h at  $500^\circ\text{C}$ .

In order to store and allow the effluent along inside walls of the reactor a PVC cup is fixed on the top of the container. A pencil type 6 W medium pressure, mercury vapour immersion lamp ( $\lambda = 365 \text{ nm}$ ) of 25 mm diameter and 270 mm height is employed as a source for UV irradiation. Provisions are also made for effluent entry and exit to the photo reactor.

### 2.2.4. Dispersion of $\text{TiO}_2$

This part consists of a magnetic stirrer (7) and the reservoir (1) containing effluent with  $\text{TiO}_2$  in suspension. The volume of the reservoir is 1000 ml.

### 2.3. Analysis of COD

In order to determine the extent of degradation of the effluent chemical oxygen demand (COD) was measured. The COD as the name implies is the oxygen requirement of a sample for oxidation of organic and inorganic matter. COD is generally considered as the oxygen equivalent of the amount of organic matter oxidizable by potassium dichromate. The organic matter of the sample is oxidized with a known excess of potassium dichromate in a 50% sulfuric acid solution. The excess dichromate is titrated with a standard solution of ferrous ammonium sulfate solution. The COD of all samples were determined by the dichromate closed reflux method using Merck Themoreactor TR620.

### 2.4. Determination of concentration of dye

The selection of suitable wavelength in the spectrum can be made during the course of preparing the calibration curve for the unknown samples. The particular wavelength, which provides a maximum absorbance value, will be considered as a best choice of wavelength. Procion blue standard solutions show maximum absorbance at a wavelength of 605 nm. The UV–vis spectra of all the effluent were measured by using a spectrophotometer Spectroquant NOVA 60 at  $\lambda_{\text{max}} = 605 \text{ nm}$ .

A series of standard solutions of procion blue dye (10–50 mg/l) was prepared along with blanks. Using the selected wavelength filter at a time, calibration curves are plotted in terms of absorbance versus concentration and the concentration of actual samples can then be read directly.

Colour removal was calculated by following formula:

$$\% \text{Colour removal} = 100 \frac{[\text{ABS}_0^{\text{M}} - \text{ABS}^{\text{M}}]}{\text{ABS}_0^{\text{M}}} \quad (1)$$

where  $\text{ABS}^{\text{M}}$  is the average of absorbance values at its maximum absorbency value of visible wavelength ( $\lambda_{\text{max}}$ ).  $\text{ABS}_0^{\text{M}}$  and  $\text{ABS}^{\text{M}}$  are the values before and after the degradation process.

## 3. Experimental

The experimental arrangement shown in Fig. 2 includes a setup for photo thin film phenomena, photo slurry process and electrochemical cell for treatment. With the aid of experimental setup the following four different schemes of experiments were conducted. For each experiment of the degradation of procion blue dye, a solution containing known concentration of dye 50 mg/l with the supporting electrolyte, usually with the mixture containing 3 g/l of NaCl and 1.5 g/l of  $\text{Na}_2\text{CO}_3$ , was prepared and it was allowed to equilibrate for 30 min in the darkness, then the prepared sample was transferred to a 1000 ml reservoir. The pH values were adjusted at desired level using dilute NaOH and HCl and thus the pH values were measured with pH meter and it was set at pH 2. The effluent was continuously stirred during the treatment process using a magnetic stirrer. Experiments were carried out under batch recirculation conditions for 7 h with the flow rate of 20 ml/min. The above conditions were fixed unless otherwise stated. COD and colour were determined periodically to know the extent of degradation of the effluent in the reservoir.

Table 1  
Conditions of experiment in each treatment process

Schemes	Dye (mg/l)	pH	Supporting electrolyte (g/l)		Flow rate (ml/min)	CD ( $\text{A}/\text{dm}^2$ )	$\text{TiO}_2$ (mg/l)
			NaCl	$\text{Na}_2\text{CO}_3$			
Photo	50	–	–	–	20	–	–
Electrochemical	50	2	3	1.5	20	2.0	–
Photo and electrochemical	50	2	3	1.5	20	2.0	–
Photocatalytic and electrochemical	50	2	3	1.5	20	2.0	40

### 3.1. Photooxidation

Photooxidation occurs when the effluent is passed through a photo reactor for degradation. In this reactor, the effluent, which contains dye without any TiO<sub>2</sub> suspension, is allowed to flow as thin film along the walls of the reactor. UV lamp is provided inside the reactor for UV irradiation to initiate the reaction. Here effluent was recirculated for further degradation. COD and colour were determined periodically to know the extent of degradation of the effluent in the reservoir. The experiment was conducted as per the conditions shown in Table 1.

### 3.2. Electrochemical oxidation

In this system, the type of degradation that was carried out by electrolysis was without lamp and TiO<sub>2</sub> in the suspension in the effluent. Anode, cathode and supporting electrolyte initiate the degradation with the conditions stated in Table 1. In this system the effluent was allowed into an electrochemical reactor. The effluent was recirculated for further degradation. COD and colour were determined periodically to know the extent of degradation of the effluent in the reservoir.

### 3.3. Photo and electrochemical oxidation

This is the combined system of degradation. In this scheme, the effluent was allowed for treatment first into the photo reactor for photooxidation. The same effluent was sent to the electrochemical reactor for further treatment. In this case both photo and electrochemical oxidation takes place at different flow rate and current density. The effluent was treated at four different current densities 0.5, 1.0, 1.5, 2.0 A/dm<sup>2</sup> as well as with different supporting electrolyte concentrations of 1, 2, 3, 4, 5 g/l of NaCl. The liquid flow rate into the system was varied as 15, 30, 45, 60, 75, 90 ml/min. The experiments were carried out under the conditions given in Table 1.

### 3.4. Photocatalytic and electrochemical oxidation

In the photocatalytic and electrochemical oxidation the suspension of TiO<sub>2</sub> was added in the effluent. TiO<sub>2</sub> acted as photocatalyst and it improves the degradation efficiency. Then the lamp was switched on to initiate the reaction. During irradiation, agitation was maintained to keep the suspension for uniform reaction and was sampled after an appropriate illumination time. The effluent was allowed into photo reactor first and electrochemical reactor next. The efficiency of degradation was studied by varying the amount of TiO<sub>2</sub> in suspension, pH and initial dye concentration. The experiment was conducted with four different amounts of catalyst concentrations in suspension, viz., 20, 30, 40, 50, 60 mg/l and pH from 2 to 12. The same effluent was recirculated for further degradation. The experiments were carried out under the conditions given in Table 1. Further adsorption experiments were also conducted to know the adsorption of dye on TiO<sub>2</sub> catalysts by the increasing the concentration of dye from 5 to 50 mg/l by measuring the absorbance at each concentration.

### 3.5. Theoretical approach

Because of batch recirculation system, the concentration of reactants or products in the reservoir varies with respect time. It is due to photochemical and electrochemical reaction taking place in the respective reactors. In the photo reactor the effluent is allowed to flow as thin film along the walls of the reactor, which is assumed to behave as plug flow reactor whereas the electrochemical reactor is assumed to behave as mixed reactor. Both the reactors can be considered to in steady state.

If  $k'$  is the heterogeneous rate coefficient for the degradation of organic matter in solution by formation of an electron-hole pair in the photo reactor and because the intensity of light and as well as the film thickness are constant, then the rate of degradation of dye depends only on the concentration of dye which can be assumed to be pseudo-first order kinetics. Treating the photo reactor unidimensionally, by the mass balance in the direction of flow along the  $y$ -axis and assuming heterogeneous pseudo-first order kinetics, the concentration of dye the degradation when leaving the photo reactor active volume,  $AL$  is given as (Fig. 2)

$$C' = C \exp \left[ -\frac{k'aAL}{q} \right] \quad (2)$$

where  $q$  is the volumetric flow rate,  $A$  the cross-section area across the flow,  $a$  the specific reaction surface area of the photo reactor ( $a = \pi dL/AL$ ),  $C$  the concentration of the dye at the inlet of the reactor and  $C'$  is the concentration at the outlet of the reactor.

As the same effluent was being passed to the electrochemical reactor, assuming heterogeneous pseudo-first order kinetic the concentration of dye the degradation when leaving the electrochemical reactor, is given as

$$C'' = C' \left[ \frac{1}{1 + k''a'(V_c/q)} \right] \quad (3a)$$

$$C'' = C \exp \left[ \frac{k'aAL}{q} \right] \left[ \frac{1}{1 + k''a'(V_c/q)} \right] \quad (3b)$$

where  $V_c$  is the volume of electrolytic cell,  $A'$  the anodic area of electrochemical reactor and  $a'$  the specific electrode surface area of the electrochemical reactor ( $A'/V_c$ ),  $C'$  the concentration of the dye at the inlet of the electro chemical reactor,  $C''$  the concentration at the outlet of the electro chemical reactor and  $k''$  is the rate coefficient for electrooxidation of dye in presence of chloride and which has been proposed and that occurs through the cycle chloride–chlorine–hypochlorite–chloride [12] in electrochemical reactor.

In a batch recirculation, if the reactors volumes are insignificant compared with reservoir inventory solution volume  $V$ , the mass balance can be written as

$$V \frac{dC}{dt} = qC'' - qC \quad (4)$$

Table 2  
K values for various photo-treatment processes

Schemes	$K \times 10^{4+}$ ( $\text{min}^{-1}$ )	
	Initial	End
Photo	25	60
Electrochemical	20	4
Photo and electrochemical	20	8
Photocatalytic and electrochemical	20	6

Substituting for  $C''$  from the above and the solution is obtained as

$$C = C_0 \exp \left[ - \left( \frac{qt}{V} \right) \left\{ \frac{1}{1 + k''a'(V_c/q)} \right\} \exp \left( \frac{-k'aAL}{q} \right) \right] \quad (5)$$

and defining

$$K = \frac{q}{V} \left\{ \frac{1}{1 + k''a'(V_c/q)} \right\} \exp \left[ \frac{-k'aAL}{q} \right] \quad (6)$$

then the expression reduces to

$$C = C_0 \exp\{-Kt\} \quad (7)$$

where  $C_0$  is the initial concentration of dye,  $V$  the reservoir volume and the plot  $\log[\text{COD}]$  versus time for procion blue was linear assuming that the degradation reaction approximately follows the first order kinetics. The constant  $K$  was estimated from the slope of the  $\log[\text{COD}]$  versus time plot and presented in Table 2. It is to be noted that  $K$  is an implicit value. The individual values of rate constants can be computed.

#### 4. Results and discussion

The effect of the parameter such as flow rate, current density, supporting electrolyte concentration, pH and weight fraction of catalysts  $\text{TiO}_2$ , etc., on rate of removal COD from the effluent was investigated depending upon the processes such as photo, photo-electrochemical and photocatalytic electrochemical.

##### 4.1. Performance of photo, electrochemical, photo-electrochemical, photocatalytic electrochemical processes

In laboratory scale results of experiments conducted under the conditions given in Table 1 are presented in Figs. 3 and 4 to show the performance of various treatment processes such as photo, electrochemical, photo-electrochemical, photocatalytic electrochemical with respect to percentage removal of COD and colour.

It can be seen from Fig. 3 the presence of both  $\text{TiO}_2$  and UV irradiation, the electrochemical treatment process indicates 98% degradation of dye at the irradiation of time of 7 h. The goal of this comparison is not to show which process is more efficient since they are different process and yields are not comparable. However, it is useful to show that when both treatments are simultaneously applied the resulting dye degradation is more

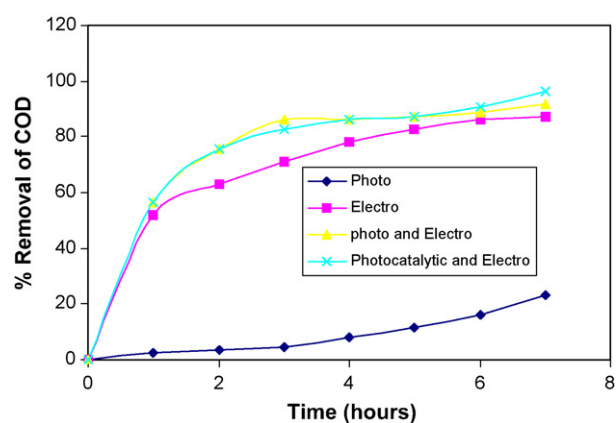


Fig. 3. Performance of various treatment processes.

effective than a single process. The synergic aspect observed by assisting electrolysis with photocatalysis or vice versa is important when one considers the need for degradation of some organic dye pollutants that usually are recalcitrant to electrochemical or heterogeneous photocatalytic treatments.

In the combined system of degradation, the effluent was allowed for treatment first into the photo reactor then the same effluent was sent to the electrochemical reactor to augment for further treatment. The results on effect of various experimental parameters such as current densities, concentration of supporting electrolyte and flow rate on the degradation efficiency of the effluent have been presented in Figs. 5 and 6.

To enumerate the effect of current density on reduction of COD, the current was varied from 0.5 to 2.0  $\text{A}/\text{dm}^2$ . The increase of flow rate reduces the power consumption of the process. This is attributable to the preferential oxidation of easily oxidizable materials. The reduction of COD was directly proportional to

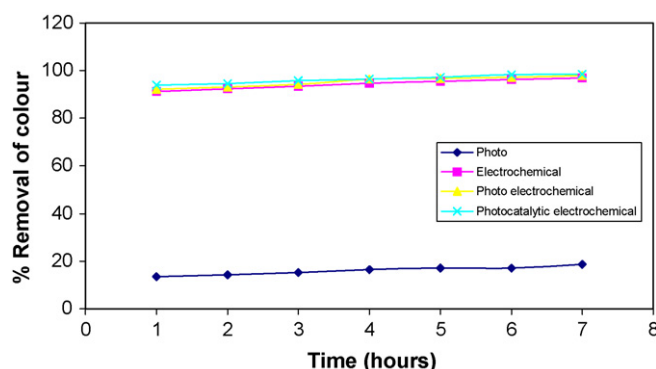


Fig. 4. Comparison of % removal of colour.

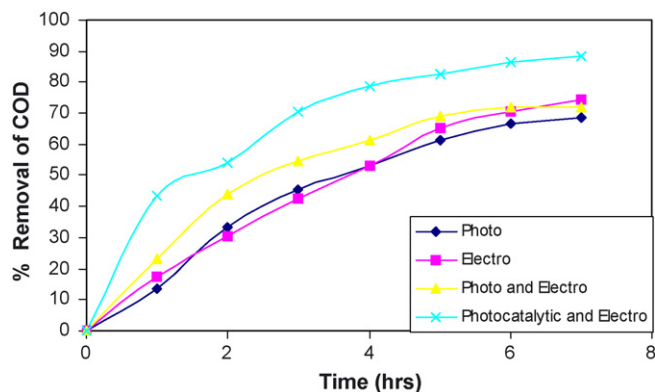


Fig. 5. Effect of current density on the % removal of COD.

the applied current. Murphy et al. [13] reported that pollutant removal efficiency at same charge loading was independent upon the value of current density in a direct electrochemical oxidation treatment process. Fig. 5 shows the effect of current density on the percentage degradation of procion blue dye along with the percentage decrease in COD after photo-electrochemical treatment. An optimum point must be carefully determined giving a faster removal of COD hence the current density  $2 \text{ A/dm}^2$  was chosen as the optimal current density for the degradation of procion blue.

As mass flux depends on the time of operation, the effect of residence time plays an important role in the process. The easily oxidizable parts present in the effluent contribute to the decrease in the COD at low flow rate. The flow rate of effluent in to the reactor is significantly affected by the reactor performance. The decrease in flow rate and increase in current density significantly increase the reduction of COD. Experiments were performed with various flow rates, i.e. 15–90 ml/min. Fig. 6 shows the effect of flow rate on the percentage degradation of procion blue along with the percentage decrease in COD after photo-electrochemical treatment. It is evident from the figure the extent of degradation of procion blue is maximum at 30 ml/min. It is evident from Fig. 5 that the extent of degradation of procion blue increases with time and higher increase in applied current density of  $2 \text{ A/dm}^2$  as compared to the other values. NaCl was used as supporting electrolyte for the electrolysis. The dye is indirectly oxidized by hydroxyl or other oxidant reagent electro

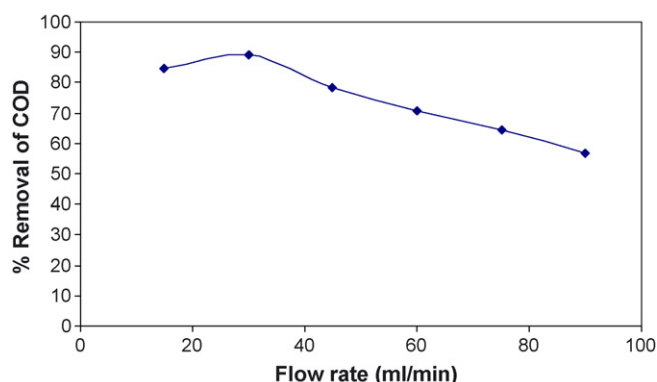


Fig. 6. Effect of flow rate on the % removal of COD.

generated from the electrolyte (mainly  $\text{ClO}^-$  ions in NaCl), reactive species in the background electrolyte. Among all the results, the redox behavior of procion blue in NaCl was good when compared to other supporting electrolytes. Experiments were performed with the different concentrations of NaCl 1–5 g/l and it was found that the photo-electrochemical efficiency increases with an increase in NaCl concentration up to 4 g/l. Among all the results, the redox behavior of procion blue in NaCl was good when compared to other supporting electrolytes.

#### 4.2. UV-vis spectra changes

The changes in the absorption spectra of procion blue solution during the photo-electrochemical process at initial and final stage are shown in Fig. 7. The spectrum of procion blue in the visible region exhibits a main band with a maximum at  $605 \text{ nm}$ . The decrease of adsorption peaks of procion blue at  $\lambda_{\text{max}} = 605 \text{ nm}$  in this figure indicates a rapid degradation of procion blue dye. The decrease is also meaningful with respect to nitrogen double bond of procion blue dye, as the most active site for oxidative attack. Complete discoloration of dye was observed after 7 h under the optimized conditions.

#### 4.3. Photocatalytic electrochemical processes

In the photocatalytic and electrochemical oxidation the suspension of  $\text{TiO}_2$  was added in the effluent, which acts as photocatalyst when the effluent was allowed into photo reactor first and electrochemical reactor next.

The photodegradation efficiency increases with an increase in the amount of photocatalyst, reaches the highest value at a catalyst amount of  $40 \text{ mg/l}$  and then decreases. The most effective decomposition of procion blue was observed with  $40 \text{ mg/l}$  of  $\text{TiO}_2$ . The reason of this observation may be due to the fact that when  $\text{TiO}_2$  adsorbs all procion blue dye molecules, the addition of higher quantities of  $\text{TiO}_2$  would have no effect on the degradation process. Another reason for this may be an increased opacity of the suspension, brought about as a result of excess of  $\text{TiO}_2$  particles [14].

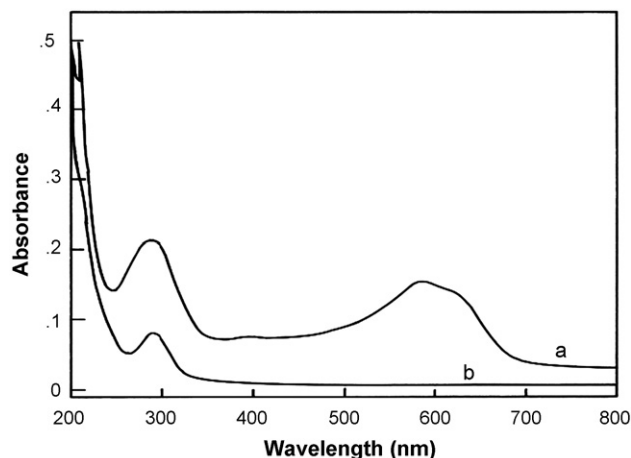


Fig. 7. Spectra of procion blue solution during the photo-electrochemical process at: (a) initial and (b) final stage of treatment.

#### 4.4. Effect of pH and initial concentration of dye on photodegradation

The photodegradation of procion blue dye at different pH values ranges from 2 to 12 was studied and it clearly indicated that the best results were obtained in acidic solution. The pH value is one of the major factors influencing the rate of degradation of some organic compounds in the photocatalytic process [15,16]. It is an important operational variable in actual wastewater treatment. According to the zero point of charge of TiO<sub>2</sub>, its surface is presumably positively charged in acidic solution and negatively charged in alkaline solution [17,18]. Since the dye has a sulfonic acid group in its structure, which is negatively charged, the acidic solution favours adsorption of dye onto the photocatalyst surface, thus the photodegradation efficiency increases. Because the difference between the degree of photodegradation of procion blue, in acidic solution (pH 2) COD removal is 100% and in neutral (pH 7) it is only 20%.

From the effect of initial procion blue concentration on photodegradation efficiency, it was observed that the photodegradation conversion of procion blue decreases with an increase in the initial concentration of procion blue. The presumed reason is that when the initial concentration of dye is increased, more and more dye molecules are adsorbed on the surface of TiO<sub>2</sub>. The large amount of adsorbed dye is thought to have an inhibitive effect on the reaction of dye molecules with photo-generated holes or hydroxyl radicals, because of the lack of any direct contact between them. Once the concentration of dye is increased, it also causes the dye molecules to adsorb light and therefore the photons never reach the photocatalyst surface, thus the photodegradation efficiency decreases.

#### 4.5. Kinetics of various photo-treatment processes

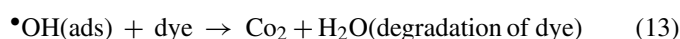
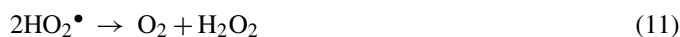
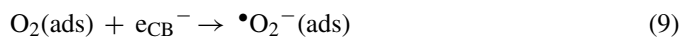
The plot log[COD] versus time for procion blue was linear assuming that the degradation reaction approximately follows the first order kinetics. The constant *K* was estimated from the slope of the log[COD] versus time plot and presented in Table 2. It is to be noted that *K* is an implicit value. The individual values of rate constants can be computed.

The reaction mechanism underlying the oxidation of dye by electrochemical method has been investigated in presence of chloride and several schemes have been proposed and reported that electrooxidation of dye in presence of chloride ions occur through the cycle chloride–chlorine–hypochlorite–chloride [12].

Both UV light and a photocatalyst (a semiconductor) as immobilized thin film or to be in slurry were needed for the degradation of dye.

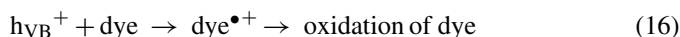
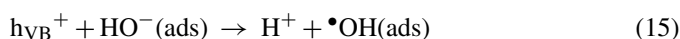
It has been established that semiconductor initiates the degradation of organic matter in solution by formation of an electron–hole pair. When TiO<sub>2</sub> is illuminated with the light of  $\lambda < 365$  nm, electrons are promoted from the valence band to the conduction band of the semiconducting oxide to give electron–hole pairs [19–22]. Electron in conduction band of the catalyst surface reduces oxygen to superoxide anion. This rad-

ical, in the presence of organic scavengers, may form organic peroxides or hydrogen peroxide.



The hydroxyl radical is a powerful oxidizing agent and attacks organic pollutants present at or near the surface of TiO<sub>2</sub>. It causes photooxidation of pollutants according to the above reactions (7)–(12).

The high oxidative potential of the hole in the catalyst permits the direct oxidation of organic matter (dye) to reactive intermediates. Very reactive hydroxyl radicals can also be formed either by the decomposition of water or by the reaction of the hole with OH<sup>−</sup>. The hydroxyl radical is an extremely strong, non-selective oxidant (*E*<sub>0</sub> = +3.06 V), which leads to the partial or complete mineralization of several organic chemicals. The hydroxyl radical is a powerful oxidizing agent and attacks organic pollutants present at or near the surface of TiO<sub>2</sub>. It causes photooxidation of pollutants according to the following reactions (13)–(16)



One of the main purposes of combining electro with photo is not only to increase overall efficiency of organic contaminant removal but also for enhancing discolouration initially by chlorination so that photo process can dominate remaining part of the process.

## 5. Conclusion

The results of the present studies showed that photocatalytic electrochemical process could be efficiently used to degrade the procion blue. Photodegradation efficiency of procion dye was small when photolysis was carried out in the absence of TiO<sub>2</sub> and negligible in the absence of the UV light. The results indicated that the degree of degradation of procion blue was obviously affected by the initial dye concentration, pH and the amount of TiO<sub>2</sub>. It is also evident that the optimal amount of photocatalyst was 40 mg/l, with dye concentration of 20 mg/l. From the COD results reduction that was found to be 96% and colour removal was nearly 100% at the current density 2.0 A/dm<sup>2</sup> for flow rate of 30 ml/m respectively. From the inhibitive effect of dye, it was concluded that hydroxyl radicals were the main reactive species, and also it is believed that the positive holes have also been involved.

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