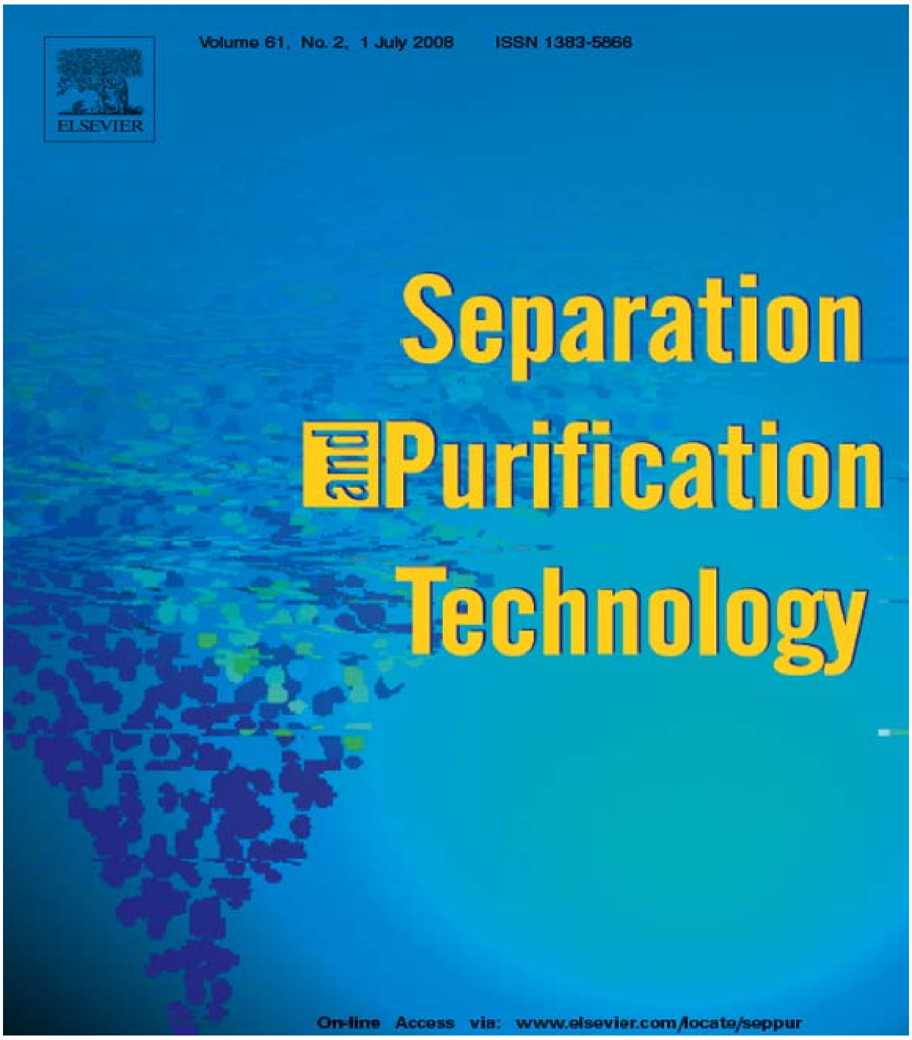
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Electrochemical-assisted photocatalytic degradation of textile washwater

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Abstract

Photocatalytic methods with TiO_2 catalyst were successfully applied to the decomposition of many organic contaminants. In this paper the performance of an electrochemical-assisted photocatalytic degradation of textile washwater containing procion blue dye was investigated. Several operational parameters to achieve optimum efficiency of this electrochemical-assisted photocatalytic degradation system have been done. The main objective was to determine the chemical oxygen demand (COD) and colour removal of the organic pollutant. The effects of pH, current density, supporting electrolyte, the irradiation time and photocatalyst on treatment efficiency were studied. The results showed that electrochemical-assisted photocatalytic process was used efficiently with 90% COD removal and complete colour removal after 7 h treatment.

Keywords: Photocatalytic oxidation; Electrooxidation; Dye; TiO_2; Textile washwater

1. Introduction

Application of electrochemical techniques in wastewater treatment has been acquiring importance in recent years. The first detailed account has been given in [1]. The 1990s photo-assisted reactions have been widely utilized in the degradation of organic pollutants in textile effluents. Their effectiveness results from the fact that the generated hydroxyl radicals ($^{\bullet}OH$) are highly reactive and non-selective such that they are able to degrade many organic pollutants [2–4].

In this field, electrochemical and photochemical technologies may offer an efficient means of controlling pollution as they provide the degradation of organic pollutants without the drawbacks observed in conventional treatments. Electrolysis, heterogeneous photocatalysis, or photo-assisted electrolysis may be used for organics abatement as a main or supplementary treatment. Indeed, electrons and photons are the only reactants added to the treatment process that generates no byproducts at all.

Literature summarizes the principles and mechanisms for the electrochemical treatment of aqueous solutions containing organic compounds with simultaneous oxygen evolution [5,6]. The key for efficient electrolytic treatments strongly based on the anode material choice. High corrosion resistances, physical and chemical stability under high positive potentials are the main requests. When properties as above are required, dimensionally stable anodes (DSA), as those discovered by Beer in the 1970s are the natural candidates [7]. This designation denotes a class of thermally prepared oxide electrodes where a titanium substrate is covered by metallic oxides. Coatings onto titanium include TiO_2, IrO_2, RuO_2, and Ta_2O_5. Combinations, such as TiO_2/RuO_2, are indicated for alkaline medium, while IrO_2/Ta_2O_5 usually shows longer service life in acidic electrolytes. On the other hand, some DSA type oxide electrodes may receive additions of SnO_2 and Sb_2O_5 in concentrations ranging from minor to main components which increase the service life [3].

Heterogeneous photocatalysis as a tool for aqueous effluent treatment is based on the oxidation of an organic pollutant on the surface of a semiconductor catalyst, especially the anatase form of TiO_2 particles. Ioannis et al. and Triantafyllos [8] reviewed recent works in this area and listed the compounds degraded by photocatalysis by various researchers.

Electrochemically assisted photocatalytic process for organics oxidation has been described in the literature demonstrating the dependence of organics mineralization rate on TiO_2 concentration; illumination intensity; organic pollutant concentration; temperature; and pH and type of anions in the solution [9–12]. As the TiO_2 catalyst is kept in suspension during illumination,

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separation of the solid phase must be carried out after treatment. Although, many studies have been reported in an effort to find the most efficient technique, coagulation with aluminum chloride allows the separation and reuse of the TiO_2 catalyst [13].

Immobilization of TiO_2 catalyst on a conductive substrate has been tried. By cycling potential, anatase has been immobilized onto an optically transparent SnO_2 conducting glass electrode for mechanistic studies of oxidation of selected organic compounds and for the determination of oxidation potentials. Sputtering has also been used for the immobilization of TiO_2, thus obtaining different stoichiometries and crystal structures [14]. Although somewhat delayed, it has been noted that the rutile form of TiO_2 may also present photocatalytic properties and, when immobilized on a conductive substrate under an applied bias potential, may have improved its oxidative efficiency due to the electron–hole recombination reduction. Similar photo-assisted processes of electrolysis have been used for the degradation of reactive dyes and for the oxidation of nitride ion and of phenol [15]. This property of the rutile structure of TiO_2 allows the use of some types of DSA oxide electrodes in which this allotropic form of TiO_2 is the major component. Fig. 1 shows the TiO_2-photosensitisation pathway under UV irradiation.

The main objective of this study is the electrochemical-assisted photocatalytic degradation of textile washwater by using TiO_2 as a photocatalyst. This is the new approach of integrating two techniques in which the process consists of electrochemical oxidation and photocatalytic degradation. The two processes concurrently operate to remove the organic pollutants from the textile washwater. The influences of some important variables on the degradation of procion blue are discussed in detail. In this paper the synthetic effluent was prepared from procion blue dye (a commercial reactive blue dye) and NaCl was used as supporting electrolyte. UV irradiation was provided by 6 W pencil type immersion lamp. During the electrolysis on a batch process, COD reduction, colour removal were investigated on TiO_2 as semiconductor at selected electrolyte medium, current densities and pH. Also a study of the potentiality of a titanium anode, coated with $70TiO_2/30RuO_2$, for the electrochemical-assisted photocatalytic process is investigated. In experiments, a synthetic solution containing procion blue dye was used in order to follow the performance of this electrode. Efficiency of electrochemical, photo, electrochemical-assisted photo, and electrochemical-assisted photocatalytic treatments were compared for the procion blue abatement and COD reduction.

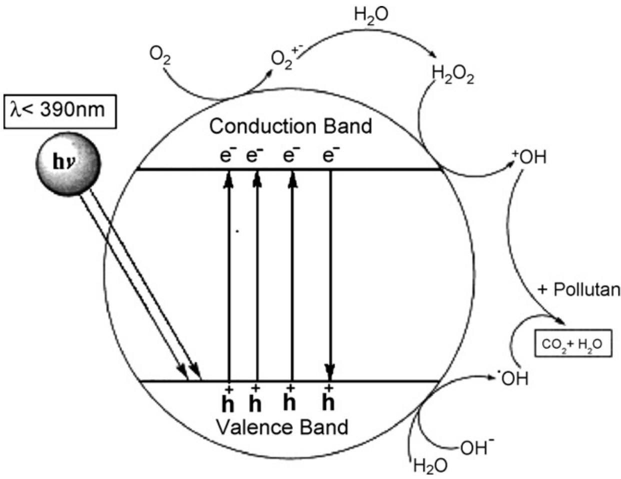

Fig. 1. TiO_2-photosensitisation pathway under UV irradiation.

2. Materials and methods

2.1. Materials

Procion blue dye, TiO_2 (Anatase form), H_2SO_4, NaOH, NaCl and Na_2CO_3 (laboratory grade) were used without further purification. Synthetic effluent was prepared from procion blue (a commercial reactive blue dye). The colour index of the dye was 61211 reactive blue which contains one chromogenic system and λ_{max} is 605 nm. The structure of procion blue is given in Fig. 2.

2.2. Apparatus

The schematic diagram of experimental setup is shown in Fig. 3. This setup consists of four parts. The effluent part which consists of stainless steel cylindrical vessel was used as a reservoir and cathode. The effluent was stored in the cathode with or without the suspension of photocatalyst and it was brought into effect by batch system. The electrical circuit part consists of a multi output dc regulated power supply together with ammeter and voltmeter connected to electrolytic batch reactor. The main component of the experimental setup is photoelectrochemical reactor, whose design was based on cylindrical cell type arrangement. The photoelectrochemical reactor consists of cathode made up of stainless steel cylinder of size 7 cm diameter and 20 cm length and the bottom was closed by a PVC disc with rubber gaskets. In the top of the cathode there is a provision for holding the UV lamp. Anode which is cylindrical in shape of 3.5 cm in diameter and 15 cm long made up of RuO_2/TiO_2 immobilized layer of about 10 μm thickness by thermal decomposition method. Anode is placed inside a cathode and the same was fixed rigidly on a PVC lid with the help of eraldite. This part also consists of a magnetic stirrer to mix the catalyst with the effluent properly. Necessary provisions were made for sampling the effluent during the investigation. The UV irradiation part consists of a pencil type 6 W medium pressure, mercury vapour immersion lamp ($\lambda = 365$ nm) of size 2.5 cm diameter and 27 cm

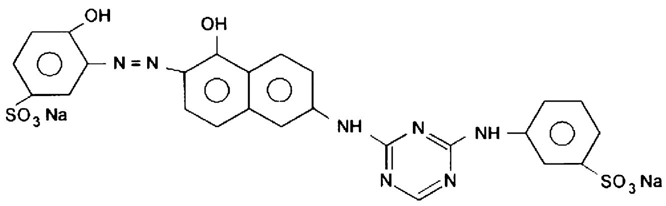

Fig. 2. Structure of procion blue.

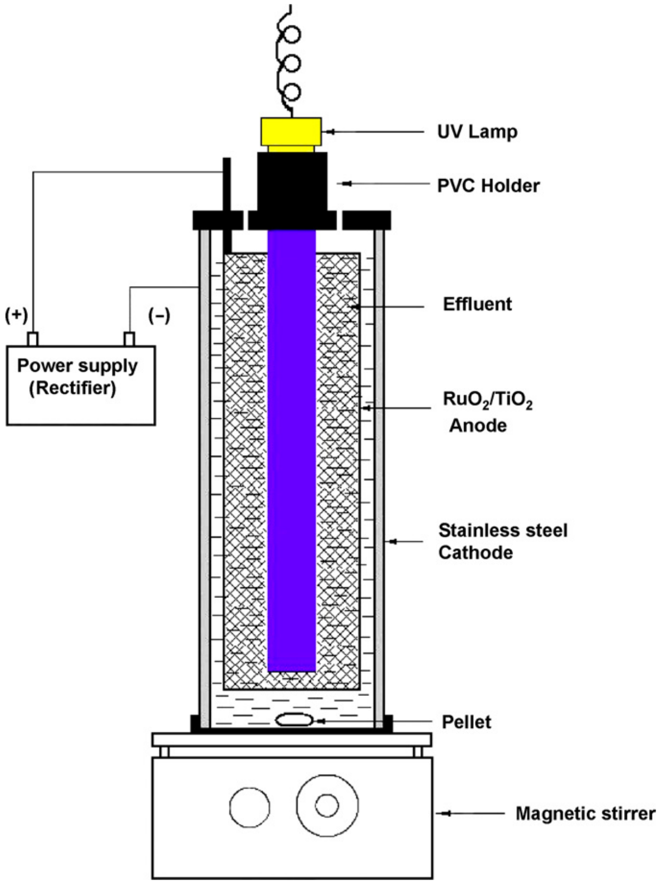

Fig. 3. Experimental setup of electrochemical-assisted photocatalytic treatment process.

height is placed inside the reactor. Dispersion of photocatalyst part consists of a magnetic stirrer and the photocatalytic reactor which contains the effluent along with photocatalysts. The volume of the batch reactor was 700 ml.

2.3. Methods

The experimental setup of electrochemical-assisted photocatalytic treatment of textile wastewater is shown in Fig. 3. 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 0.1 g/l with the supporting electrolyte, usually with the mixture containing 3 g/l of NaCl and 1.5 g/l of Na_2CO_3, was prepared and it was allowed to equilibrate for 30 min in the darkness. The prepared sample was transferred to a photoelectrochemical reactor of volume 700 ml. The pH of the effluent was adjusted to a desired level using dilute NaOH and HCl. The pH values were measured by using pH meter (Dot 491) and it was set at pH 4. The effluent was continuously stirred during the treatment process using a magnetic stirrer. Experiments were carried out under batch conditions for 7 h. The above conditions were fixed unless otherwise stated. COD and colour removal were determined periodically to know the extent of degradation of the effluent. The experiment was conducted as per the conditions shown in Table 1.

2.3.1. Electrochemical oxidation

In this system, the effluent was treated electrochemically without UV lamp and photocatalyst (TiO_2). Anode, cathode and supporting electrolyte initiate the degradation as per the conditions stated in Table 1. In this system, the effluent was allowed into the reactor for the degradation of pollutants by electrolysis at different current densities. Reduction of COD and colour removal were determined periodically to know the extent of degradation of the effluent in the reservoir.

2.3.2. Electrochemical-assisted photooxidation

This is the combined system of both electrochemical and photodegradation. In this scheme, the effluent was allowed to the reactor for electrolysis. In addition to this the effluent was irradiated by a 6 W UV lamp emitting 365 nm wavelength for photooxidation. In the present system the effluent was treated without any suspensions of semiconductor. In this case both photo and electrochemical oxidation takes place simultaneously. The effluent was treated at four different current densities 0.5, 1.0, 1.5, 2.0 A/dm^2 under the conditions given in Table 1.

2.3.3. Electrochemical assisted photocatalytic oxidation

In this electrochemical-assisted photocatalytic oxidation, the suspension of TiO_2 was added in the effluent at different concentration. TiO_2 acted as photocatalyst and improves the degradation efficiency. The lamp was switched on to initiate the reaction. During irradiation, agitation was given by magnetic stirrer to keep the suspension for uniform reaction and samples were collected after an appropriate illumination time. The efficiency of degradation was studied by varying the concentration of catalyst in suspension, pH and initial dye concentration. The experiment was conducted with four different amounts of catalyst concentrations in suspension viz., 35–85 mg/l and three different pH, i.e., 3.5, 6.9 and 9.8. The same effluent was allowed to carryout electrochemical-assisted photocatalytic oxidation for further degradation as per the conditions given in Table 1.

Table 1
Conditions of experiment in each treatment processes

Schemes	Dye (mg/l)	pH	Supporting electrolyte		CD (A/dm^2)	TiO_2 (mg/l)
			NaCl g/l	Na_2CO_3 (g/l)		
Photo	100	–	–	–	–	–
Electrochemical	100	3.5	3	1.5	2.0	–
Electrochemical-assisted photo	100	3.5	3	1.5	2.0	–
Electrochemical-assisted Photocatalytic	100	3.5	3	1.5	2.0	65

2.4. Analysis of COD

To know the extent of degradation of the effluent chemical oxygen demand (COD) was measured according to the standard methods. The COD of all samples were determined by the dichromate closed reflux method using Merck Themoreactor TR620.

2.5. Determination of colour

The selection of suitable wavelength in the spectrum can be made during the course of preparing of 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 $\lambda_{\max} = 605$ nm.

A series of standard solutions of procion blue dye (100–500 mg/l) was prepared along with blanks. Using the selected wavelength filter at a time, calibration curves are plotted and the concentration of actual samples calculated directly.

Colour removal was calculated by following formula:

$$\%\,\text{color removal} = \frac{100\,[\text{ABS}_0^{\text{M}} - \text{ABS}^{\text{M}}]}{\text{ABS}_0^{\text{M}}}$$

where ABS^{M} is the average of absorbance values as it is maximum absorbency value of wavelength: ABS_0^{M} the value ABS^{M} value before and after the degradation process.

2.6. Kinetics of various treatment processes

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 [16].

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_2 is illuminated with the light of $\lambda < 365$ nm, electrons are promoted from the valance band to the conduction band of the semiconducting oxide to give electron–hole pairs [17]. Electron in conduction band of the catalyst surface reduces oxygen to super oxide anion. This radical, in the presence of organic scavengers, may form organic peroxides or hydrogen peroxide

$$TiO_2 + h\upsilon\,(\lambda < 365\,\text{nm}) \rightarrow TiO_2(e_{CB}^- + h_{VB}^+) \quad (1)$$

$$O_2(\text{ads}) + e_{CB}^- \rightarrow {}^{\bullet}O_2^-\,(\text{ads}) \quad (2)$$

$${}^{\bullet}O_2{}^-\,(\text{ads}) + H_2O \rightarrow HO_2{}^{\bullet} \quad (3)$$

$$2HO_2{}^{\bullet} \rightarrow O_2 + H_2O_2 \quad (4)$$

$${}^{\bullet}O_2{}^-\,(\text{ads}) + H_2O_2 \rightarrow O_2 + OH^- + {}^{\bullet}OH\,(\text{ads}) \quad (5)$$

$${}^{\bullet}OH\,(\text{ads}) + \text{dye} \rightarrow CO_2 + H_2O\,(\text{degradation of dye}) \quad (6)$$

The hydroxyl radical is a powerful oxidizing agent and attacks organic pollutants present at or near the surface of TiO_2. It causes photooxidation of pollutants according to the above reactions (1)–(6).

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^-. The hydroxyl radical is an extremely strong, non-selective oxidant ($E_o = +3.06$ 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_2. It causes photooxidation of pollutants according to the following reactions (7)–(9)

$$h_{VB}^+ + H_2O\,(\text{ads}) \rightarrow H^+ + {}^{\bullet}OH\,(\text{ads}) \quad (7)$$

$$h_{VB}^+ + HO^-(\text{ads}) \rightarrow H^+ + {}^{\bullet}OH\,(\text{ads}) \quad (8)$$

$$h_{VB}^+ + \text{dye} \rightarrow \text{dye}^{\bullet +} \rightarrow \text{oxidation of dye} \quad (9)$$

The objective of electro-assisted photocatalytic is that not only to increase overall efficiency of organic pollutant removal but also for enhancing discolouration initially by chlorination so that photoprocess can dominate remaining part of the process.

Because of batch system, the concentration of reactants or products in the reactor varies with respect time. It is due to photochemical and electrochemical reaction taking place in the same reactor. In this reactor the effluent was allowed under go degradation due photo as well as electrochemical reaction following heterogeneous pseudo first order kinetics. The dye degradation the reactor active volume due to photochemical and electrochemical reaction simultaneously, the concentration of unreacted dye can be obtained from the following equation

$$C = C_0 \exp\,[-k_p a_p t] + C_0 \exp\,[-k_e a_e t] \quad (10)$$

where a_e is the specific electrode reaction area, $[A_e/V_r]$, a_p is the specific surface area of the UV lamp, $[A_p/V_r]$, k_e is the rate coefficient for electrochemical l reaction, k_p is the rate co-efficient for photoreaction and C is the concentration of the dye in the reactor.

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.

Table 2
K-values for various treatment processes

Schemes	$K \times 10^4$ min^{-1}	
	Initial	Final
Photo	13.2	1.8
Electrochemical	44.4	9.6
Electrochemical-assisted Photo	6	12.6
Electrochemical-assisted Photocatalytic	12.6	22.8

It is to be noted that k is an implicit value. The individual values of rate constants can be computed.

3. Results and discussion

The effect of the parameters such as pH, current density, the presence of TiO_2 in the effluent on rate of COD removal and removal of colour were investigated depending upon, electrochemical, photo, electrochemical-assisted photodegradation and electrochemical-assisted photocatalytic degradation processes.

3.1. Comparison among various process.

Fig. 4 shows the performance of various treatment process such as electrochemical, photo, electrochemical-assisted photo and photo with the presence of TiO_2 with respect to percentage removal of COD and colour as per the conditions displayed in Table 1.

It can be seen in Fig. 4 that the electrochemical-assisted photocatalytic treatment process indicates 90% degradation of dye at the irradiation of time of 7 h. The objective of this comparison is not to show which process is more efficient since they are different process and the yields are not comparable. However, it is useful to show that when both treatments are simultaneously applied the resulting dye degradation is more 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.

3.2. Electrochemical-assisted photocatalytic process

Some dyes are degraded by direct UV radiation [18]. Therefore, it should be examined to what extent the dyes are 'photolyzed' in absence of photocatalyst. In other words, it is important to estimate the contribution of direct 'photolysis' in the overall PCD. Blank experiments were carried out without catalyst for this purpose. It is also interesting to determine, the minimum amount of catalyst required to decolourize the maximum amount of dye at a particular experimental condition. For this, experiments were carried out varying the photocatalyst like TiO_2.

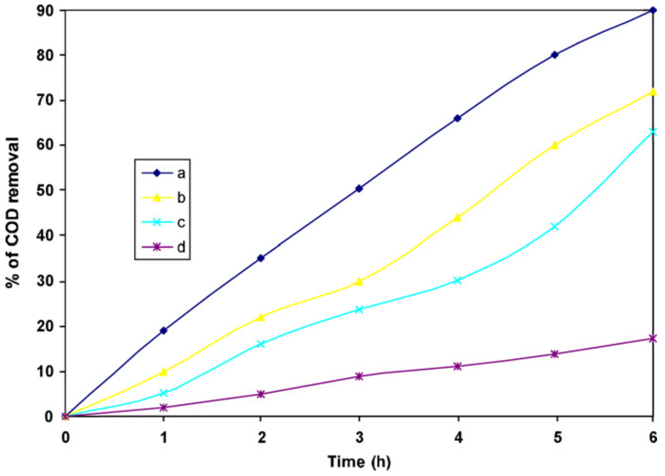

Fig. 4. Performance of various treatment processes. a = electro-assisted photocatalytic degradation, b = electro-assisted photodegradation, c = electro-oxidation, and d = photodegradation.

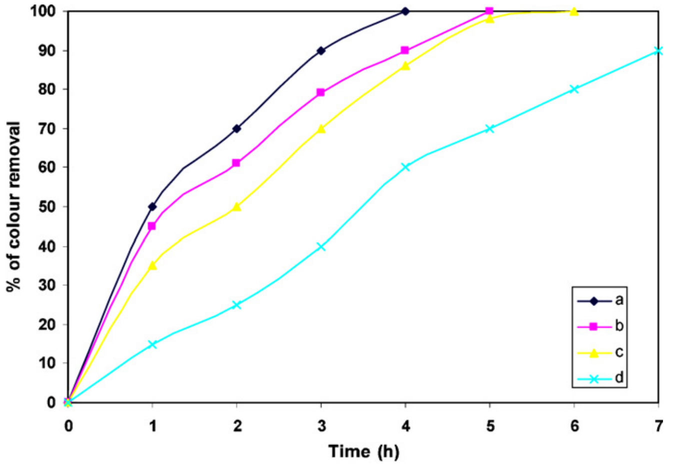

Fig. 5. Effect of colour removal for various process. a = electro-assisted photocatalytic degradation, b = electro-assisted photodegradation c = electro-oxidation, and d = photodegradation.

In this electrochemical-assisted photocatalytic process, the suspension of TiO_2 was added in the effluent which acts as photocatalyst. The effect of electrochemical-assisted photocatalytic process on the procion blue removal was shown in Fig. 5. From this figure it can be seen that better colour removal took place by electrochemical-assisted photocatalytic process. The irradiation time increases the dye degrades to compounds of lower molecular weight, and the intermediates gradually disappear during the remaining period of irradiation. In this process 100% removal of colour was achieved at 4th hour. Fig. 6 shows the effect of loading of TiO_2. A series of experiments were carried out to assess the optimum catalyst loading by varying the amount of catalyst from 35 to 85 mg/l. In a set of runs, the percentage removal of COD was increased upto the loading of photcatalyst reaches 75 mg/l. The photocatalytic degradation efficiency increases with an increase in the amount of photocat-

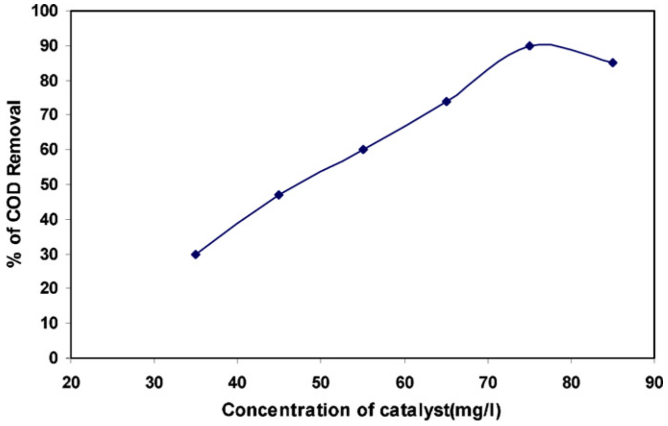

Fig. 6. Effect of photocatalyst loading on % removal of COD.

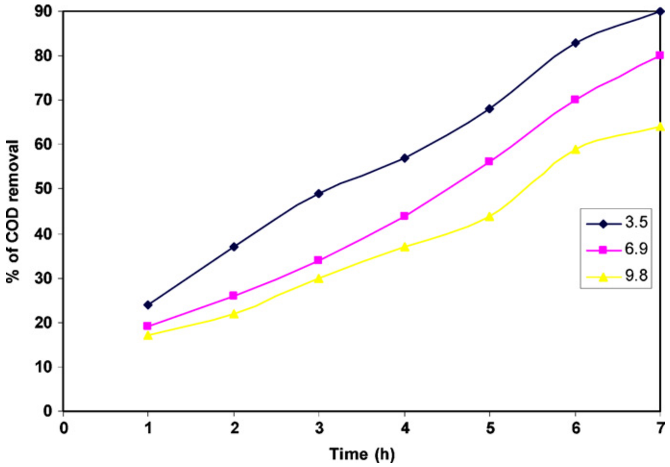

Fig. 7. Effect of pH on the % removal of COD.

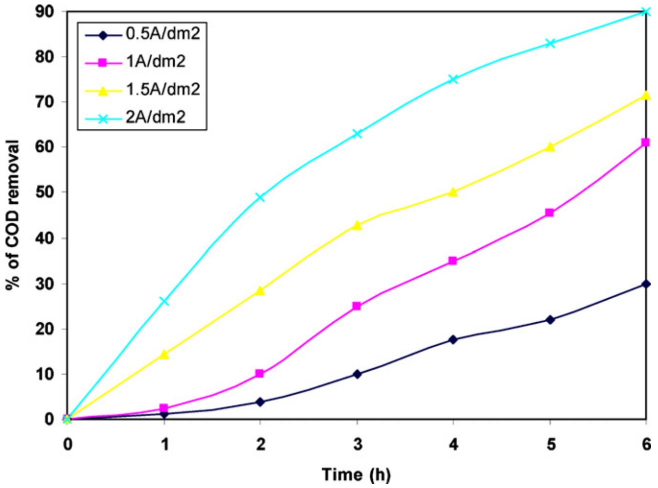

Fig. 8. Effect of current density on the % removal of COD.

alyst, reaches the highest value at a catalyst amount of 75 mg/l and then decreases. The most effective decomposition of procion blue was observed at 75 mg/l of TiO_2. The reason of this observation may due to the fact that when TiO_2 adsorbs all procion blue dye molecules, the addition of higher quantities of 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 TiO_2 particles [19].

3.3. *Effect of pH*

Because of the amphoteric behaviour of most semiconductor oxides, an important parameter governing the rate of reaction taking place on semiconductor particle surfaces is the pH of the dispersions, since; it influences the surface-charge-properties of the photocatalyst [20]. Further, industrial effluents may not be neutral. Therefore, the effect of pH on the rate of degradation needs to be considered. Experiments were carried out at pH values of 3.5, 6.9, and 9.8, using 0.1 g/l procion blue solutions. Fig. 7 shows the effect of pH on removal of COD. As it can be seen, strong acid conditions favor dye degradation by photocatalytic process. Thus, the highest decolourization and mineralization extents were obtained at pH 3.5. According to the zero point charge of semiconductors its surface is presumably positively charged in acidic and negatively in basic medium. When the organic dye as a contaminant contains negatively charged sulfonate groups in the structure, acidic solution favors adsorption of the dye on to the semiconductor surface, thus increasing degradation efficiency of photocatalytic process. Change in pH shifts the redox-potentials of valance and conduction bands, which may affect interfacial charge-transfer [15,21–23].

3.4. *Effect of current densities and supporting electrolyte*

To enumerate the effect of current density on reduction of COD, the current was varied from 0.5 to 2.0 A/dm^2. The reduction of COD was directly proportional to the applied current. Murphy et al. [24] 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. 8 shows the effect of current density on the percentage degradation of procion blue dye along with the percentage decrease in COD after electrochemically assisted photocatalytic treatment. An optimum point must be carefully determined giving a faster removal of COD. Hence the current density 2 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 under batch condition. In this study experiments were performed under batch conditions. It is evident that the extent of degradation of procion blue increases with time and higher increase in applied current density of 2 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 generated from the electrolyte (mainly 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 concentration of 3 g/l of NaCl. Among all the results, the redox behaviour of procion blue in NaCl was good when compared to other supporting electrolytes.

3.5. *UV–vis spectra changes*

Typical UV spectra and of untreated and treated effluent has been done for the effluent used in the present investigation. The changes in the absorption spectra of procion blue solution during the photoelectrochemical process at initial and final stage are shown in Fig. 9. The spectrum of procion blue in the visible region exhibits a main band with a maximum at 605 nm. The decrease of adsorption peaks of procion blue at $\lambda_{max} = 605$ 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

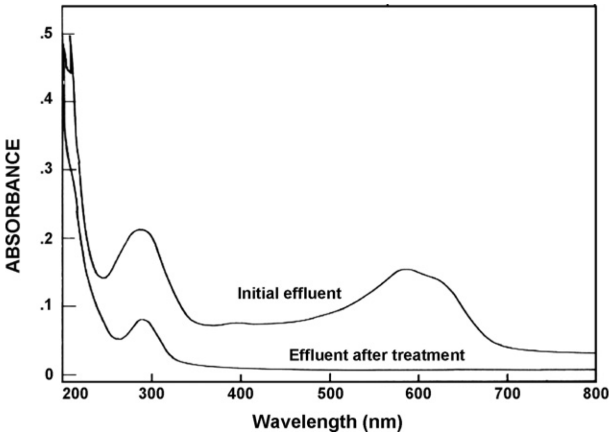

Fig. 9. Spectra of procion blue solution during the electrochemical-assisted photocatalytic process.

attack. Complete discolouration of dye was observed after 7 h under the optimized conditions.

4. Conclusions

The results indicate the importance of the operational parameters towards obtaining high electrochemical-assisted photocatalytic degradation rate. It has been found that type of process used was the main factor that has strong influences on degradation of textile washwater containing procion blue. Stirring of the effluent acts to promote the degradation rate by bringing more dye molecules closer to the electrode surface and hydroxyl radical produced at the interface can also react more randomly with the dye in the washwater. The additives such as sodium carbonate and sodium chloride are hindering the rate of electrochemical-assisted photocatalytic degradation but it can be removed by diluting the dye solution to appropriate concentration. The percentage removal of COD 90% and 100% colour removal were found to be the presence of TiO_2. It is evident that TiO_2 catalyzed photodegradation using UV irradiation with electrochemical treatment is a better technique for removal of porcion blue dye in waste water from textile industries.

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