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 TiO₂ 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 TiO₂.

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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 yams 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-
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 corrosive and inert nature.

Advanced oxidation process like photocatalysis system which includes a combination of semiconductor (e.g., TiO2, ZnO, CdS, Fe2O3 and ZnS) and UV light [9]. Due to a faster electron less transfer to molecular oxygen, TiO2 is found to be more efficient for photocatalytic degradation of pollutants [10]. However, widespread use of TiO2 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 Ti/TiO2/RuO2-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 TiO2.

2. Materials and methods

2.1. Materials

Procion blue dye, TiO2 (Anatase form), H2SO4, NaOH, NaCl and Na2CO3 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 contains 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. 1. Structure of procion blue.](image-url)

![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 Ti/RuO2-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.](image-url)
reactor consists of titanium expanded mesh anode coated with TiO₂/RuO₂ and has an area of 0.4 dm² and the stainless steel cathode of size 70 mm × 70 mm × 1 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.

2.2.4. Dispersion of TiO₂

made for effluent entry and exit to the photo reactor. Provisions are also employed as a source for UV irradiation. Provisions are also 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 RuO₂/TiO₂ catalytically active immobilized layer of about 10 μ thickness by thermal decomposition technique [12] which consisted of the following steps: dissolution in isopropanol of RuCl₃; varnish application on the pre-treated titanium base; drying at 80 °C; thermal decomposition at 500 °C; cooling and repeating the above operation till we get the required layer thickness, finally post-heat treat for 2 h at 500 °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 (λ = 365 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 TiO₂

This part consists of a magnetic stirrer (7) and the reservoir (1) containing effluent with TiO₂ 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 λ_max = 605 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:

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

where ABS₀ is the average of absorbance values at its maximum absorbency value of visible wavelength (λ_max). ABS₀ and ABS 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 Na₂CO₃, 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>
<thead>
<tr>
<th>Schemes</th>
<th>Dye (mg/l)</th>
<th>pH</th>
<th>Supporting electrolyte (g/l)</th>
<th>Flow rate (ml/min)</th>
<th>CD (A/dm²)</th>
<th>TiO₂ (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>NaCl Na₂CO₃</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Photo</td>
<td>50</td>
<td>–</td>
<td>–</td>
<td>20</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Electrochemical</td>
<td>50</td>
<td>2</td>
<td>3 1.5</td>
<td>20</td>
<td>2.0</td>
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</tr>
<tr>
<td>Photo and electrochemical</td>
<td>50</td>
<td>2</td>
<td>3 1.5</td>
<td>20</td>
<td>2.0</td>
<td>–</td>
</tr>
<tr>
<td>Photocatalytic and electrochemical</td>
<td>50</td>
<td>2</td>
<td>3 1.5</td>
<td>20</td>
<td>2.0</td>
<td>40</td>
</tr>
</tbody>
</table>
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\(_2\) 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\(_2\) 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\(^2\) 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\(_2\) was added in the effluent. TiO\(_2\) acted as 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. Further adsorption experiments were also conducted to know the adsorption of dye on TiO\(_2\) 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)

\[
C' = C \exp \left[ - \frac{k' a L}{q} \right]
\]

(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 \((a = \pi d L / A L)\), \(C\) 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

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

(3a)

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

(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

\[
\frac{dC}{dt} = q C'' - qC
\]

(4)
Table 2

<table>
<thead>
<tr>
<th>Schemes</th>
<th>$K \times 10^4$ (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
</tr>
<tr>
<td>Photo</td>
<td>25</td>
</tr>
<tr>
<td>Electrochemical</td>
<td>20</td>
</tr>
<tr>
<td>Photo and electrochemical</td>
<td>20</td>
</tr>
<tr>
<td>Photocatalytic and electrochemical</td>
<td>20</td>
</tr>
</tbody>
</table>

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

$$C = C_0 \exp \left[ - \left( \frac{q t}{V} \right) \left\{ \frac{1}{1 + k'' a'(V_c/q)} \right\} \exp \left( - k' a A L \right) \right]$$

and defining

$$K = \frac{q}{V} \left\{ \frac{1}{1 + k'' a'(V_c/q)} \right\} \exp \left( - k' a A L \right)$$

then the expression reduces to

$$C = C_0 \exp \{- K t\}$$

where $C_0$ is the initial concentration of dye, $V$ the reservoir volume and 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.

4. Results and discussion

The effect of the parameter such as flow rate, current density, supporting electrolyte concentration, pH and weight fraction of catalysts 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 TiO$_2$ and UV irradiation, the electrochemical treatment process indicates 98% degradation of dye at the irradiation of time of 7h. 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 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 A/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
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 A/dm² 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 dye 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 A/dm² 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 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 nm. The decrease of adsorption peaks of procion blue at λmax = 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 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 TiO₂ 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 mg/l and then decreases. The most effective decomposition of procion blue was observed with 40 mg/l of TiO₂. The reason of this observation may be due to the fact that when TiO₂ adsorbs all procion blue dye molecules, the addition of higher quantities of TiO₂ 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 TiO₂ particles [14].
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 TiO2, 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 TiO2. The large amount of adsorbed dye 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 TiO2 is illuminated with the light of λ < 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 radical, in the presence of organic scavengers, may form organic peroxides or hydrogen peroxide.

\[
\text{TiO}_2 + h\nu (\lambda < 365 \text{ nm}) \rightarrow \text{TiO}_2(e_{\text{CB}}^- + h\nu^+) \quad (8)
\]
\[
\text{O}_2(\text{ads}) + e_{\text{CB}}^- \rightarrow \text{O}_2^-(\text{ads}) \quad (9)
\]
\[
\text{O}_2^- (\text{ads}) + \text{H}_2\text{O} \rightarrow \text{HO}_2^- \quad (10)
\]
\[
2\text{HO}_2^- \rightarrow \text{O}_2 + \text{H}_2\text{O} \quad (11)
\]
\[
\text{O}_2^- (\text{ads}) + \text{H}_2\text{O}_2 \rightarrow \text{O}_2 + \text{OH}^- + \text{OH}(\text{ads}) \quad (12)
\]
\[
\text{OH}(\text{ads}) + \text{dye} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad \text{(degradation of dye) (13)}
\]

The hydroxyl radical is a powerful oxidizing agent and attacks organic pollutants present at or near the surface of TiO2. 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−. The hydroxyl radical is extremely reactive, non-selective oxidant (Eo = +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 TiO2. It causes photooxidation of pollutants according to the following reactions (13)–(16)

\[
h\nu^+ + \text{H}_2\text{O(ads)} \rightarrow \text{H}^+ + \text{OH}(\text{ads}) \quad (14)
\]
\[
h\nu^+ + \text{HO}^- (\text{ads}) \rightarrow \text{H}^+ + \text{OH}(\text{ads}) \quad (15)
\]
\[
h\nu^+ + \text{dye} \rightarrow \text{dye}^+ \rightarrow \text{oxidation of dye} \quad (16)
\]

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 discoloration 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 TiO2 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 TiO2. 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/dm2 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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References

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Abstract

Photocatalytic methods with TiO₂ 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; TiO₂; 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 (•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 TiO₂, IrO₂, RuO₂, and Ta₂O₅. Combinations, such as TiO₂/RuO₂, are indicated for alkaline medium, while IrO₂/Ta₂O₅ usually shows longer service life in acidic electrolytes. On the other hand, some DSA type oxide electrodes may receive additions of SnO₂ and Sb₂O₅ 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 TiO₂ 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 TiO₂ concentration; illumination intensity; organic pollutant concentration; temperature; and pH and type of anions in the solution [9–12]. As the TiO₂ catalyst is kept in suspension during illumination,
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 TiO2 catalyst [13].

Immobilization of TiO2 catalyst on a conductive substrate has been tried. By cycling potential, anatase has been immobilized onto an optically transparent SnO2 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 TiO2, thus obtaining different stoichiometries and crystal structures [14]. Although somewhat delayed, it has been noted that the rutile form of TiO2 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 TiO2 allows the use of some types of DSA oxide electrodes in which this allotropic form of TiO2 is the major component. Fig. 1 shows the TiO2-photosensitisation pathway under UV irradiation.

The main objective of this study is the electrochemical-assisted photocatalytic degradation of textile washwater by using TiO2 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 6W pencil type immersion lamp. During the electrolysis on a batch process, COD reduction, colour removal were investigated on TiO2 as semiconductor at selected electrolyte medium, current densities and pH. Also a study of the potentiality of a titanium anode, coated with 70TiO2/30RuO2, 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.

2. Materials and methods

2.1. Materials

Procion blue dye, TiO2 (Anatase form), H2SO4, NaOH, NaCl and Na2CO3 (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 λmax 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 RuO2/TiO2 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 6W medium pressure, mercury vapour immersion lamp (λ = 365 nm) of size 2.5 cm diameter and 27 cm
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 Na2CO3, 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 (TiO2). 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 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/dm² under the conditions given in Table 1.

2.3.3. Electrochemical assisted photocatalytic oxidation

In this electrochemical-assisted photocatalytic oxidation, the suspension of TiO2 was added in the effluent at different concentration. TiO2 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

<table>
<thead>
<tr>
<th>Schemes</th>
<th>Dye (mg/l)</th>
<th>pH</th>
<th>Supporting electrolyte</th>
<th>CD (A/dm²)</th>
<th>TiO2 (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photo</td>
<td>100</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Electrochemical</td>
<td>100</td>
<td>3.5</td>
<td>3</td>
<td>1.5</td>
<td>2.0</td>
</tr>
<tr>
<td>Electrochemical-assisted photo</td>
<td>100</td>
<td>3.5</td>
<td>3</td>
<td>1.5</td>
<td>2.0</td>
</tr>
<tr>
<td>Electrochemical-assisted Photocatalytic</td>
<td>100</td>
<td>3.5</td>
<td>3</td>
<td>1.5</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Fig. 3. Experimental setup of electrochemical-assisted photocatalytic treatment process.
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 \(\lambda_{\text{max}} = 605\) 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:

\[
\% \text{ color removal} = 100 \left[ \frac{\text{ABS}^M_0 - \text{ABS}^M}{\text{ABS}^M_0} \right]
\]

where \(\text{ABS}^M\) is the average of absorbance values as it is maximum absorbency value of wavelength; \(\text{ABS}^M_0\) the value \(\text{ABS}^M\) 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

\[
\text{TiO}_2 + h\nu (\lambda < 365 \text{ nm}) \rightarrow \text{TiO}_2(e^-_{\text{CB}} + h^+_\text{VB})
\]

\[
\text{O}_2(\text{ads}) + e^-_{\text{CB}} \rightarrow \text{O}_2^- \ (\text{ads})
\]

\[
\text{O}_2^- (\text{ads}) + \text{H}_2\text{O} \rightarrow \text{HO}_2^* \ (\text{ads})
\]

\[
2\text{HO}_2^* \rightarrow \text{O}_2 + \text{H}_2\text{O}_2
\]

\[
\cdot\text{O}_2^- (\text{ads}) + \text{H}_2\text{O}_2 \rightarrow \text{O}_2 + \text{OH}^- + \cdot\text{OH} (\text{ads})
\]

\[
\cdot\text{OH} (\text{ads}) + \text{dye} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \ (\text{degradation of dye})
\]

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 \(\text{OH}^-\). The hydroxyl radical is an extremely strong, non-selective oxidant \((E_o = +3.06 \ \text{V})\), 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).

\[
h^+_{\text{VB}} + \text{H}_2\text{O} (\text{ads}) \rightarrow \text{H}^+ + \cdot\text{OH} (\text{ads})
\]

\[
h^+_{\text{VB}} + \text{HO}^- (\text{ads}) \rightarrow \text{H}^+ + \cdot\text{OH} (\text{ads})
\]

\[
h^+_{\text{VB}} + \text{dye} \rightarrow \text{dye}^{*+} \rightarrow \text{oxidation of dye}
\]

The objective of electro-assisted photocatalytic is not only to increase overall efficiency of organic pollutant removal but also for enhancing discoloration 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

\[
C = C_0 \exp \left[ -k_e a_e t \right] + \frac{C_0}{V} \left[ -k_p a_p t \right]
\]

where \(a_e\) is the specific electrode reaction area, \(A_e/V_l\), \(a_p\) is the specific surface area of the UV lamp, \(A_p/V_l\), \(k_e\) is the rate coefficient for electrochemical I reaction, \(k_p\) is the rate co-efficient for photoreaction and \(C\) is the concentration of the dye in the reactor.

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.

Table 2

<table>
<thead>
<tr>
<th>Schemes</th>
<th>(K \times 10^4) (\text{min}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>Final</td>
</tr>
<tr>
<td>Photo</td>
<td>13.2</td>
</tr>
<tr>
<td>Electrochemical</td>
<td>44.4</td>
</tr>
<tr>
<td>Electrochemical-assisted Photo</td>
<td>6.0</td>
</tr>
<tr>
<td>Electrochemical-assisted Photocatalytic</td>
<td>12.6</td>
</tr>
</tbody>
</table>
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 processes 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$_2$.

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 photocatalyst reaches 75 mg/l. The photocatalytic degradation efficiency increases with an increase in the amount of photocat-

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.

Fig. 6. Effect of photocatalyst loading on % 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 TiO₂. The reason of this observation may due to the fact that when TiO₂ adsorbs all procion blue dye molecules, the addition of higher quantities of TiO₂ 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 TiO₂ 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/dm². 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/dm² 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/dm² 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 λ 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
attack. Complete discoloration 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 TiO2. It is evident that TiO2 catalyzed photodegradation using UV irradiation with electrochemical treatment is a better technique for removal of porcion blue dye in waste water from textile industries.

Acknowledgement

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References

The photocatalytic degradation of Procion blue H-B dye in biodegraded textile washwater has been investigated for the complete removal of color and maximum reduction of chemical oxygen demand (COD). Pseudomonas putida was utilized for obtaining biodegraded textile washwater. In this process, silver-doped TiO₂ photocatalyst was prepared and experiments were carried out to study the effects of UV and mercury lamp irradiations on COD reduction and removal of color. The thus prepared silver-doped TiO₂ catalyst was characterized by thermogravimetric and differential thermal analysis, UV-visible spectrometer, X-ray diffraction, scanning electron microscope, energy dispersive X-ray microanalysis, and BET surface area techniques. Adsorption studies were also carried out to evaluate the fitness of isotherm models. The results show that the silver-doped TiO₂ has enhanced the photodegradation of Procion blue H-B dye under UV and mercury lamp irradiations. The enhanced activity of silver-doped TiO₂ is due to the enrichment of electron–hole separation by electron trapping of silver particles.

**Keywords:** Procion blue H-B dye; photocatalysis; silver doping; TiO₂; washwater; COD

**Introduction**

Discharge of dyehouse effluents with biocalcitrant organic pollutants has led to the development of new technologies for the treatment of wastewater. Dye effluents can be treated by biological methods, flocculation, adsorption on activated carbon, chemical oxidation methods, reverse osmosis, and advanced oxidation processes (Slokar and Marechal 1998). Biological methods alone have been proved to be unsuccessful for the treatment of textile wastewater (Pearce, Lloyd, and Guthrie 2003). Flocculation, reverse osmosis, and adsorption methods transfer the pollutants to other media, thus causing secondary pollution (Goutley, Buckley, and Groves 1983). Moreover, chemical oxidation methods are not cost effective (Baban et al. 2003).

In this effort, heterogeneous photocatalysis has been identified as one of the most potential pollution remedial technologies in recent decades (Corma and Garcia 2004; Oller et al. 2006). Semiconductor photocatalyst generates electron and hole
pair (e\(^{-}\)/h\(^{+}\)) upon irradiation of light energy that could be utilized in initiating oxidation and reduction reactions, respectively. Low electron transfer rate to oxygen and high electron–hole pairs’ recombination rate limit the rate of photo-oxidation of organic compounds on the catalyst surface significantly (Linsebiger, Lu, and Yates 1995). The effects of various factors influencing photocatalytic degradation, such as pH, concentration of dye, dosage of photocatalyst on the photodegradation of Procion blue by electro-assisted photocatalytic degradation have been studied (Neelavannan, Revathi, and Basha 2007).

Considerable investigations have been focused on improving photocatalytic activity of titania using dopants and surface deposition of noble metals to broaden the absorption of UV by TiO\(_2\) and reduce recombination odds of photoexcited carriers. Emerging techniques, such as ozonation treatment using Fenton’s reagent, electrochemical destruction, and photocatalysis may have considerable potential for discoloration. However, such technologies either usually involve complicated procedures or are economically unfeasible (Chang and Lin 2000). Biological and/or combination treatment systems that can effectively remove dyes from large volumes of wastewater at a low cost are considered to offer a preferable alternative (Robinson et al. 2001). Several researchers have studied the degradation of different textile dyes using silver-doped titanium dioxide by photocatalytic methods (Arabatzis et al. 2003; Ozkan et al. 2004; Sahoo, Gupta, and Pal 2005; Rupa et al. 2007).

The photocatalytic activity with silver deposit was less augmented than with platinum deposit and at times is even detrimental (Vamathevan et al. 2002). It is also found that the presence of nanosized silver particles on the TiO\(_2\) surface could augment the activity of TiO\(_2\) by a factor of 4.0 for the mineralization of sucrose. For the treatment of dye wastewater, TiO\(_2\) modified with silver loading enables the catalyst to be more effective and shortens the illumination period (Sokmen and Ozkan 2002). Separation of TiO\(_2\) from the effluent after dye degradation, however, is difficult due to its fine size. Therefore, it needs a costly filtration process before disposal. To combat this difficulty, TiO\(_2\) is sometimes immobilized on transparent supports (Naskar, Pillay, and Chanda 1998), or it is doped with either metal or metal ions (Arabatzis et al. 2003).

The enhancement of photocatalytic activity of TiO\(_2\) in the oxidative degradation procion by silver deposition may be achieved through the following mechanisms:

1. Silver particles deposited on TiO\(_2\) act as electron traps, enhancing the electron–hole separation and the subsequent transfer of the trapped electron to the adsorbed O\(_2\) acting as an electron acceptor (Herrmann 1986).

2. More dye molecules were adsorbed on the surface of silver-doped TiO\(_2\) than on the TiO\(_2\) surface, enhancing the photo-excited electron transfer from the visible light sensitized dye molecule to the conduction band of TiO\(_2\), thereby subsequently increasing the electron transfer to the adsorbed O\(_2\).

In this work, biodegradation of Procion blue H-B dye in textile washwater is carried out to obtain biodegraded textile washwater, which is amenable for photocatalytic oxidation. For the first time, we report Ag–TiO\(_2\) doped photocatalytic degradation of Procion blue H-B dye in biodegraded textile washwater. All the intermediates and unreacted compounds formed during biodegradation will be oxidized by photocatalytic oxidation and the bacteria presented in the effluent will also be killed. Prepared silver-doped TiO\(_2\) catalyst was characterized by thermo gravimetric and differential thermal analysis (TG and DTA), UV-Visible
spectrometer, X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive X-ray microanalysis (EDX), and Brunauer–Emmett–Teller (BET) surface area techniques.

**Experimental**

**Materials**

The biodegraded textile washwater containing Procion blue H-B dye (reactive blue 2, C.I. no., 61211 and $\lambda_{max}$ of Procion blue dye of 605 nm) was used in this study. Titanium dioxide (anatase 98.0%) and silver nitrate (99.5 wt%) analytical grade from Merck were used for the preparation of silver-doped TiO$_2$ photocatalysts.

**Photocatalytic degradation studies**

In this study, the washwater after biodegradation was subjected to photocatalytic degradation by two types of irradiation.

**Mercury lamp irradiation method**

The experimental setup consists of a 500 mL glass beaker that contains washwater with photocatalysts, placed on a magnetic stirrer. This setup is kept inside a reflecting mirror box. A 125 W mercury lamp is provided on top of the mirror box, which serves as the light source. The length, breadth, and height of the reflecting mirror box are 40, 25, and 25 cm, respectively. A volume of 400 mL of the washwater is taken in the beaker and the TiO$_2$ or silver-doped TiO$_2$ is added to it. Washwater with a photocatalyst is continuously stirred by a magnetic stirrer for complete mixing of reaction mixture. The volume of washwater taken in the beaker is 400 mL. Figure 1(a) shows the mercury lamp irradiation setup.

**UV lamp irradiation method**

For this work, washwater containing Procion blue H-B dye is obtained after biodegradation. The experimental setup of pencil-type UV lamp irradiation is shown in Figure 1(b). This setup consists of a 700 mL cylindrical stainless steel reactor placed on a magnetic stirrer. An immersion type 6 W UV lamp of size 2.5 cm diameter and 27 cm height (emitting UV light, $\lambda = 365$ nm) is placed inside the reactor and the same serves as the light source. The height and diameter of the reactor are 21 and 8 cm, respectively. A volume of 700 mL of the washwater is taken in the reactor and to it is added TiO$_2$ or Ag$^+$ doped TiO$_2$. The washwater with a photocatalyst is continuously stirred by a magnetic stirrer for complete mixing of reaction mixture. The height of the dye solution in the reactor is 20 cm.

**Chemical oxygen demand analysis**

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. The COD of all samples were determined by the dichromate closed reflux method using Thermoreactor TR 620 (Merck). The reaction time was 2 h at 148°C.

The experiments are repeated until the difference observed is less than 3%.

**Biodegradation**

Biodegradation of textile washwater was carried out for 5 days to study the partial removal of color and COD reduction. *Bacillus cereus* and *Pseudomonas putida* was inoculated on the nutrient agar slant and incubated at 37°C for 24 h, and it was maintained in refrigeration condition and it has been subcultured routinely for 15 days.

Nutrient broth culture of 100 mL (*P. putida*) was taken in a 250 mL Erlenmeyer flask and incubated at 37°C for 24 h. Then, textile washwater of 100 mL was taken and added to a flask that contains nutrient broth culture at a pH of 9.0 and shaken at 120 rpm at a temperature of 28°C. The flask was kept in a shaker for 5 days. Discoloration and degradation of washwater in biological treatment based on bacterial activities thus require aerobic condition. For the sequential treatment, aerobic environment can be provided in a rotating biological conductor (orbital shaker). After completion of 24h, 1 mL of sample was collected every day from the flask for COD analysis, and 5 mL sample was collected for absorbance with the
help of NOVA 60 (Merck). The results thus obtained in a batch setup are shown in Table 1.

### Instrumentation

A Varian Cary 500 UV–VIS–NIR spectrophotometer equipped with an integrated sphere was used to record the diffuse reflectance spectra (DRS) and to measure the absorbance data of the solution samples. The baseline correction was performed using a calibrated reference sample of barium sulfate. The reflectance spectra of TiO₂ and silver-doped TiO₂ catalysts were analyzed under ambient conditions in the range λ = 200–800 nm.

Powder XRD patterns of TiO₂ and Ag-doped TiO₂ catalysts were obtained using a Philips PAN analytical X’pert PRO diffractometer equipped with a copper tube for generating a Cu-Kα radiation (λ = 1.5406 Å) at 40 kV, 25 mA. The particles were spread on a glass slide specimen holder and the scattered intensity was measured between 20° and 85° at a scanning rate of 2θ = 1.2° min⁻¹. Peak positions were compared with the standard files to identify the crystalline phases.

SEM analysis was performed on samples using a Hitachi, Model S-3000H, equipped with an INCA EDX probe for the EDX microanalysis.

TG and DTA analyser, TA Instruments Model SDT Q600 Model, was used to measure weight changes in Ag–TiO₂ as a function of temperature (or time) under a controlled nitrogen atmosphere. Its principal uses include measurement of thermal stability and composition of Ag–TiO₂. Data were collected during cooling also.

The specific surface areas of TiO₂ and silver-doped TiO₂ were determined according to the BET method through nitrogen adsorption at liquid nitrogen temperature (77 K) using a NOVA 1000 series instrument.

### Preparation of photocatalyst

The Ag-doped TiO₂ catalysts were prepared by photo reducing Ag⁺ ions to Ag metal on the TiO₂ surface as per the following procedure. First, 0.2 g of AgNO₃ was dissolved in 100 mL of water in a glass beaker. Then 10 g of TiO₂ was added to the solution and the solution was stirred well and allowed to stand for 24 h. The system was then irradiated under a 6 W UV lamp with a maximum emission at 365 nm for 2 h. After irradiation, the powder was filtered and washed to remove residual ions and finally dried in vacuum oven at 95°C for 16 h (Liu et al. 2004).

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>COD (mg L⁻¹)</th>
<th>% of COD removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>3280</td>
<td>5</td>
</tr>
<tr>
<td>48</td>
<td>2960</td>
<td>14</td>
</tr>
<tr>
<td>72</td>
<td>2640</td>
<td>23</td>
</tr>
<tr>
<td>96</td>
<td>2480</td>
<td>28</td>
</tr>
<tr>
<td>120</td>
<td>2320</td>
<td>33</td>
</tr>
</tbody>
</table>

Table 1. Biodegradation using P. putida.
Results and discussion

**XRD and EDX analysis**

Figure 2 shows the XRD patterns of TiO\textsubscript{2} and Ag–TiO\textsubscript{2}. From the figure, we found that the XRD patterns of silver-doped TiO\textsubscript{2} samples almost coincide with that of pure TiO\textsubscript{2} and show no diffraction peaks due to silver species, thus suggesting that the metal particles are well dispersed on the TiO\textsubscript{2} surface. Anatase-type structure is kept in all silver-doped TiO\textsubscript{2} catalysts, indicating that the metal dopants are merely placed on the surface of the crystals without being covalently anchored into the crystal lattice. There are no diffraction patterns characteristics of the doped metals in the XRD patterns. Hence these metal sites are expected to be below the visibility limit of X-ray analysis (Sclafani and Herrmann 1998). The crystallite size was determined from the diffraction peak broadening by employing the following equation:

\[
D = \frac{K\lambda}{(\beta_c - \beta_s) \cos \theta}
\]

where \(D\) is the crystallite size of the catalyst, \(\lambda\) the X-ray wavelength, and \(\beta_c\) and \(\beta_s\) the FWHM of the catalyst and the standard, respectively; \(K=0.89\) is a coefficient and \(\theta\) the diffraction angle. It is noted that all the catalysts are in the form of nanoparticulates with sizes ranging from 20 to 40 nm. The TiO\textsubscript{2} used in this study was pure anatase phase. There was no change in the structure of TiO\textsubscript{2} after the photocatalytic reaction.

We observed maximum photocatalytic degradation of Procion blue by 2% of Ag-doped TiO\textsubscript{2}. We have performed EDX analysis on the Ag-doped TiO\textsubscript{2} catalyst and from the analysis, we notice that in Ag–TiO\textsubscript{2}, the Ag content of 0.42 wt% was present in the selected region. This confirms that the deposition of silver on TiO\textsubscript{2} is non-uniform.
UV-visible DRS

The spectrum of TiO$_2$ consists of a single absorption around 350 nm, usually ascribed to charge-transfer from the valence band (mainly formed by 2p orbitals of the oxide anions) to the conduction band (mainly formed by 3d$_{2g}$ orbital of the Ti$^{4+}$ cations) (Gerischer and Heller 1991). The addition of silver ions and subsequent UV irradiation cause significant changes to the absorption spectrum of TiO$_2$ resulting in high absorbance from 370 nm to the entire visible region, a characteristic of surface plasmon absorption where a band usually appears at 400 nm. As this band is not as strong as reported in literature (Herrmann et al. 1997; Stathatos et al. 2000), the red shift may not be due to surface plasmon absorption. Hence the extended absorption must be from band gap absorption. This band gap absorption of all silver-doped TiO$_2$ catalysts slightly shifts to higher wavelength. The absorbance in the visible region for the metallized system shows that lower energy transitions are possible. This is due to the metal clusters giving rise to localized energy levels in the band gap of TiO$_2$ into which valence band electrons of TiO$_2$ are excited at wavelength longer than 350 nm. If equal-sized metal clusters are formed, constant absorption in the visible region corresponding to the excitation from the valence band of TiO$_2$ to the unoccupied level of metal cluster will occur. Since there is a small gradual decrease in absorption from 400 to 800 nm in the DRS of silver-doped TiO$_2$ catalyst, the metal clusters in the catalyst are not of equal size. The spectra reveal that silver doping has a marked effect on the absorption properties of TiO$_2$ and that the absorption of light in the visible region by TiO$_2$ increases with an increase in the silver content.

BET surface area analysis

In general, the surface area of the catalyst is the most important factor in influencing the catalytic activity. The surface area of TiO$_2$ particles before and after surface modification was determined. It was observed that the surface area decreases with increase in the silver content of the silver-doped TiO$_2$ catalyst. The surface area of the titanium dioxide and silver-doped TiO$_2$ were 22.19 and 17.52 m$^2$/g, respectively. The decrease in the surface area of silver-doped TiO$_2$ may be due to blocking of fine capillaries of parent TiO$_2$ surface by metal film islands (Sakthivel et al. 2004).

Thermo gravimetric and differential thermal analysis

Thermal stability is critically important for silver-based multilayered structures such as silver/TiO$_2$. In this work, it has been proved that silver deposition can effectively improve the thermal stability of TiO$_2$ but does not adversely affect the optical transmission through the multilayer from the near ultraviolet to near infrared spectral region. The TG and DTA patterns were obtained on TiO$_2$ and silver-doped TiO$_2$. An endothermic peak is observed around 35°C with a corresponding weight loss of about 0.5%. This is attributed to the dehydration of the catalyst. No weight loss was observed beyond 1000°C. A similar observation has been reported by Nagaveni et al. (2004) on the photocatalytic degradation of nano TiO$_2$. Although the silver-doped TiO$_2$ gave a similar trend in the latter case, an irreversible decomposition takes place at 1200°C. In both cases, the weight losses observed...
between 150 and 500°C are attributed to the strongly bonded water or surface hydroxyl groups (Nagaveni et al. 2004).

**Adsorption of Procion blue on TiO$_2$ and Ag-doped TiO$_2$ catalysts**

Adsorption is usually described through isotherms, that is, the amount of adsorbate on the adsorbent as a function of its concentration at constant temperature. For the photodegradation of Procion blue dye on silver-doped TiO$_2$ under UV irradiation, silver metals act as electron traps, thereby enhancing the charge separation. To find out the mechanism, an adsorption study was carried out with 20–100 mg L$^{-1}$ of the aqueous solution of Procion blue H-B dye in darkness for 12 h. It was found that there was no measurable decrease in the dye concentration. This indicates that the adsorption of dye is not significant over silver-doped TiO$_2$.

An adsorption isotherm of TiO$_2$ is shown in Figure 3(a) and (b). From the figures, a substantial increase in the relative amount adsorption was observed as the dosage was increased from 60 to 100 mg L$^{-1}$. Linear plots of $C_e/q_e$ versus $C_e$ (Langmuir) and $\ln(qe)$ versus $\ln(C_e)$ (Freundlich) show that the adsorption obeys both Langmuir and Freundlich isotherm models. The high values of coefficient of regression ($R^2$) for both the models indicate good agreement between experimental

![Figure 3. An adsorption isotherm of TiO$_2$. (a) Langmuir isotherm. (b) Freundlich isotherm.](image-url)
and predicted data. The applicability of both the isotherm models to TiO₂ and silver-doped TiO₂ system implies that both monolayer sorption and heterogeneous surface conditions exist under the experimental conditions used. The sorption of dye on the TiO₂ and silver-doped TiO₂ is thus complex, involving more than one mechanism. From the measurement, we found that the values of Langmuir constant ‘\(Q^0\)’ (\(Q^0\) is the maximum amount of the Procion blue dye adsorbed per unit weight of catalysts to form a complete monolayer, a practical limiting adsorption capacity when the surface is fully covered with Procion blue dye) increases with the increase of dosage of TiO₂ from 8.56 to 47.3, whereas the constant related to the affinity of the binding sites ‘\(b\)’ decreases from 0.041 to 0.039. In Freundlich isotherm, the values of \(K_f\) and \(n\) (\(K_f\) and \(n\) are the Freundlich constants characteristic on the system. \(K_f\) and \(n\) are indicators of adsorption capacity and adsorption intensity, respectively) increase with the increase of dosage of Procion blue dye from 2.9 to 5.5 and 1.42 to 1.83.

**Photocatalytic activities of TiO₂ and Ag-doped TiO₂ catalysts on Procion blue degradation**

The degradation profile of Procion blue under various catalysts loading under irradiation is shown in Figure 4. Compared to pure TiO₂, the silver-doped TiO₂ catalysts with both irradiations exhibited a significant increase in the Procion blue H-B dye degradation. As there is no significant difference in the adsorption of dyes between TiO₂ and the silver-doped TiO₂ catalysts, mechanism (2) is ruled out. Hence the increase in efficiency by Ag deposition is due to mechanism (1).

It is observed that the photonic efficiency increases with an increase in the silver loading up to 600 mg L\(^{-1}\) of Ag–TiO₂ (optimum metal loading) and then decreases. There is no considerable change in further loading of catalyst because further addition of catalyst made the effluent dense, and penetration of UV into the effluent was poor. It is also observed that the photonic efficiency increases with an increase in the silver loading up to 600 mg L\(^{-1}\). More silver contents could be detrimental to the photonic

![Figure 4. Effect of catalysts loading on COD removal.](image-url)
It may be explained that up to maximum metal loading, the silver particles deposited on the TiO$_2$ surface can act as electron–hole separation centers. The electron transfer from the TiO$_2$ conduction band to metallic silver particles at the interface is thermodynamically possible because the Fermi level of TiO$_2$ is higher than that of silver metals (Sclafani and Herrmann 1998). This results in the formation of Schottky barrier at the metal–semiconductor contact region, which improves the charge separation and thus enhances the photocatalytic activity of TiO$_2$. In contrast, at the silver content above its maximum, the silver particles can also act as recombination centers thereby decreasing the photocatalytic activity of TiO$_2$. It has been reported that the probability for the hole capture is increased by the large number of negatively charged silver particles on TiO$_2$ at high silver content, which reduces the efficiency of charge separation (Zhao et al. 1996; Stathatos and Lianos 2002). The photodegradation of Procion blue H-B Dye against the irradiation time is shown in Figure 5. From this figure, it was found that the rate of photodegradation increased linearly with time of irradiation and mercury lamp with silver-doped TiO$_2$ irradiation shows maximum Procion blue H-B dye degradation. It is due to the emission area in mercury lamp setup and attained temperature is more that that of UV lamp setup. The source (mercury lamp) was surrounded by mirrors and the reflections influence the photodegradation. The total energy absorbed per unit area during a given exposure time is also more in mercury lamp irradiation setup. Because of the high wattage of the mercury lamp, heat is generated in the reaction chamber, which leads to more photolytic yields. Also the plot reveals that there is no significant difference at each sampling points. During photocatalytic oxidation, all the pollutants (organic contaminants, dyes, and intermediates) were converted to CO$_2$.

**Conclusion**

In this article, silver-doped TiO$_2$ photocatalyst was prepared and used for the treatment of textile washwater with UV and mercury lamp irradiations. The
characterization of TiO₂ and silver-doped TiO₂ using diffuse reflectance spectroscopy, XRD, SEM, EDX, TG and DTA, and BET surface area techniques revealed the dispersion of silver metal on the surface of TiO₂. The photonic efficiency increases with increase in the metal loading up to 600 mg L⁻¹ due to the effect of decreasing recombination of electron and hole. From this study, we found that the mercury lamp irradiation with silver-doped TiO₂ results in maximum discoloration (86%) and COD removal (69%). Both Langmuir and Freundlich isotherms are fitted well for the degradation of Procion blue H-B dye. An integrated biological–photocatalytic system for the discoloration and COD reduction seems a logical choice for the treatment of textile washwater. The presence of bacteria was checked by plate method and there was no colony found in the photodegraded washwater and can be recycled and used for the rinsing purpose.

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References
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