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Studies on the photocatalytic decolorization of pararosanilne chloride dye and its simulated dyebath effluent

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ABSTRACT

In the present study the photocatalytic decolorization of pararosaniline chloride dye (unhydrolysed and hydrolysed forms) and its simulated dyebath effluent has been investigated by employing heterogeneous photocatalysis process. The photocatalytic activity of different semiconductors viz. TiO_2, ZnO, CdS and ZnS has been compared in order to select the most active catalyst for the decolorization of this dye. It was observed that ZnO exhibits better photocatalytic activity than the others. Thereafter different operational parameters which affect the decolorization process like catalyst dose, pH, initial dye concentration have been optimized. The maximum decolorization of the dye solutions was noticed in alkaline conditions and the optimum value of catalyst dose was found to be 1 g L^{-1}. Further the study has been extended to explore the applicability of this system for the decolorization of the dye in its hydrolysed form and simulated dyebath effluent. The decolorization rate as well as chemical oxygen demand (COD) reduction of the hydrolysed dye solutions was higher than that of the unhydrolysed dye solutions, whereas the simulated dye bath effluent decolorized at a somewhat slower rate than hydrolysed and unhydrolysed dye solutions.

Keywords: Decolorization; Pararosaniline chloride; Photocatalysis; Titanium dioxide; Zinc oxide

1. Introduction

Textile industries produce large volume of colored dye effluents which are toxic and non biodegradable [1]. Among the different types of dyes, triphenylmethane dyes are used extensively for dyeing nylon, polyacrylonitrile modified nylon, wool, silk, and cotton. Paper and leather industries are also major consumers of these dyes. This group of dyes is also used for coloring plastics, gasoline, varnish, fats, oil, and waxes. Some of the triphenylmethane dyes are used as medicine and biological stains. Food and cosmetic industries also use different types of triphenylmethane dyes.

Environmental regulations in most of the countries now have made it mandatory to decolorize the dye wastewater prior to discharge. Increasing concerns about color in the effluents are leading to the worldwide efforts to develop more effective color removal processes. Various chemical and physical processes such as precipitation, adsorption, air stripping, flocculation, reverse osmosis and ultrafiltration can be used for color removal from textile effluents [2–5]. However these techniques are nondestructive, since they only transfer the non biodegradable matter into sludge, giving rise to new type of pollution, which needs further treatment [6–8]. Recently there has been considerable interest in the utilization of advanced oxidation processes (AOPs) for the complete destruction of dyes. AOPs are based on generation of reactive species

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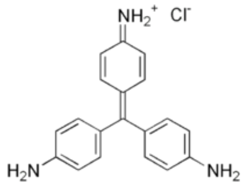
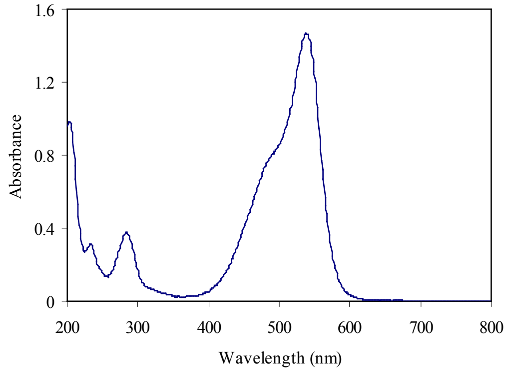
such as hydroxyl radicals that oxidizes a broad range of organic pollutants quickly and non selectively [9,10]. AOPs include photocatalysis systems such as combination of semiconductors and light, and semiconductor and oxidants. Heterogeneous photocatalysis has emerged as an important destructive technology leading to the total mineralization of most of the organic pollutants including organic reactive dyes [11–20].

Titanium dioxide (TiO_2) is generally considered to be the best photocatalyst and has the ability to detoxificate water from a number of organic pollutants [15–17]. However widespread use of TiO_2 is uneconomical for large scale water treatment, thereby interest has been drawn towards the search for suitable alternatives to TiO_2. Many attempts have been made to study photocatalytic activity of different semiconductors such as SnO_2, ZrO_2, CdS and ZnO [18–22]. Lizama et al. [21] reported the photocatalytic decolorization of reactive blue 19 (RB-19) in aqueous solutions containing TiO_2 or ZnO as catalysts and concluded that ZnO is a more efficient catalyst than TiO_2 in the color removal of RB-19. Daneshvar et al. [23] reported that zinc oxide (ZnO) is a suitable alternative to TiO_2 for the degradation of Acid Red 14, an azo dye, since its photodegradation mechanism has been proven to be similar to that of TiO_2.

Although various reports deal with the photodecolorization of several dyestuffs, only a handful studies have been reported for the photocatalytic decolorization of pararosaniline chloride dye. Pararosaniline chloride is a derivative of the triphenylmethane structure and is also known as benzeneamine 4-(4-aminophenyl)(4-imino-2,5-cyclohexadian-1-ylidene)-methyl monohydrochloride, paramagenta, magenta or basic fuchsin. The properties, structure and absorption spectra of pararosaniline chloride dye are given in Table 1. It is an important dye used in biological and chemical assays. It is one of three components of commercial magenta which is used as a dye for coloring textiles (cotton, wool, silks, and acrylics), china clay products, leather, printing inks, and as a filter dye in photography [24,25]. Its special applications include tinting automobile antifreeze solutions and toilet sanitary preparations [26]. This dye is suspected to be carcinogenic in animal experiments [27]. Its occupational and environmental issues are therefore of concern especially the treatment and final disposition of pararosaniline wastes. Kosanić and Tričković [28] investigated the photoassisted degradation of pararosaniline chloride dye using titanium dioxide under visible light illumination. Degradation of pararosaniline chloride dye by ozonation and sonolysis was reported by Martins et al. [29].

In the present study, the photocatalytic decolorization efficiency of various catalysts (TiO_2, ZnO, ZnS and CdS) was compared for the decolorization of pararosaniline chloride dye. After the selection of the most active catalyst for its decolorization, subsequent experiments were conducted to investigate the effects of various process parameters (catalyst loading, pH, and initial dye concentration) on the process performance. Further the study has been extended to explore the applicability of this system for the decolorization of hydrolysed dye solution and simulated dyebath effluent.

Table 1
Properties and absorption spectra of pararosaniline chloride dye

Name	Pararosaniline chloride
Other name	Para magenta
C. I. name	Basic Red 9
Nature	Basic dye
λ_{max}	540 nm
Empirical formula	$C_{19}H_{18}C_lN_3$
Molecular mass	323.82 g mol^{-1}
Molecular structure	
UV-visible spectra	

2. Experimental methods

2.1. Materials

Titanium PC-105 (Average elementary crystallites — 15–25 nm) was gifted by Millennium Inorganic Chemicals, France and was used as received. ZnO (5 $m^2 g^{-1}$, assay (ZnO) 99%) was purchased from Merck, India and was used without further purification. CdS (assay (CdS) 99%) and ZnS (assay (ZnS) 98%) were purchased from S.D. Fine Chem. Limited, India. Pararosaniline chloride dye was obtained from Loba Chemie (India) and was used as received. Other chemicals required for the preparation of the simulated dyebath effluent (NaCl, Na_2CO_3, NaOH, EDTA and CH_3COOH) were obtained from Merck, India. Double distilled water was used for preparation of vari-

Table 2
Composition of the simulated dyebath effluent

Dye, mg L^{-1}	25
NaCl, g L^{-1}	1.2
Na_2CO_3, mg L^{-1}	5
NaOH, mg L^{-1}	5
EDTA, mg L^{-1}	10
CH_3COOH, mg L^{-1}	5

ous solutions. The pH value of the solutions was adjusted with 1 M HCI or 1 M NaOH.

Three types of dye solutions were prepared, all at a dye concentration of 25 mg L^{-1}: (a) the unhydrolysed dye in aqueous phase; (b) the hydrolysed dye in aqueous phase; (c) the unhydrolysed dye in simulated dyebath liquor. The composition of the simulated dyebath effluent is given in Table 2. A solution of unhydrolysed dye in this medium was prepared by mixing the components at room temperature and used as such. Conversion of the dye into its hydrolysed form was ensured by heating the solution near the boiling point for 5 min and allowing it to cool overnight.

The spectra were taken with UV-vis spectrophotometer (Systronics Model 2202) and chemical oxygen demand (COD) was analyzed with COD meter (WTW Photoflex with thermoreactor CR 3200).

2.2. Photocatalytic reactor

Photochemical degradation of the model compound was carried out in a specially designed double walled reaction vessel (volume 500 mL) in the UV chamber equipped with seven UV tubes each of 18 W (Philips) having a wavelength of 365 nm (detail is given elsewhere – [30]). UV light intensity was measured by UVA light meter (Model UVA-365, Lutron) and it was found to be 0.5 mW cm^{-2}. Constant stirring of the solution was ensured by using a magnetic stirrer. The temperature was maintained constant throughout the reaction time by circulating water in the jacketed wall reactor.

2.3. Irradiation experiments

The photocatalyst was added to 100 mL of dye solution and the suspension was irradiated under UV light. At different time intervals the aliquot was taken out with a syringe and then filtered through Millipore syringe filter of 0.45 µm. Then absorption spectra of the dye solutions were recorded and rate of decolorization was observed in terms of change in intensity at λmax of the dye.

The decolorization efficiency (%) has been calculated as:

$$\text{Decolorization efficiency (\%)} = \frac{C_o - C}{C_o} \times 100 \quad (1)$$

where C_o is the initial concentration of dye and C is the concentration of dye after photoirradiation.

Various parameters which effect the decolorization efficiency such as catalyst loading (0.25 –1.25 g L^{-1}), pH (3–11), initial concentration of dye (5–100 mg L^{-1}) and time (0–30 min) of decolorization were assessed.

3. Results and discussion

3.1. Photodecolorization of pararosaniline chloride dye using different catalysts

Investigations were carried out with different semiconductors viz. TiO_2, ZnO, CdS and ZnS in order to select the most active catalyst for the decolorization of pararosaniline chloride dye. The experiments were carried out using different catalysts at a fixed dye concentration (25 mg L^{-1}), and fixed catalyst loading (1 g L^{-1}) for 30 min of irradiation. Fig. 1 depicts the percentage decolorization of pararosaniline chloride dye using various photocatalysts. The results indicate that ZnO exhibits higher photocatalytic activity than the others. The same trend has been observed in earlier findings with azo reactive dyes [31,32]. Since the bandgap of ZnO is 3.17 eV, the quantum efficiency of ZnO powder is significantly larger than TiO_2 powder and hence higher efficiencies have been reported for ZnO [33]. ZnS has 3.6 eV bandgap energy, the light energy is not sufficient to activate the catalyst. On the other hand CdS has bandgap energy 2.4 eV. The smaller bandgap permits rapid recombination of hole and electron and hence a lesser photocatalytic activity for decolorization is observed. Moreover, the metal sulphide semiconductors are unsuitable based on the stability requirements in that they readily undergo photoanodic corrosion. Besides higher efficiency, the other advantage of ZnO is its low cost. Thus subsequent experiments were carried out with ZnO to optimize the different operational

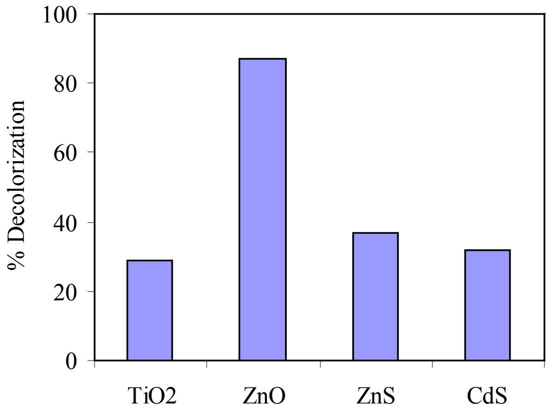


Fig. 1. Comparison for the decolorization of pararosaniline chloride dye using different catalysts (25 mg L^{-1} dye solution, pH-natural (pH 5.26)).

parameters viz. catalyst dose, pH and initial concentration of the substrate affecting the decolorization of dye solutions.

3.2. Decolorization of pararosaniline chloride dye using ZnO as photocatalyst

The experiments were carried out to study the decolorization of pararosaniline chloride dye employing ZnO as catalyst under UV light. Various parameters which affect the decolorization efficiency such as catalyst dose, pH, initial concentration of dye and time of decolorization were assessed.

3.2.1. Effect of catalyst dose

The effect of catalyst loading on the decolorization efficiency of pararosaniline chloride dye was examined by varying its dose from 0.25 gL^{-1} to 1.25 gL^{-1}. The results are presented in Fig. 2. The decolorization efficiency increased with increase in the catalyst dose up to 1 gL^{-1} of ZnO and then decreased. The photocatalytic destruction of other organic pollutants has also exhibited the same dependency on catalyst dose [32]. This can be explained on the basis that optimum catalyst loading is found to be dependent on initial solute concentration because with the increase of catalyst dosage, total active surface area increases, hence availability of more active sites on catalyst surface [34]. At the same time, due to an increase in turbidity of the suspension with high dose of photocatalyst, there will be decrease in penetration of UV light and hence photoactivated volume of suspension decreases [23]. Thus it can be concluded that higher dose of catalyst may not be useful both in view of aggregation as well as reduced irradiation field due to light scattering.

3.2.2. Effect of pH

Fig. 3 depicts the color removal efficiency of pararosaniline chloride dye solution as a function of pH in the range varying from 3 to 11. The maximum decolorization was seen at higher pH (pH ~11). Natural pH (pH 5.26) was also found to be favorable for the decolorization of dye solutions. The interpretation of pH effects on the efficiency of the photodegradation is a very difficult task because three possible reaction mechanisms can contribute to dye decolorization namely hydroxyl radical attack, direct oxidation by the positive hole and direct reduction by the electron in the conducting band. The importance of each one depends upon the substrate nature and pH [19]. The maximum decolorization achieved at pH 11 might be because of the amphoteric behavior of ZnO. At higher pH, electrostatic interactions between the negative ZnO surface and pararosaniline chloride dye cations lead to strong adsorption and thus enhancing the decolorization rate. More efficient formation of hydroxyl radicals also takes place in alkaline conditions. In the acidic pH there was poor adsorption because the catalyst and dye both are positively charged in the acidic media. Therefore decrease in pH causes decrease in decolorization rate. Similar findings have been reported by other workers for the photocatalytic degradation of ethyl violet and basic blue dyes using ZnO [35,36].

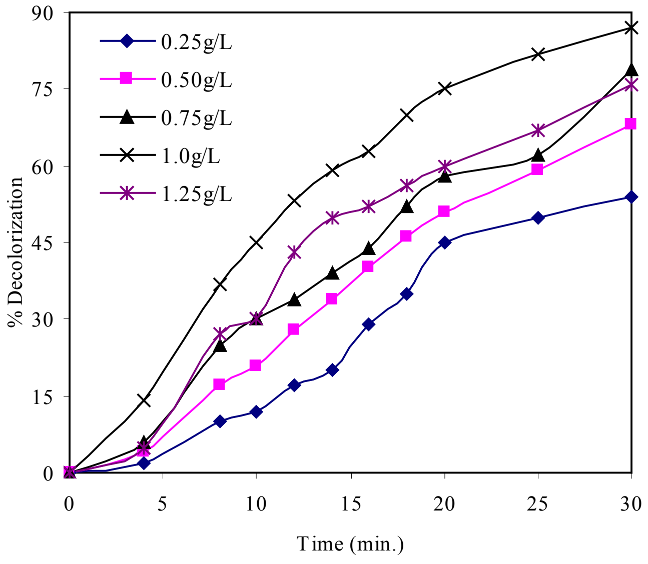


Fig. 2. Effect of catalyst dose (ZnO) for the decolorization of pararosaniline chloride dye (25 mgL^{-1} dye solution, pH natural).

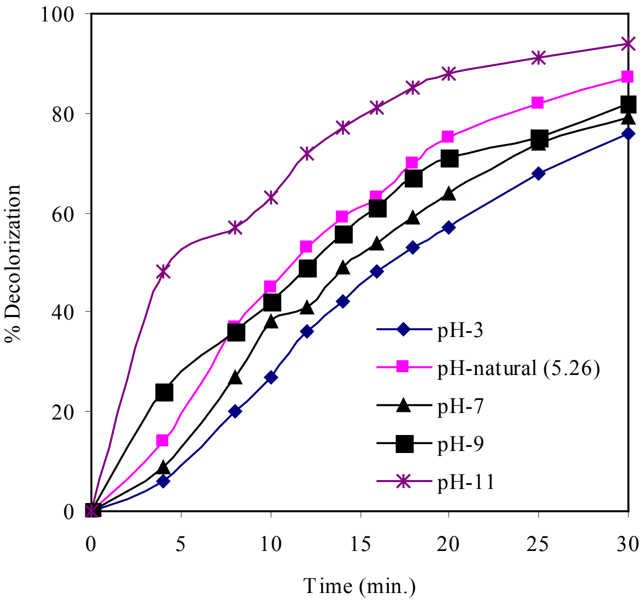


Fig. 3. Effect of pH for the decolorization of pararosaniline chloride dye (25 mg L^{-1} dye solution, ZnO 1 g L^{-1}).

3.2.3. Effect of concentration of dye

After optimizing the catalyst dose and pH (catalyst dose 1 g L^{-1} and pH 11), the photocatalytic decolorization of the dye was carried out by varying the initial concentration from 5 to 100 mg L^{-1} in order to assess the appropriate amount of catalyst dose. As the concentration of the dye was increased, the rate of photodecolorization decreased indicating for either to increase the catalyst dose or time span for the complete removal. Fig. 4 depicts the time dependent graphs of decolorization of pararosanilne chloride dye at different initial concentrations. It can be seen that it takes only 10 min for the complete decolorization of dye, for the initial dye concentration of 10 mgL^{-1}. For 25 mg L^{-1} and 50 mg L^{-1} of the dye solution, the decolorization was 94% and 86% respectively after 30 min of irradiation. The possible explanation for this behavior is that as the initial concentration of the dye increases, the path length of the photons entering the solution decreases and in low concentration the reverse effect is observed, thereby increasing the number of photon absorption by the catalyst in lower concentration [19].

3.2.4. Adsorption studies

In order to investigate the adsorption behavior of pararosaniline chloride dye (unhydrolysed and hydrolysed forms) and its simulated dyebath effluent using ZnO as photocatalyst, the suspension was kept under dark conditions of stirring for a given time under optimized conditions (catalyst dose 1 g L^{-1}, pH 11). The results are shown in Fig. 5. It was noticed that the adsorption equilibrium of the dye solutions was reached in about 15 min of equilibration time. The adsorption was seen to be 21%, 24%, 16% for unhydrolysed, hydrolysed dye solutions and simulated dyebath effluent respectively.

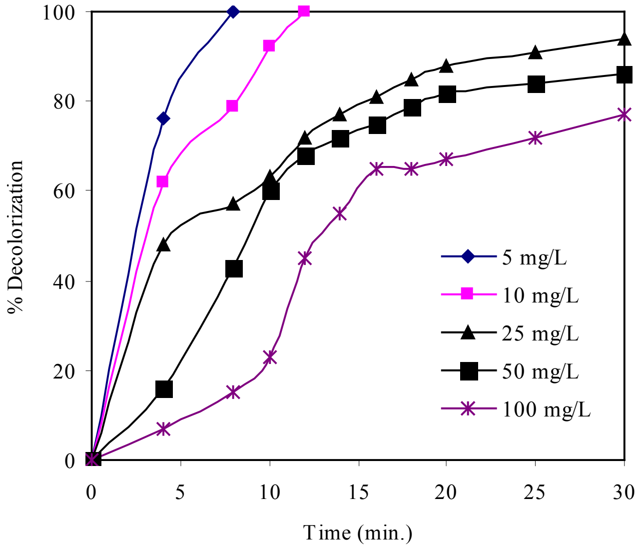


Fig. 4. Effect of initial concentration of dye for the decolorization of pararosaniline chloride dye (ZnO 1 g L^{-1}, pH 11).

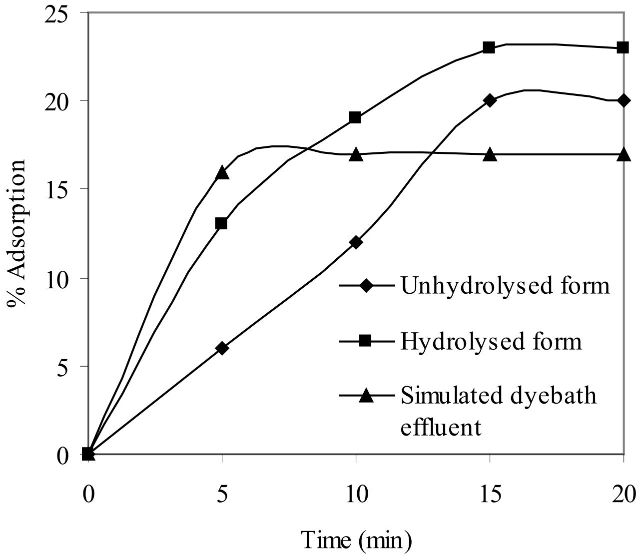


Fig. 5. Adsorption studies for pararosaniline chloride dye in unhydrolysed form, hydrolysed form and silulated dyebath effluent under optimized conditions (ZnO dose 1g L^{-1}, pH 11).

3.2.5. Kinetic study

Fig. 6 shows the kinetics of disappearance of pararosanilne chloride dye for an initial concentration of 25 mgL^{-1} under optimized conditions. The results show that the photocatalytic decolorization of this dye in aqueous ZnO can be described by the first order kinetic model, $\ln (C_0/C) = kt$, where C_0 is the initial concentration and C is the concentration at any time, t. The semi logarithmic

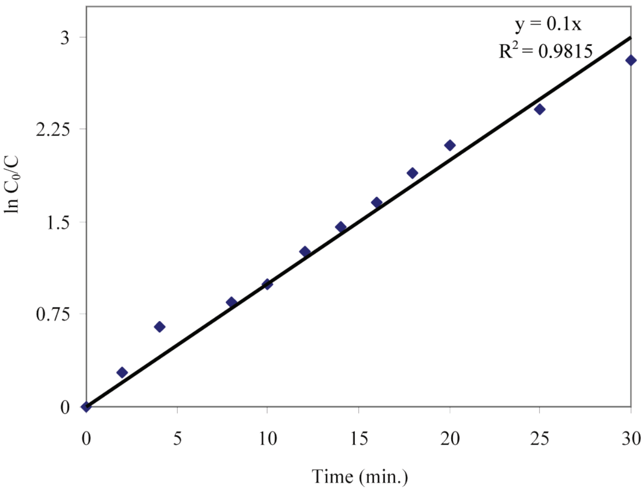


Fig. 6. Kinetic analysis (25 mgL^{-1} dye solution, ZnO 1 gL^{-1}, pH 11).

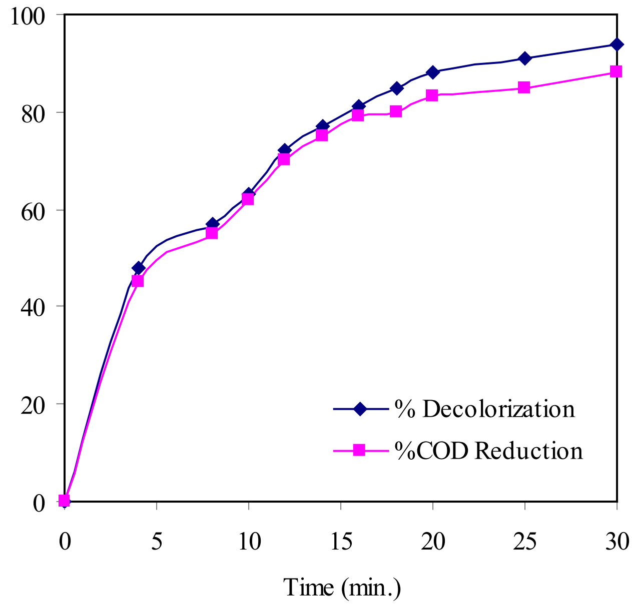


Fig. 7. Comparison of percentage decolorization and percentage COD reduction for pararosaniline chloride dye.

plots of the concentration data gave a straight line. The correlation constant for the fitted line was calculated to be $R^2 = 0.9787$. The rate constants were calculated to be 1.6×10^{-3} s^{-1}.

3.2.6. Mineralization studies

As the reduction of chemical oxygen demand (COD) reflects the extent of degradation or mineralization of an organic species, the percentage change in COD was studied for pararosanilne chloride dye (initial concentration 25 mg L^{-1}) under optimized conditions for 30 min of irradiation. Fig. 7 shows the percentage decolorization and percentage COD reduction as a function of irradiation time. It can be seen that the COD reduction is lesser than percentage decolorization which may be due to the formation of smaller uncolored products. Therefore, it seems that to achieve complete mineralization of dyes, longer irradiation time is required.

Fig. 8 shows the percentage decolorization and percentage COD reduction for the hydrolysed dye solutions. From the results (Figs. 6 and 7), it can be seen that the decolorization rate as well as COD reduction of the hydrolyzed dye solutions is higher than that of the unhydrolysed dye solutions. This is due to the higher concentration of hydroxide ions in the hydrolysed form of dye which lead to the photogeneration of more reactive hydroxyl radical species [37].

3.3. Photodecolorization of simulated dyebath effluent

In an attempt to relate our present study to the real situation arising with effluent from the commercial dyeing of cotton with reactive dyes, it was decided to formulate the simulated dyebath effluent and to test its response to photocatalytic decolorization. The results for the photocatalyzed decolorization and COD reduction of the prepared dyebath effluent under optimized conditions (catalyst dose 1 g L^{-1} and pH 11) are shown in Fig. 9. It was observed that the simulated dyebath effluent decolorized at a somewhat slower rate than hydrolysed

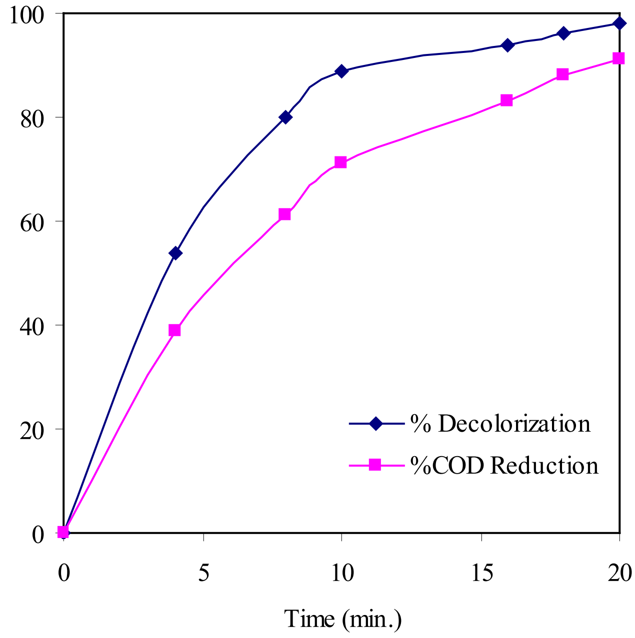


Fig. 8. Comparison of percentage decolorization and percentage COD reduction for hydrolysed pararosaniline chloride dye.

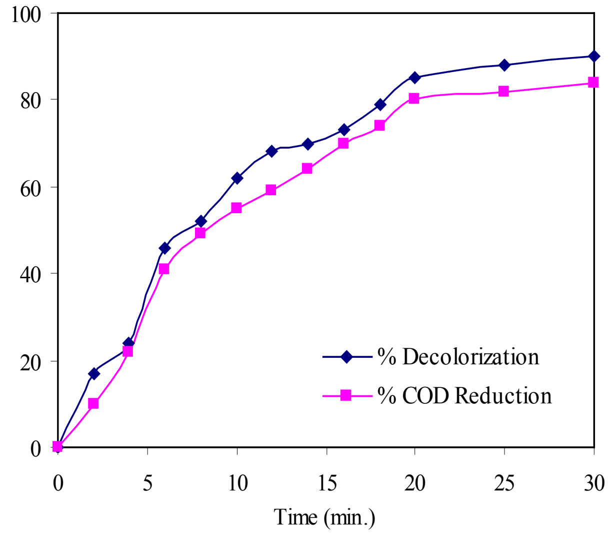


Fig. 9. Comparison of percentage decolorization and percentage COD reduction for simulated dyebath effluent.

and unhydrolysed dye solutions, presumably due to competition from the additives/chemicals in the dye bath. The reduction in COD of the dyebath effluent also confirmed its degradation/mineralization with irradiation time.

4. Conclusions

Heterogeneous photocatalysis has been found to be a promising method for the degradation of pararosaniline chloride dye (either alone or in its hydrolysed form) and its dyebath effluent. Comparison of photocatalytic activity of different semiconductors indicated ZnO to be the most active photocatalyst for the decolorization of this dye. Maximum decolorization of the dye was noticed in basic region with a catalyst dose of 1.0 g L^{-1}. The decolorization of dye solutions followed first order kinetics. The correlation constant for the fitted line was calculated to be $R^2 = 0.9787$ and the rate constant value was calculated to be 1.6×10^{-3} s^{-1}. The rate of decolorization as well as COD reduction was higher for the hydrolysed form of dye than its unhydrolysed solution. It is due to the presence of more hydroxyl radical species in the hydrolysed dye solutions. Simulated dyebath effluent was decolorized at a slower rate as compared to dye solutions either in the hydrolysed form or in unhydrolysed form, presumably due to competition from the additives in the dyebath.

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