

Decolorization of simulated spent reactive dye bath using solar / TiO₂ / H₂O₂

¹S. Sreedhar Reddy and ²B. Kotaiah

¹Center for Environmental Engineering, Vellore Institute of Technology, Vellore, India

²Department of Civil Engineering, S.V.U.College of Engineering, Tirupati, India

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Abstract

Different parameters were investigated to evaluate their effect on the process removal efficiency of reactive dye from simulated spent reactive dye bath, by solar / TiO₂ / H₂O₂, including H₂O₂ concentration, TiO₂ loading and pH. As a result 99% of reactive dye can be removed at a TiO₂ loading of 400mg/l, H₂O₂ concentration of 150 mg/l and of pH: 5.2. The effect of photo-catalytic deactivation of TiO₂ on reactive dye removal was studied for ten number of cycles, and found that the extent of deactivation was high for each consecutive repeated use.

Key words: solar / TiO₂ / H₂O₂, photo catalytic deactivation, irreversible electron acceptors, electron-hole reversal process

*Corresponding Author, E-mail: sreedharreddysajjala@yahoo.co.uk

Introduction

In the last twenty years, an increase of attention has been directed towards the environment. It has been increasingly noticeable the growing awareness of the public in general and particularly of the entrepreneurs, concerning the conditions that have a negative impact over the environment, water quality being one of their main preoccupations (Leonas and Leonas, 1994). This change is due to the deterioration, both qualitative and quantitative, of the existing natural resources caused by the high-untreated discharges from industrial activities and urban agglomerates. Color removal from dyeing plant effluents has been the target of great attention in the last few years, not only because of its toxicity but mainly due its visibility, even at lower concentrations, than many other chemicals found in wastewater (Zollinger, 1987).

Reactive dyes are commercially, a very important class of textile dyes, whose losses through processing are particularly significant and difficult to treat. Under typical reactive dyeing conditions (pH > 10, temperature > 65°C and salt: 60 – 100 g/l) as much as 20-50 percent of the initial mass of the reactive dye remains in the spent reactive dye bath in the hydrolyzed form which has no affinity for the fiber (Swadesh, *et al.*, 2000). Both their low fixation level and removal rate in treatment plants make these dyes a unique and separate class that must be treated as such. Although some existing technologies may have certain efficiency in the removal of

reactive dyes, their initial and operational costs are so great, that they constitute an inhibition of dyeing and finishing industries. On the other hand, low cost technologies do not allow a wishful color removal or have certain disadvantages, being consequently, necessary their integration in a more complex and complete treatment plan, therefore more onerous such as a combination of biological, chemical and physical procedures (Yeh, *et al.*, 1993). Hence, research has been directed to other non-conventional materials and procedures of color removal that will combine effectiveness with cheapness (Laszlo, 1994).

In this study, solar/TiO₂/H₂O₂ oxidation process was employed to see how it resolves the above issues of concern. This photochemical process can generate hydroxyl radicals of very strong oxidizing power, leading to complete destruction of organic contaminants in to innocuous products such as carbon dioxide, water and other non-hazardous halide ions. As reported, this process has been successfully applied in the treatment of jet fuel contaminants from ground water (Turchi, 1993). It appears very attractive to use as an advanced treatment for the decolorization of spent reactive dye bath. Therefore, the purpose of this study was emphasized on the capability of solar/TiO₂/H₂O₂ process to meet the discharge standards for the disposal of spent reactive dye effluents in to water courses.

Materials and Methods

Hydrogen peroxide (30% w/v), and Titanium dioxide used in this study of commercial grade, were purchased from G.G.K. chemicals, Chennai. chemicals used in the preparation of simulated reactive dye bath and in analytical methods were of LR grade, procured from MPM Scientifics, Vellore. Dyes used in the preparation of simulated spent reactive dye bath were procion brilliant blue M. R, procion brilliant Red H-8G and procion turquoise M.G, which are being most commonly used in cotton dyeing industries. They were obtained from ATIC industries, Atul, Gujarat, India.

Preparation of the spent reactive dye bath

To simulate industrial processing the following operating conditions were considered:

Temperature: 65 °C Na₂CO₃: 5 g/l
Time: 1hr. NaCl: 60 g/l
NaOH: 2 g/l HCl: 8.4 ml. of 20% HCl
in one litre

Dye: 6 g/l (2g of procion brilliant Blue M-R + 2 g. procion brilliant Red H-8G + 2g of procion turquoise Blue M-G)

The appropriate amount of dye, NaCl, NaOH and sodium carbonate were weighed and transferred into a beaker and the approximate volume of HCl and tap water added to it. The solution was heated on a stirring plate at 65°C for one hour. Before the treatment experiments could be performed, it is necessary to choose the appropriate concentration of dye solution in the effluent. By assuming 20% dye remains in the combined effluent, 120 mg/l of dye concentration was maintained for all the decolorization studies, by diluting the dye bath by five times.

Scanning Curve

The removal of dye from spent reactive dye bath was determined colorimetrically using spectronic made spectro photometer. The absorbance values of the dye, before and after treatment were measured at corresponding maximum wavelength (max) of 605 nm. Absorbance and dye concentration relationship was determined from the exponential equation. Maximum absorbance and absorbance-dye concentration relationship are given in Figs. 1 and 2.

Procedure for Decolorization Studies

In decolorizing simulated spent reactive dye bath by solar/ TiO₂/ H₂O₂, experiments were carried out in a one litre capacity flexi glass reactor attached

with a speed controlled mechanical stirrer in the open atmosphere. In a typical run, flexi glass reactor was filled with 500 ml. of simulated spent reactive dye bath of known dye concentration. Just after the addition of a known amount of concentrated H₂O₂ [Strength was measured by standard idometric method (Vogel, 1978)] and TiO₂, the reaction mixture was agitated at a speed of 100 rpm. Samples were withdrawn at regular intervals after stopping the agitation for a few seconds to allow the titanium dioxide particles to settle. The concentration of untreated dye in drawn samples was estimated using spectronic made visible spectrophotometer.

Experiments were also done in the absence of TiO₂ and H₂O₂ individually. The effect of operating variables like catalyst concentration, H₂O₂ concentration and pH on decolorization was studied. The effect of catalyst reuse on decolorization was studied for ten cycles. After each batch, the reaction mixture was quantitatively transferred in to a separating funnel, and titanium dioxide particles were allowed to settle by gravity. After complete separation of titanium dioxide particles from reaction mixture, titanium dioxide particles were directly used for the next cycle without pre-treatment.

Results

Decolorization of Simulated spent reactive dye bath by solar / H₂O₂

Experiments for the decolorization of simulated spent reactive dye bath were conducted in the open atmosphere with H₂O₂ alone. Before dosing H₂O₂, the pH of the simulated dyeing plant effluent was adjusted to 7 using 0.1N H₂SO₄ solution. It can be seen from Fig. 3, that with H₂O₂ alone, the percentage decolorization of simulated dyeing plant effluent was nominal, even after three hours of reaction period.

Decolorization of Simulated spent reactive dye bath by solar/TiO₂

Decolorization of simulated spent reactive dye bath was studied with TiO₂ alone for an initial concentration of 1000 mg/l at neutral pH conditions, under open sunlight. From Fig. 4 it is observed that, there was no significant reduction in color in the presence of TiO₂ alone, even after three hours of reaction period.

Decolorization of Simulated spent reactive dye bath By solar / TiO₂ / H₂O₂

The capability of solar / TiO₂ / H₂O₂ for the decolorization of simulated dyeing plant effluent is

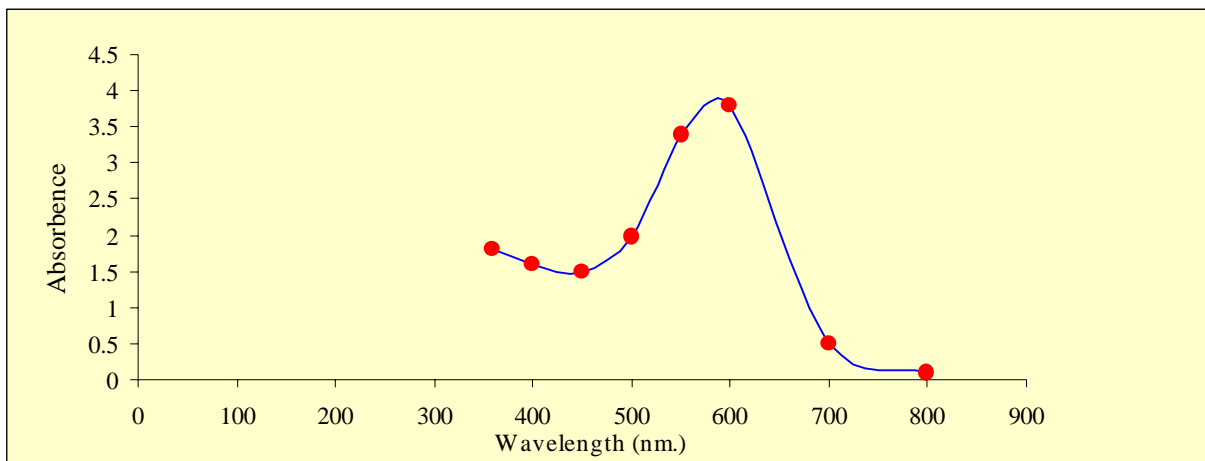


Fig. 1: Wave length Vs Absorbance for simulated spent reactive dye bath

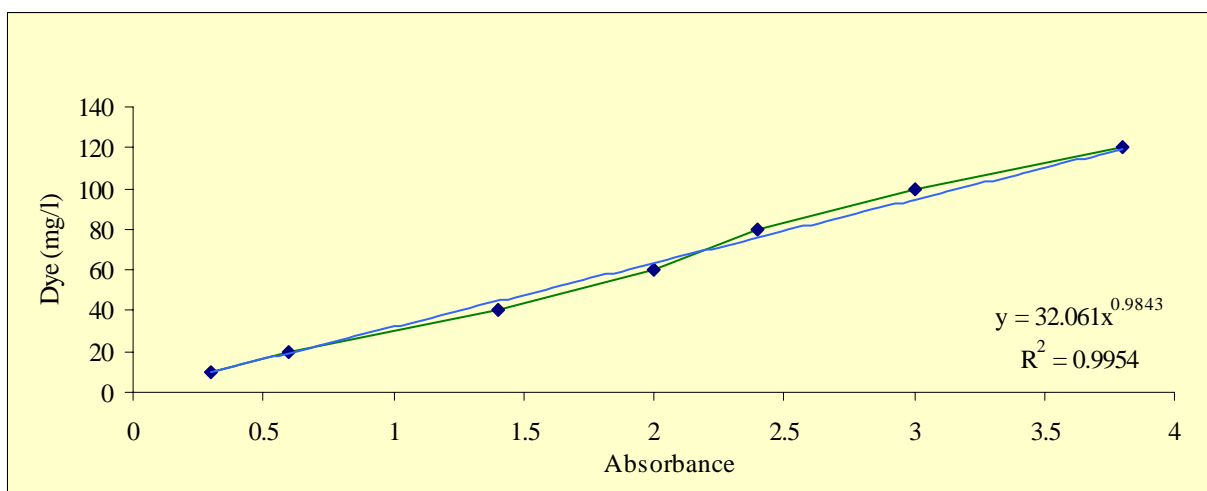


Fig. 2: Absorbance Vs dye concentration

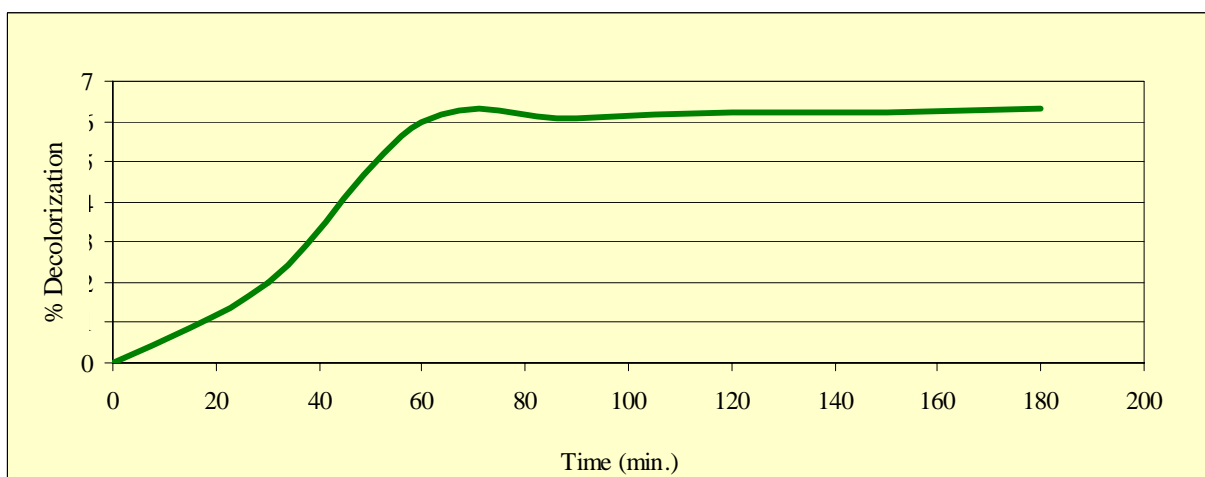


Fig. 3: Decolorization of simulated dyeing plant effluent by solar/H₂O₂

shown in Fig. 5. With 100 mg/l and 1500 mg/l of TiO₂ and H₂O₂, at neutral pH conditions, 60% of the color was removed, in one hour of reaction period. Further, there was no much improvement in the color removal even after three hours of reaction period.

Effect of TiO₂ Loading

The effect of TiO₂ loading in the range of 100 mg/l – 1000 mg/l at neutral pH conditions was studied on the decolorization capability of solar/ TiO₂/ H₂O₂. As shown in Fig. 6 the percentage decolorization was increased up to a TiO₂ loading of 400 mg/l

and beyond that a relative decrease in percentage decolorization was observed.

Effect of pH

The effect of pH in the range of 2 – 7 was studied for the decolorization of simulated dyeing plant effluent at a TiO₂ loading of 400 mg/l and H₂O₂ dosage of 1500 mg/l from Fig. 7, it is observed that lowering the pH of the simulated dyeing plant effluent, significantly improved the color removal efficiency of solar / TiO₂ / H₂O₂ methodology. Lowering the pH from 7.2 to 5.2 improved the color removal efficiency from 91 to 99 percent.

Effect of initial concentration of H₂O₂

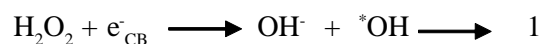
The effect of initial concentration of H₂O₂ in the range of 500 mg/l – 4000 mg/l was tested on the rate of decolorization, for an initial dye concentration of 120 mg/l and 400 mg/l of TiO₂ loading. Fig. 8 illustrate that rate of color removal was improved with H₂O₂ concentration up to 1500 mg/l At this concentration color removal efficiency was 99 %. A further increase in H₂O₂ dosage did not increase the color removal efficiency. Another series of experiments was also conducted in parallel using 1000 mg/l of TiO₂ and H₂O₂ dosage ranging from 400 mg/l – 5000 mg/l Results are similar to those using 400 mg/l of TiO₂ as illustrated in Fig. 8. The extra dosage of TiO₂ did not appear to have any benefit in color removal.

Effect of reuse of TiO₂

The photo-catalytic deactivation of TiO₂ was studied for the decolorization of simulated dyeing plant effluent under operating conditions reported in Table 1. After each batch (batch time equals to one hour of reaction period), the reaction mixture was quantitatively transferred in to a separating funnel having whattman 42 filter paper and TiO₂ particles were separated by filtration. After complete separation, TiO₂ particles were directly taken from separating funnel in to the reactor and used without washing and drying after each repeated use. In the repeated use, the rate of decolorization (k, mg/l.s) of simulated dyeing plant effluent was lowered by 10% than the corresponding value of K for fresh TiO₂. There after, from Fig. 9 it was found that the extent of deactivation was high for each consecutive repeated use. The value of 'K' in the tenth repeated use was found to be less than 90 percent, compared to the corresponding fresh TiO₂.

Discussion and Conclusion

In the absence of TiO₂ in solar / TiO₂ / H₂O₂ only nominal amount of color was removed from simulated spent reactive dye bath, even after three hours of reaction period, due to lack of sufficient hydroxyl radicals. Low molar absorption coefficient of H₂O₂ in the visible region is responsible for the generation of insufficient number of hydroxyl radicals (EPA, 1998). Electron hole reversal process in semiconductor photoconductivity results in the production of photons or heat, instead of hydroxyl radical in aqueous solutions, in the visible region (EPA, 1998). This reversal process significantly decreases the photo catalytic activity of a semiconductor, so that no significant reduction in color was observed in the absence of H₂O₂ in solar / TiO₂ / H₂O₂ process. One possible method of improving the photo-catalytic activity of a semiconductor is by adding Irreversible Electron Acceptors (IEA). Once IEA accepts an electron in the conduction band, dissociate and provide an additional route for hydroxyl radical generation. H₂O₂ is an IEA and illustrates the role that IEA's may play in the advanced photochemical oxidation processes. When H₂O₂ accepts an electron in the conduction band, it dissociates as shown in equation (1).



Therefore H₂O₂ not only inhibits the electron - hole reversal process but also prolongs the life time of the photo-generated hole and generates additional hydroxyl radicals (EPA, 1998).

TiO₂ loading rate, pH of dye bath and initial concentration of H₂O₂ plays a significant role in decolorization of spent reactive dye bath by solar / TiO₂ / H₂O₂. The rise in percentage of decolorization with increase in TiO₂ loading up to 400 mg/l was

Table 1: Operating conditions for photo-catalytic deactivation of TiO₂

Parameter	Condition
Dye	120 mg/l
TiO ₂	400 mg/l
H ₂ O ₂	1500 mg/l
pH	5.2
N	100 rpm
Reaction period	One hour

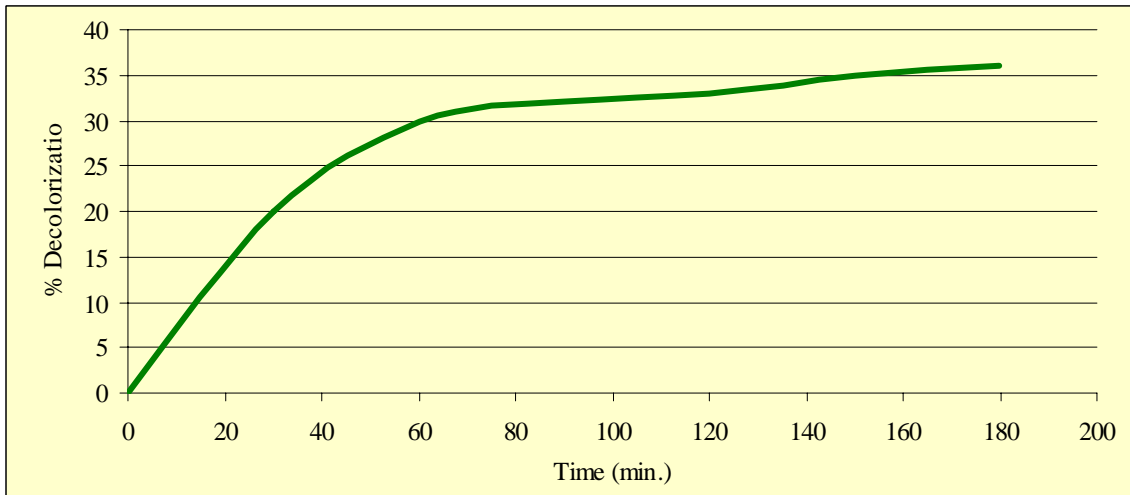


Fig. 4: Decolorization of simulated dyeing plant effluent by solar/ TiO₂

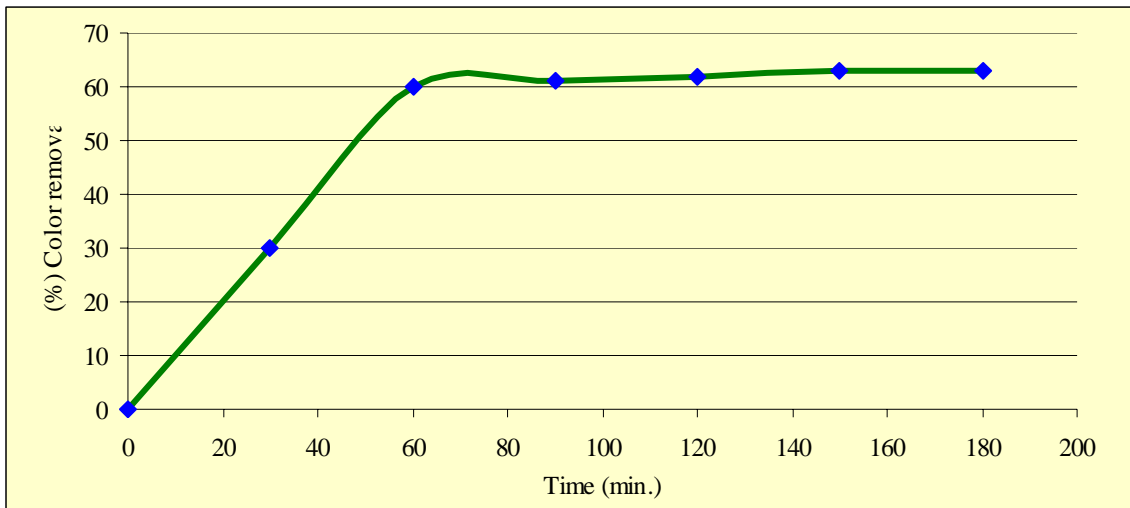


Fig. 5: Percentage color reduction with time using solar/ TiO₂/ H₂O₂ (Operating conditions: dye: 120 mg/l; H₂O₂: 1500 mg/l; TiO₂: 100 mg/l; N: 100 RPM; pH: 7)

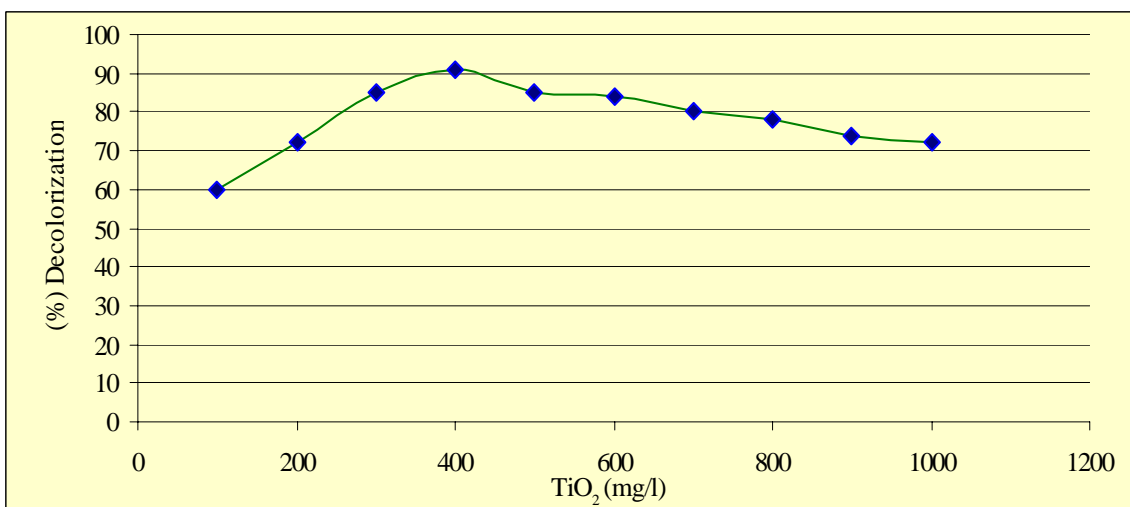


Fig. 6: Effect of TiO₂ loading on decolorization (operating conditions: Dye: 120 mg/l; H₂O₂: 1500 mg/l; N: 100 RPM; pH: 7)

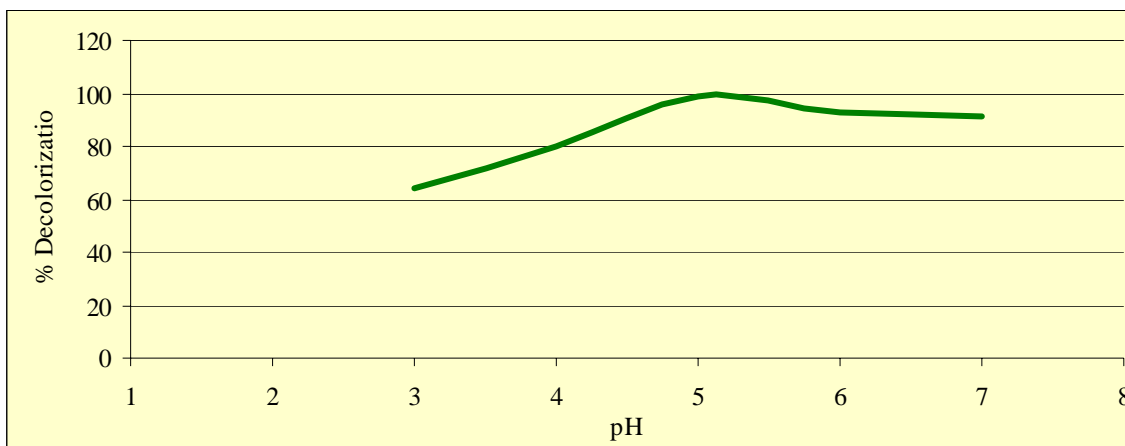


Fig. 7: Effect of pH on decolorization of simulated dyeing plant effluent by solar/ TiO_2 / H_2O_2

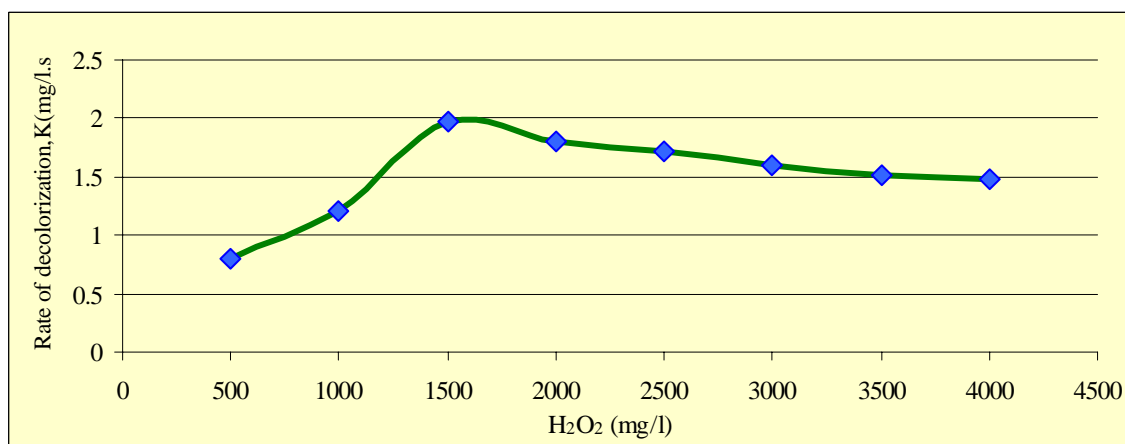


Fig. 8: Effect of initial concentration of H_2O_2 on rate of decolorization (K, mg/l.s)

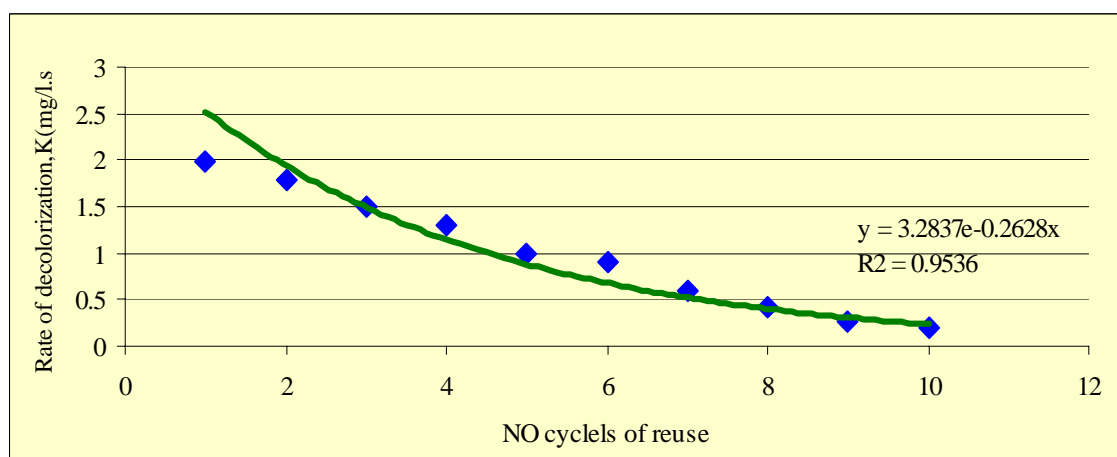


Fig. 9: Effect of TiO_2 reuse on rate of decolorization

primarily due to the availability of higher total surface area of the semiconductor (EPA, 1998). However, a relative decrease in decolorization rates at higher TiO_2 loadings, i.e. beyond 400 mg/l may be due to a fraction of both H_2O_2 and dye molecule being adsorbed on separate particles rather than at

adjacent sites of the same particle and there by not reacting each other (Swadesh, *et al.*, 2000). Lowering the pH from 7.2 to 5.2 improved the color removal efficiency of solar / TiO_2 / H_2O_2 from 91 to 99 percent, due to reduction in the concentration of bicarbonate ion, a known scavenger of hydroxyl

radical in aqueous dye solution (EPA, 1998). Turchi (1993) also observed the similar effect of pH in treating jet fuel contaminants from ground water using solar / TiO₂ / H₂O₂. The drop in color removal efficiency on acidic region i.e. pH<5, is because of the undissociated functional groups of dye molecule (Ivan *et al.*, 2001). The color removal efficiency of solar / TiO₂ / H₂O₂ was improved as the dosage of H₂O₂ increased from 500 mg/l – 1500 mg/l, by keeping TiO₂ loading constant. A further increase in H₂O₂ dosage did not increase the color removal efficiency due to the scavenging of hydroxyl radical by hydrogen peroxide at high concentrations (Buxton, *et al.*, 1988). Effect of reuse of TiO₂ on decolorization capability of solar / TiO₂ / H₂O₂ was studied for ten number of cycles. In the repeated use, the rate of decolorization (k, mg/l.s) of simulated dyeing plant effluent was lowered by 10% than the corresponding value of K for fresh TiO₂. The value of 'K' in the tenth repeated use was found to be less than 90 percent, compared to the corresponding fresh TiO₂. This catalytic deactivation is possible due to the undecomposed dye molecules, which occupies the sites of TiO₂ (Kanmani, *et al.*, 2003).

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