UV Photolytic Decolorization Study of Synthetic Waste Water Containing Indigo Carmine Dye in Presence of H_2O_2

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Abstract

The waste waters containing synthetic dyes could not be treated effectively using conventional technologies owing to the complex molecular structure and stability of synthetic dyes. Use of high energy radiations like UV rays either alone or in presence of H_2O_2 *is considered as the novel technique for treating such effluents. In this work, the photolytic decoloration of aqueous solutions of Indigo carmine dye with UV rays in presence of* H_2O_2 *has been investigated. The extent of decoloration was followed as a function of decrease in absorbance, spectrophotometrically at the* λ_{max} *of 612 nm. The influence of factors such as exposure time, dye concentration and dose of* H_2O_2 *was studied. Results revealed that the effective decoloration could be achieved only in the presence of both i.e. UV rays and* H_2O_2*.The dose of* H_2O_2 *has significant effect on the rate of degradation. There is a critical value of* H_2O_2 *to achieve effective decoloration. As the dose of* H_2O_2 *increased beyond this critical value it was found to have retarding effect on efficiency of decoloration. It was observed that, as the dye concentration increases, the rate of decoloration decreases. For all the dye concentrations, the rate of decoloration was quite high initially, but as the time of exposure was increased, the rate of decoloration was found to be slow and steady.*

Keywords: synthetic dyes, AOP, photolysis, degradation

Introduction

The beauty of colors has fascinated the mankind since ages. Initially the colorants used were natural, obtained from plants, animals and minerals by extraction processes for example, Alizarin is extracted from madder, tyrian purple from snail and ochre, a mineral of Fe_2O_3[1]. These natural dyes had various advantages such as(i) they need no special care(ii) beautiful and rich in tones (iii) need no disposal and hence environment friendly(iv) non carcinogenic (v) requires mild reaction conditions in their extraction and applications etc.[2]. These colors went on to rule the world of colors for many years. But owing to their limitations like lesser availability of colors, poor color yield, poor fastness properties , complex dyeing processing etc.[3]were soon replaced by synthetic dyes around nineteenth century. Due to their superior characteristics like variety of reproducible shades and colors, production in bulk, economical etc. [4], the synthetic dyes gained the popularity in no time and made the world aesthetically more beautiful with their wide range of shades. Soon these synthetic dyes were used extensively in diverse applications that included textile, paper, medicine, leather, cosmetics, and food and beverage industries [5].

Most of these dyes have a complex chemical structure and are very stable and hence persists in nature for a long. The synthetic dyes are produced in extremely large quantities for use in diverse industries mentioned above. There are more than 100,000 commercially available dyes with an estimated annual production of over 7 x10^5 tons [6], and around fifteen percent of these are lost during the manufacturing and application processes [7]. Most of these dyes are toxic and potential carcinogenic, thus posing a severe threat to the environment. Hence their removal from the industrial wastes or effluents is a major concern from environmental point of view [8].

The methods that are generally employed to effect the removal of dyes from effluents include biodegradation, adsorption, coagulation and membrane processes [9-13].But these methods are inadequate to achieve the effective degradation of dyes from industrial wastes [14].Moreover, and they are not environment friendly, as they lead to secondary pollution.

The advanced oxidation processes(A.O.P.'s) has been reported to hold promising future as they are capable of achieving almost complete degradation of dyes from waste waters[15-25].The
common AOP's involve Fenton (Fe^{2+}/H_2O_2, R1) and Fenton-like (Fe^{3+}/H_2O_2, R2) processes, ozonation, photochemical and electrochemical oxidation, photolysis with H_2O_2 and O_3, high voltage electrical discharge (corona) process,TiO_2 photo catalysis, radiolysis, wet oxidation, water solutions treatment by electronic beams or γ-beams and various combinations of these methods [26]. All these techniques are capable of degradation of contaminants to less harmful compounds like oxygenated organic products and low molecular weight acids [27].The functioning of A.O.P.'s involve the generation of highly reactive hydroxyl radical ($^{\cdot}OH$) at a certain stage, which is supposed to be capable for the destruction of pollutants [28].Owing to their high standard reduction potential (2.8V), these $^{\cdot}OH$ radicals are able to oxidize almost all the organic compounds to CO_2 and water. In addition to this, other simple organic compounds such as acids, acetone or simple chloride derivatives are also generated [29] which can be further degraded by various chemical or photochemical reactions.

The present communication explores the effectiveness of UV-H_2O_2 advanced oxidation process in bringing about the efficient decolonization of aqueous solutions of Indigo carmine dye. Some important properties of dye are given in Table 1. The primary use of Indigo Carmine is as a pH indicator. Indigo Carmine is also a redox indicator. It is also used as a dye in the manufacturing of capsules, and in obstetrics, Indigo Carmine-based dye is used to detect amniotic fluid leaks. In surgery, intravenous Indigo Carmine is used to highlight the urinary tract. However, the dye can cause a potentially dangerous increase in blood pressure in some cases. Indigo Carmine is harmful to the respiratory tract if inhaled. It is also an irritant to the skin and eyes.

Table 1 Properties of dye

Sr.	Properties	Description
1.	Molecular formula	$C_{16}H_8N_2Na_2O_8S_2$
2.	Molar mass	466.36 g/mol
3.	C.I.Number	C.I. 73015
4.	Absorption maximum (water)	608 - 612 nm
5.	CAS number	860-22-0
6.	Bulk density	700 - 900 kg/m3

An effort to determine the critical value of H_2O_2 in achieving the efficient decoloration is also made as this dose has found to have major impact on the rate and extent of decolorization.

Experimental

Materials

All chemicals used were of AR grade. The Indigo carmine was procured from HiMedia and was used without any further purification. All the solutions were prepared afresh using double distilled Water.H_2O_2 was used a 30% solution.

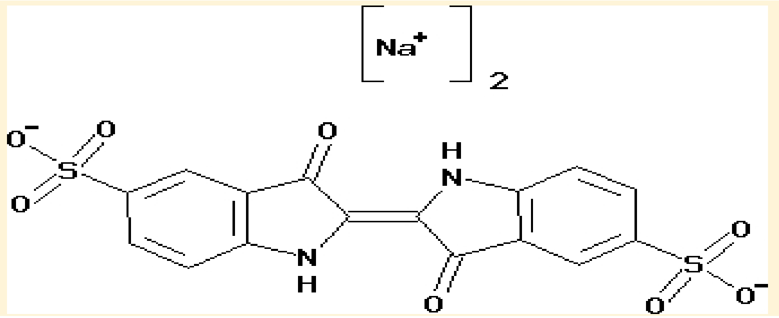

Fig.1 Structure of Indigo carmine Dye

Methodology

The stock solution of Indigo carmine dye was prepared by dissolving 10 mg of dye in 50 ml of doubly distilled water. Three different systems of Indigo carmine dye were prepared by appropriate dilutions to 50 ml. The sample solutions were prepared by transferring 10 ml of each of these concentrations to 50 ml beaker and were exposed to different doses of UV rays alone by placing them in a UV Ray source fabricated, using Hg lamp(12 W). Decolorization of dye solutions was followed as a function of decrease in absorbance of irradiated samples and was measured using Spectronic-D20 spectrophotometer at λ_{max} *of 612 nm.*

In order to study the effect of H_2O_2 on the rate and extent of decolorization, an appropriate concentration of dye solution was selected having medium absorbance. The sample solutions were prepared by transferring 10 ml each of this selected dye concentration to 50 ml beakers and quantity of 30% H_2O_2 was directly added in increasing order to these solutions. On repeating the same procedure, the decolorization was studied. Change in process parameters like pH, conductance on irradiation was noted.

Results and Discussion

Calibration plot

In order to determine the concentration of residual Indigo carmine dye in solution after irradiation, the calibration curve for Indigo carmine dye (as shown in Fig.2.) is prepared .The calibration curve between concentration and corresponding absorbance was found to be linear with regression coefficient of 0.99 at 619 nm.

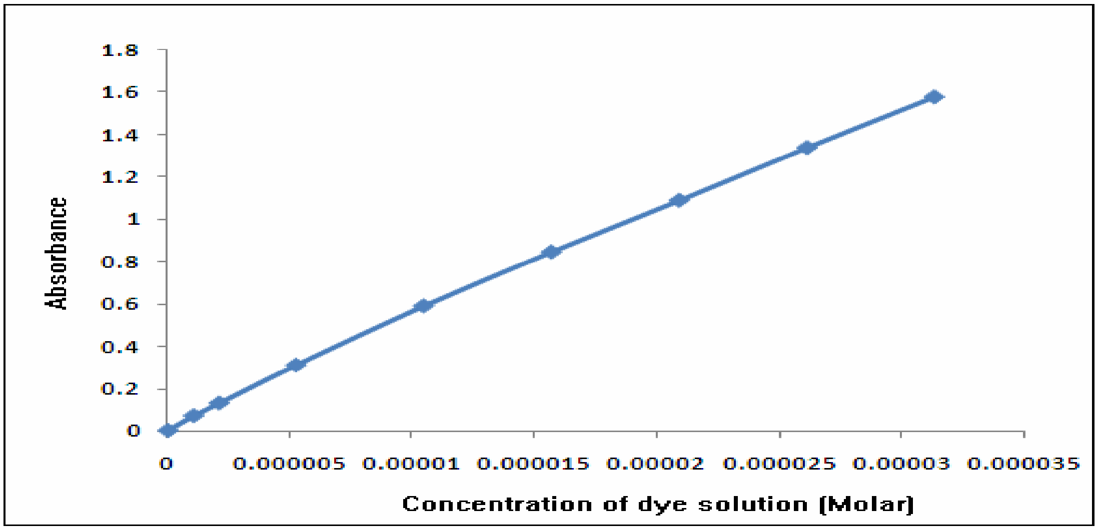

Fig.2 Calibration plot of Indigo carmine dye

Decolorization study using UV rays alone

Fig. 3 shows the percent decolorization of Indigo carmine dye occurred against dose of UV rays exposed without H_2O_2 for different dye concentrations. It can be seen from the graph that, UV rays alone are not effective in bringing about efficient decolorization as only10-25 % decolorization is achieved. For all the concentrations, initially the rate of decolorization is quite slow, which improved for the exposure time between 60-120 minutes indicating that as the dose of UV rays increases, the rate of decolorization also increases and beyond a particular dose there is no significant increase in the rate. It is further observed that, as the concentration of dye increases, the dose of UV rays required for achieving the same extent of decolorization also increases.

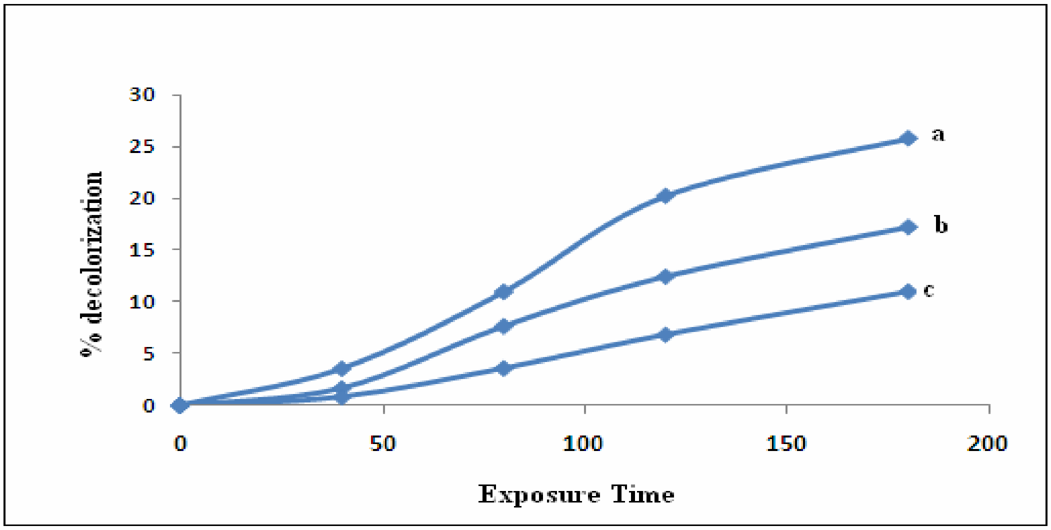

Fig.3 Extent of dye decolorization with only UV-Ray dose exposed

[**a,b & c** represents the concentrations of dye solutions where **a**=$3.43X10^{-5}$M, **b**=$5.46X10^{-5}$M & **c**=$6.86X10^{-5}$M respectively.]

Effect of H_2O_2 on rate and extent of decolorization

The use of UV rays or H_2O_2 alone is not efficient in oxidizing more complex and recalcitrant materials like synthetic dyes. The effectiveness of H_2O_2 can be enhanced when it is used in presence of other reagents or energy sources that are capable of dissociating it to generate hydroxyl radicals, which acts as oxidizing agent. In presence of UV irradiation in wavelengths shorter than 300 nm, H_2O_2 can decompose and generate hydroxyl radicals, as shown in Eq.(1).

$H_2O_2 + h\upsilon \longrightarrow 2HO^{\cdot}$ Eq.(1)

Hydrogen peroxide can also react with hydroxyl radicals and the intermediary products formed thereby, according to the reaction mechanism as described in a simplified way by equations
2-6[30].

$H_2O_2 + HO\bullet \rightarrow HO_2\bullet + H_2O$ Eq.(2)

$H_2O_2 + HO_2\bullet \rightarrow HO\bullet + H_2O + O_2$ Eq.(3)

$2HO\bullet \rightarrow H_2O_2$ Eq.(4)

$2HO_2\bullet \rightarrow H_2O_2 + O_2$ Eq.(5)

$HO\bullet + HO_2\bullet \rightarrow H_2O_2 + O_2$ Eq.(6)

Fig. 4 depicts the effect of addition of H_2O_2 on the rate and extent of decolorization of Indigo carmine dye at a constant dye concentration. Here plots ***p,q,r,s*** and ***t*** represents the extent of decolorization of dye with quantity of 30% H_2O_2 that was added directly to sample solutions in increasing order while plot ***u*** represents the extent of decolorization of dye without H_2O_2.

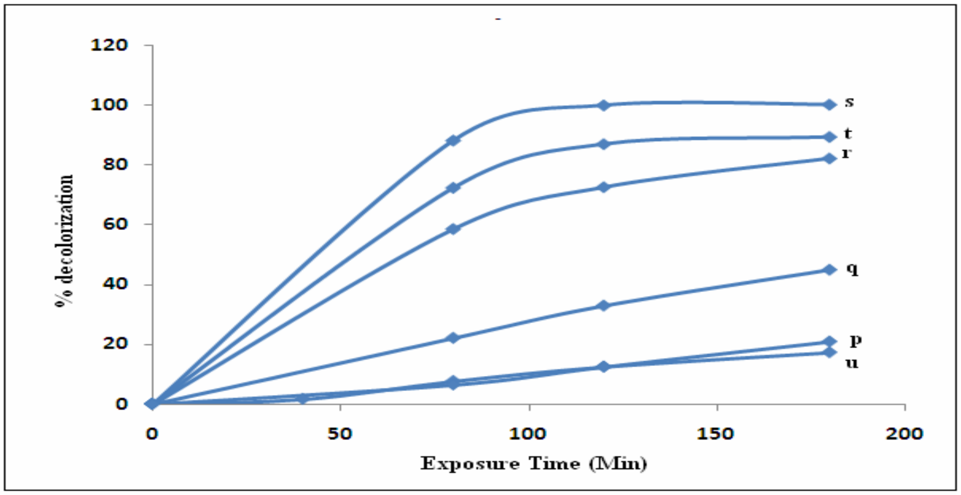

Figure 4 Comparison of extent of decolorization with and without H_2O_2
(Here, p = 1.75mM, q = 17.5mM, r = 90mM, s= 175 mM & t= 350 mM of H_2O_2.)

From the graph it can be seen that, the sudden change in extent of decolorization is observed on addition of H_2O_2 to the solutions. As the dose of H_2O_2 increases, the rate and extent of decolorization also increases. This drastic change in rate and extent of decoloration can be attributed to the generation of highly reactive $OH^{\cdot}$ radicals, which are generated on incidence of UV photon on H_2O_2 as per the eq.(1) above.

It was further observed that, as the quantity of H_2O_2 was increased, the rate and extent of decolorization also increased. For the dose of 175 mM of H_2O_2 the extent of decolorization was maximum. However when dose exceeded this value the rate and extent of decolorization started decreasing. Hence, it can be treated as a critical amount of H_2O_2 in bringing about the effective decolorization in the present study. This decrease in extent may be due to the scavenging of $OH^{\cdot}$ radicals due to H_2O_2 at higher concentration as per equation (2) above.[31-34]

$$HO^{\cdot} + H_2O_2 \longrightarrow HO_2 + H_2O \qquad \text{Eq..(7)}$$

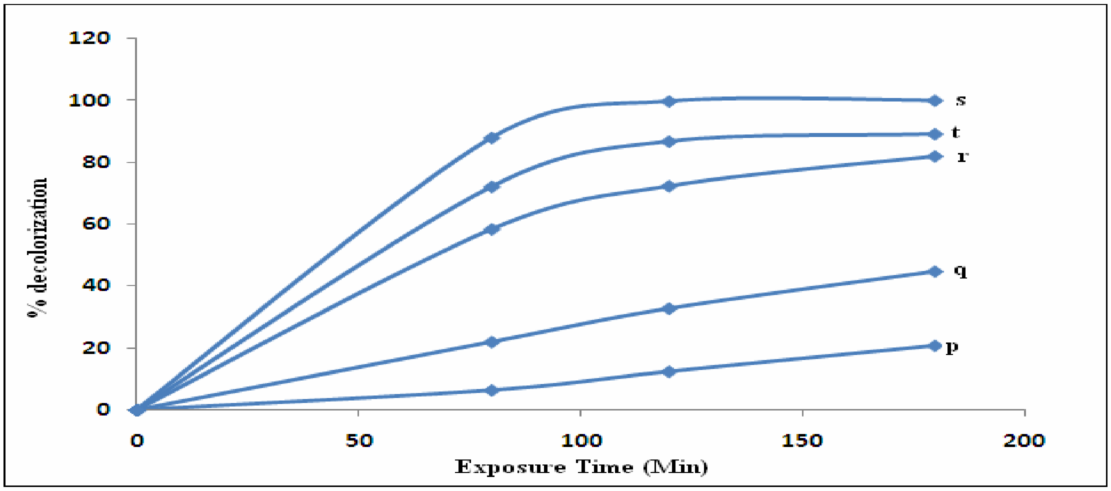

Figure 5 Effect of addition of H_2O_2 on extent of decolorization

The very low extent of decolorization of dye using UV rays alone may be due to fact that the energy of UV rays in this study may not be sufficient to bring about the destruction of dye molecules. The combination of UV –H_2O_2 results into formation of highly reactive $^{\cdot}OH$ radicals in sufficient amounts which are capable of degradation and subsequent decolorization of dye.

Conclusion

In the present study, the decoloration of Indigo carmine dye solutions was achieved effectively only when both UV rays and H_2O_2 were used. The degradation rate and extent increased with increase in concentration of H_2O_2 and reached the limiting value of H_2O_2. At the higher concentration of H_2O_2 the rate and extent of decoloration decreased. This can be explained on the basis of scavenging of OH^- radicals by H_2O_2 at higher concentrations. The pH and conductance of the irradiated solutions was found to change slightly.

Thus, decolorization of dye containing effluents can be achieved effectively by using UV Rays-H_2O_2 advanced oxidation process. The major advantage of this process is that it is a environment friendly clean process as it do not involve formation of any precipitate as well as do not increase the dissolved solid in solutions.

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