



PHOTOCATALYSIS AND PHOTOOXIDATIVE DEGRADATION OF ENVIRONMENTALLY HAZARDOUS CONGO RED (A DIAZO DYE) USING TiO₂

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ABSTRACT

Photocatalysis and photooxidative degradation of congored (CR) diazo dye using UV-light with TiO₂ is reported. CR is a direct dye of diazo series. Samples of oven dried, anatase, rutile and degussa P-25 TiO₂ were used for the photocatalytic degradation experiments. The presence of anatase form of TiO₂ seems to be faster than any other types of TiO₂.

Key words : Photocatalytic degradation, TiO₂, Diazo dye, Photooxidation, Congo red

INTRODUCTION

Azo colouring matters are not only largest chemical class by number but also by volume and weight. A detailed survey of various azo dyes shows a general classification according to the number of azo groups present, which can be divided into mono, bis-, tris-, tetrakis- and higher azo derivatives. Mono and diazo colouring matters are of approximately equal importance, but triazo are less important. Hence, the substance with more than 3 azo groups generally put together as polyazo dyes. Further subdivision is done, first according to whether the sample is water soluble or not, secondly, according to the type of component used. The second method of subdivision is particularly important in diazo compound. Here primary and secondary types are distinguished. The primary type covers compounds made from two molecules of a diazo derivative and one of a bifunctional coupling component. In both the cases the mono functional agents consists of two molecules of the same compound or one molecule of each of two substance used stepwise. The first alternative yielding symmetrical products. In stepwise reaction, it is the rule to carry out the coupling with greater difficulty. Since generally the components contain one or more azo group, they become progressively inert.

In the present study, congo red being a red coloured dye has been chosen for photodegradation. This dye contain two azo ($-N=N-.....-N=N-$) groups. Since, the number of azo groups increased in the molecule, it becomes more inert. Photocatalytic degradation of azo dyes seems to be significantly influenced by their polar nature, the number of azo bonds present

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in the dye molecule and the types of auxiliary groups attached to the azo bond. In literature, it is reported that the triazo dyes were the most difficult to degrade and the monoazo dyes most readily degrade, while the degradation of diazo dyes lies in between¹. It is also reported that other diazo dyes like Disperse yellow and Disperse orange dyes undergoes photodegradation, which will produce a mixture of disubstituted mono azobenzene, partially reduced diazo benzene and many more other intermediates². Since there are many more controversial and ambiguous reports regarding the photocatalytic degradation, the study of this diazo dye has been undertaken. These dyes have strong affinity for protein material and cellulose. Its industrial uses include the dyeing of leather and paper and even for dyeing cotton directly. Congo red is sensitive to acid and it turns from red to deep blue in the presence of strong mineral acids and dull purple by organic acids. This change in colour of congo red is attributed to the occurrence of resonance.

EXPERIMENTAL

Congo red (CR) is a symmetrical primary diazo dye from tetraazo component. Its molecular formula is $C_{32}H_{22}N_6O_6S_2Na_2$. The molecular weight is 697. It is a simple benzidine diazo dye. This red dye can be converted into blue dye by converting it into disodium salt (process of salting out with NaCl). The red salt is used extensively to dye cotton directly. The change in the colour from red to blue in the presence of acid is due to the occurrence of resonance. The preparation of fine grained powders of anatase and rutile has been prepared^{3,4}. The standard solution of CR is prepared by dissolving 1 g/litre of water. The photocatalytic degradation experiments were carried out in a standard quartz cell using a mercury vapour lamp. The amount of CR taken for experiment is 10 ppm with 0.1% by weight of TiO_2 used for the experiment at a constant temperature.

The photocatalytic degradation experiments performed under deaerated condition shows that even after 14 to 15 hours, the amount of CR present in the solution is unaltered. This is an evidence that degradation process is possibly occur only in the presence of oxygen. Samples for analysis were taken out at any desired time interval during the degradation experiment and solution was centrifuged for about 50 minutes to eliminate TiO_2 .

RESULTS AND DISCUSSION

The kinetic data are shown in Figure 1. The photo catalytic degradation experiments were carried out using anatase form of TiO_2 , rutile form of TiO_2 , commercially available degussa P-25 and in the absence of any catalyst. The photocatalysis process without the catalyst takes 12 hours. This is monitored only by measuring O.D. and not with spectroscopy. Anatase form of TiO_2 takes 1.5 hours, rutile form of TiO_2 takes 8 hours and degussa P-25 takes around 5 hours for complete mineralisation. 600°C annealed TiO_2 seems to be the best catalyst even in the case of congo red⁵⁻⁷.

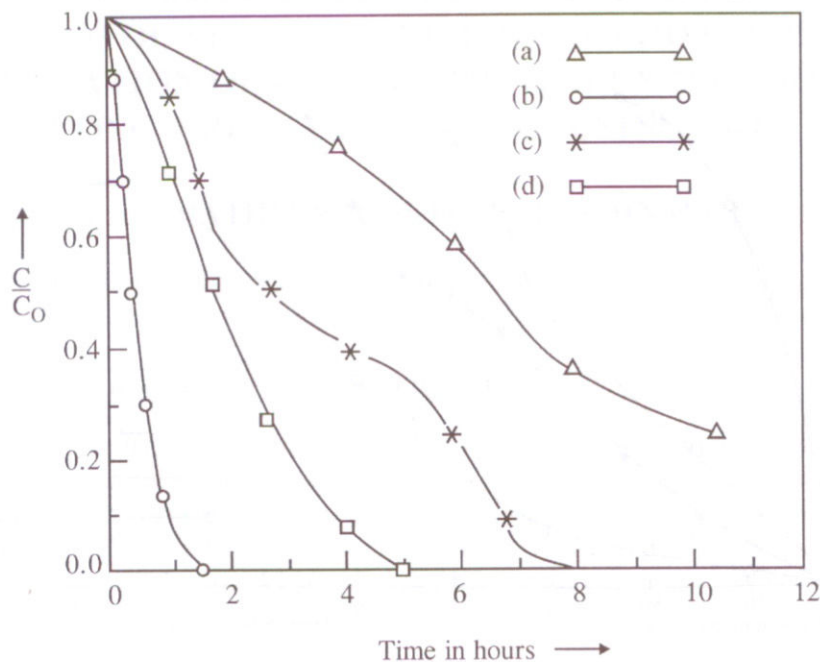


Figure 1. Concentration versus time curves for CR using photocatalyst TiO₂ (a) without catalyst (b) with anatase TiO₂ (c) with rutile TiO₂ (d) with degussa P-25 TiO₂

Further, the samples were taken out from the reaction mixture during irradiation of UV-light at different time intervals. From these data, the amount of congo red dye solution is calculated. The concentrations of CR in original solution is C_0 and the concentration at any desired interval of time is C . The α is calculated using $1-C/C_0$ values. The $d\alpha$ varies with dt , which is tabulated. The rate, $v = d\alpha/dt$ is also tabulated. The photocatalysis and photooxidative degradation of environmentally hazardous congo red dye is faster with anatase form of TiO₂. Therefore, anatase (annealed at 600–650°C) TiO₂ seems to be the best photocatalyst. The plots of α versus time t and rate versus time t for this system are shown in the Figure 2 and Figure 3, respectively. The rate value for anatase form of TiO₂ (600°C annealed) is 1.28 hr⁻¹ whereas it is around 0.18 and 0.28 hr⁻¹ for rutile and Degussa P-25 TiO₂ samples, respectively, which is nowhere comparable to the anatase form of TiO₂.

The degradation process was followed by UV-Visible spectrophotometry. The samples were withdrawn at different intervals of time during the irradiation of UV-light. Four prominent peaks were observed. The peaks at 190.0 nm and 235.5 nm is because of E₂ and B-band of benzene ring present in the CR^{10,11}. The peak at 341.1 nm should be because of azo (-N=N-) group. The peak at 496.3 nm is due to λ_{max} for CR (expected peak at 497 nm)^{12,13}. After illumination for 30 minutes, only one peak persists, this peak is due to the presence of benzene

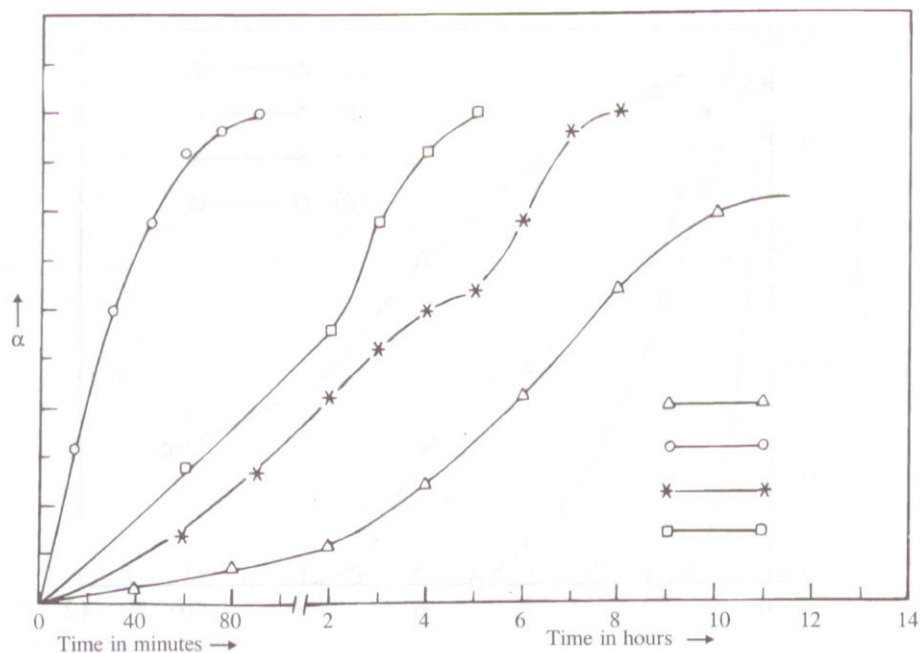


Figure 2. α versus time curves for CR degradation using different types of TiO_2 (a) without catalyst (b) with anatase TiO_2 (c) with rutile TiO_2 (d) with degussa P-25 TiO_2

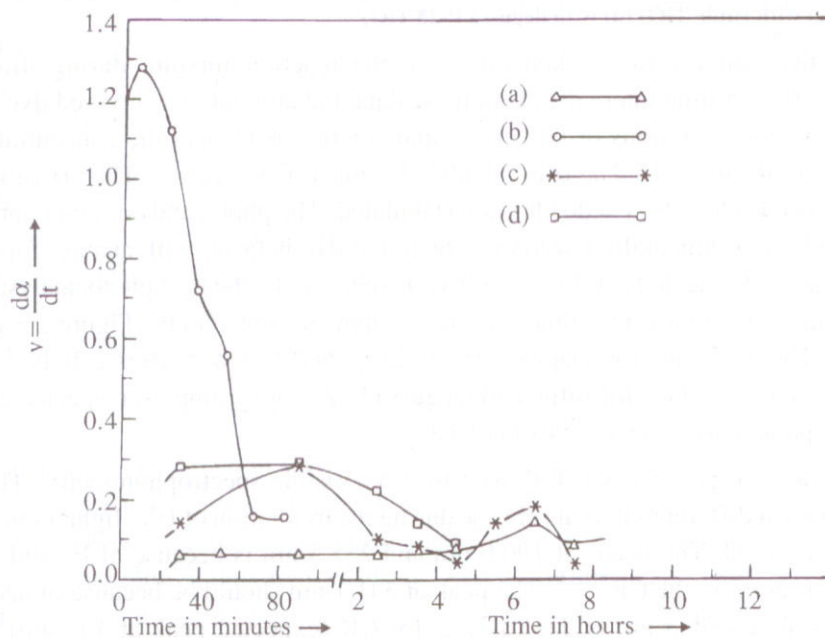


Figure 3. Rate (v) versus time curves for CR degradation using different types of TiO_2 (a) without catalyst (b) with anatase TiO_2 (c) with rutile TiO_2 (d) with degussa P-25 TiO_2

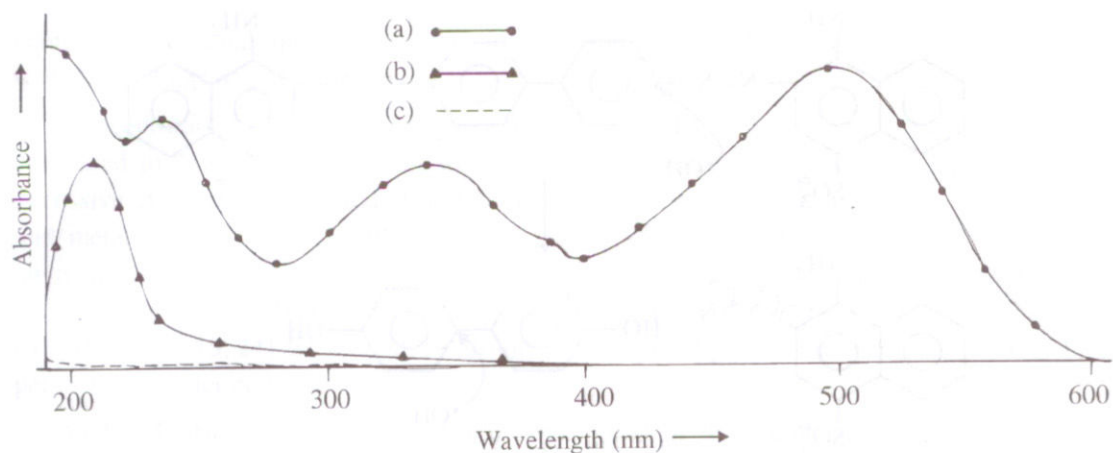


Figure 4. UV-Visible spectra of CR taken during the process of degradation using TiO_2 as the catalyst. (a) pure CR (b) after 30 min (c) after 60 min

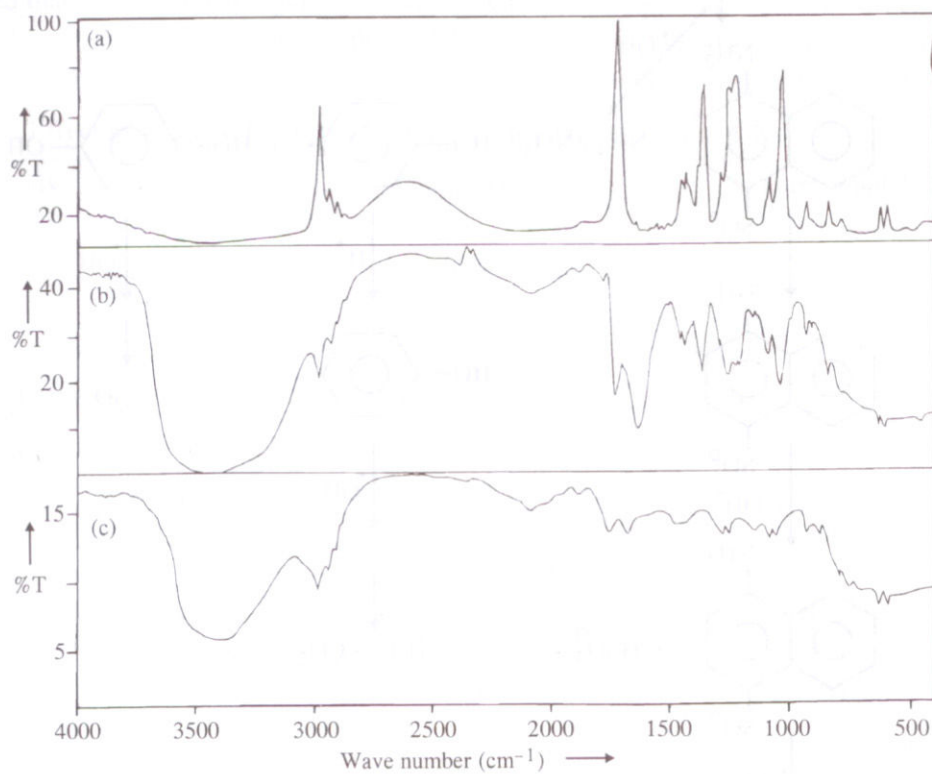
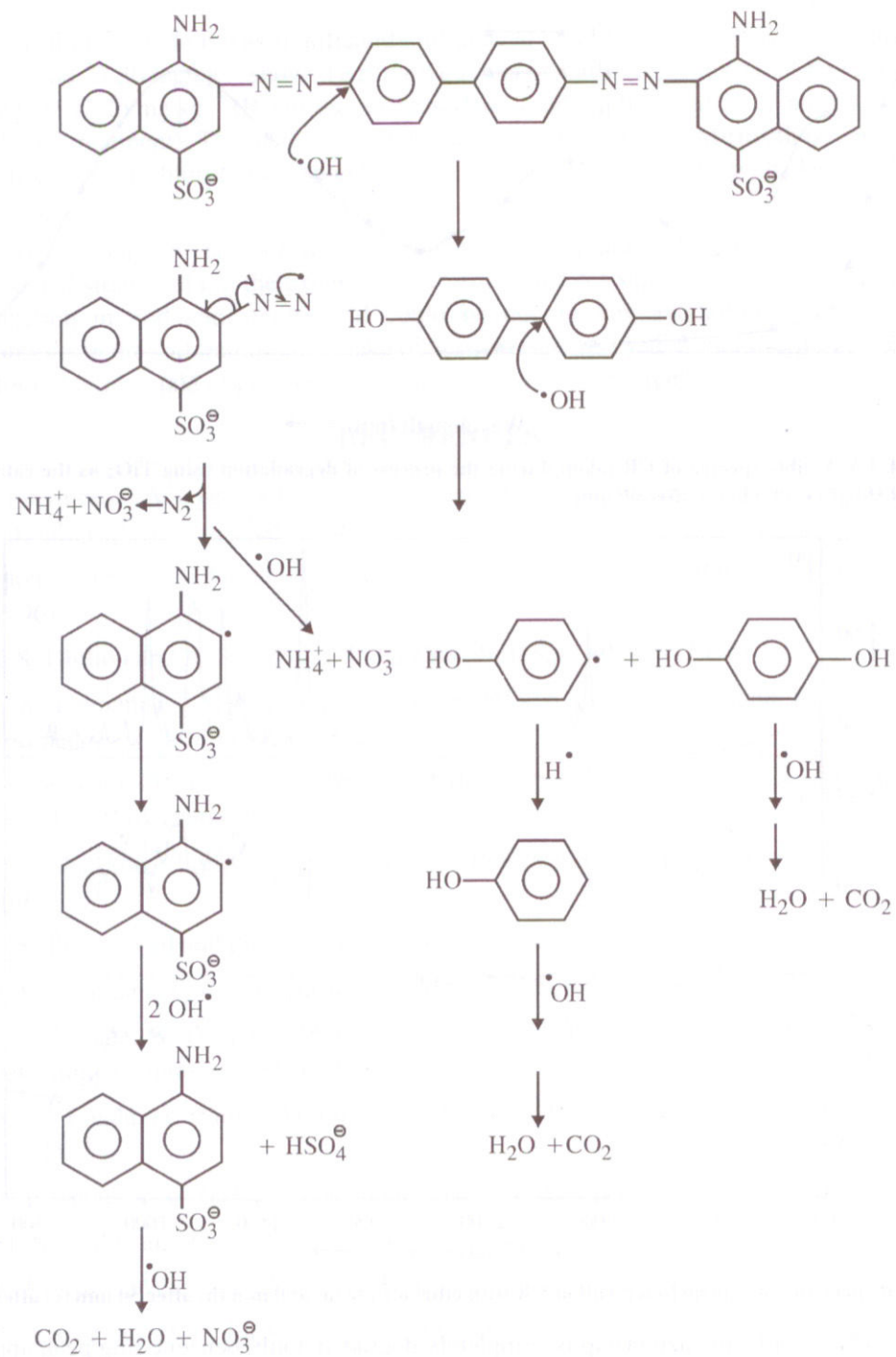


Fig. 5. IR spectrum of subtraction result of CR with ethylacetate (a) at 0 min (b) after 30 min (c) after 60 min ring. In other words, the azo group is completely degraded. Only benzene ring peak appears at 208 nm. This also completely disappeared after 1 hour illumination.



Scheme-I

In the IR spectral analysis, the spectrum was recorded for solution of 10 ppm concentration of CR. The CR from aqueous medium is extracted into ethyl acetate. The spectra obtained for this non-aqueous solution is as shown in Figure 5 (a). The spectra at 30 minutes is shown in the Figure 5 (b). The broad peak in the region 3500 cm^{-1} should be because of $-\text{NH}$ group. The peak observed between $2000\text{--}1500\text{ cm}^{-1}$ is due to the azo group present in the CR. The peaks at $1500\text{--}500\text{ cm}^{-1}$ should be because of benzene ring with its substituents¹³. The spectra taken at 60 minutes, the subtraction result showed no prominent peak at all (subtracting result means, the spectral solution in ethyl acetate minus spectra of ethylacetate), which confirms the complete degradation of CR at 60 minutes.

CONCLUSION

Reaction mechanism for congo red (CR) has been proposed (Scheme I). Reverse phase separation of the photodecomposition products were performed on a High Performance Liquid Chromatography (HPLC) with $150 \times 4.6\text{ mm}$ spherisorb 5 micron Cg column. Gradient elution was performed with 90:10 acetonitrile and water, the flow rate is 1.0 mL/minute. CR takes around 1.5 hours for complete degradation. It was observed that sulphur and nitrogen atoms are converted into sulphate, ammonium and nitrate ions. The other degradation products are not identified^{14,15}. Based on the spectroscopic and HPLC analyses, the following reaction mechanism has been proposed. First the congo red molecule is broken, and in the next step, the destruction takes place within the time period of 30 minutes.

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