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Synthesis, Characterization and Application of $Cu\text{-}TiO_2$ Nanaocomposites in Photodegradation of Methyl Red (MR)

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Abstract: TiO_2 is used as photo catalyst because of its high oxidation power, stability and non toxicity.$Cu\text{-}TiO_2$ nanocomposites was prepared by a adopting the solution impregnation method. After characterization for crystalline phase and particle size by XRD analysis, SEM analysis was carried out to seen morphology of samples, Surface area of TiO_2 and $Cu\text{-}TiO_2$ were analysed by BET. Both the prepared TiO_2 and synthesized $Cu\text{-}TiO_2$ nanocomposites were used as photo catalyst in the photo-degradation of methyl red. The Photo-degradation of methyl red in the presence of pure TiO_2 and synthesized $Cu\text{-}TiO_2$ was done. The Photo-degradation of methyl red were investigated at different condition of temperature, concentration and pH. The effective photo-degradation was found in case of methyl red in the presence of $Cu\text{-}TiO_2$ as compared to pure TiO_2 at different conditions. Photo-degradation of methyl is following the pseudo first order kinetics.

Keyword: Photo degradation, methyl red, photo-catalyst.

I. INTRODUCTION

Synthetic dyes are found in a wide range of products such as clothes, leather accessories, and furniture. These dyes are commonly used every day. However, a side effect of their widespread use is that up to 12% of these dyes are wasted during the dying process and enters in the environment. Most of the dyes used in the pigmentation of textiles, leather, paper, ceramics, and food-processing are derived from azo dyes. Dyes are lost with waste water during synthesis and processing [1]. This represents a great hazard to human and environmental health due to the toxicity of azo dyes [2]. The treatment of such pollutants can be achieved by heterogeneous photocatalysis due to its efficiency and low cost as well as to the fact that it allows complete degradation of pollutants to carbon dioxide and inorganic acids [3]. The standard experimental set up for dye degradation, photocatalysis is by using a UV lamp to provide energy for the formation of oxidizing radicals. Photocatalysis is the addition of light to a semiconductor oxide/sulphide that results in electrons moving from the valence band to the conduction band. The electron-hole pairs formed will react with oxygen and water molecules to create superoxide anions and hydroxide radicals that have increased oxidizing and reducing abilities to be used on numerous industrial dye compounds.

Titanium dioxide TiO_2 is a most important nanomaterial which has attracted a great interest due to its unique properties. Titanium dioxide TiO_2 have excellent merits in solar energy transferring and photocatalysis of poison compounds in environment. Further, the strong oxidizing power of the photogenerated holes, the chemical inertness, and the non-toxicity of TiO_2 has also made it a superior photocatalyst [4]. Titania has a large band gap (3.20 ev for anatase TiO_2) and therefore, only a small fraction of solar light can be absorbed [5]. Many attempts have been made to sensitize titanium dioxide to the whole visible region, such as doping with transition metals [6-7], transition metal ions [8], nonmetal atoms [9] and organic materials [10]. Introduction of dopants allows titania to absorb in the visible region but this does not necessarily mean that the doped catalyst has a better photocatalytic activity. In photocatalysis, light is absorbed by an adsorbed substrate. Today, semiconductors are usually selected as photocatalysts, because semiconductors have a narrow gap between the valence and conduction bands. In order for photocatalysis to proceed, the semiconductors need to absorbed energy equal to or more than its energy gap. When tio_2 is irradiated by UV light (400 nm or less), electron is excited to generate electron ($e^–$) hole (h+) pairs. This movement of electrons forms e^-/h^+ or negatively charged electron/positively charged whole pairs. The hole can oxidize donor molecules. In photogenerated catalysis the photocatalytic activity (PCA) depends on the ability of the catalyst to create electron–hole pairs, which generate free radicals able to undergo secondary reactions [11-16].

II. METHODOLOGY

A. Synthesis of Titania by wet chemical method.

In this method, both $TiCl_4$ solution (200 g/l) and NaOH solution (64.5 g/l) was added drop wise to water with stirring. After the resulting solution reaches pH to 7, the slurry was filtered, and the filter cake of tio_2 was washed

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and redispersed in water to prepare 1 M of TiO_2 slurry. Resulting TiO_2 slurry and an aqueous solution of HNO_3 were refluxed at 95°C for 2 h, cooled to room temperature and neutralized with 28% of aqueous ammonia. Then, it was filtered, washed and calcined at 400 °C [17].

$$TiCl_4 + 4NaOH + NH_3 \longrightarrow Ti(OH)_4 + 4NaCl$$
$$Ti(OH)_4 \longrightarrow TiO_2 + 2H_2O$$

B. Synthesis of Cu-TiO_2 nanocomposites

In this study, Cu-TiO_2 nanocomposites were prepared by solution impregnation method. In this method suitable quantity of prepared tio_2 (10 g) was dispersed in alcoholic copper acetate 10% (w/v). The dispersion is agitated continuously for 4 hour at temperature which is just below of boiling point of alcohol. After the treatment the residue was removed through filtration and was sintered for 4 hour in presence of air at 600 °C by kipping it in a silica boat inside muffle furnace. After sintering and slow anilling to room temperature, content was taken out from furnace and was stored in closed and air tight bottles and was used as photocatalyst [18].

$$TiO_2 + Cu(CH_3COO)_2 \longrightarrow Cu - TiO_2$$

C. Characterization

The physical properties of metal oxide semiconductor nanocomposites that may influence significantly their use as photocatalyst are dependent on nature of crystalline phase present. Thus, phase analysis is an important parameter for this study and the prepared samples were subjected to x-ray diffraction analysis on Powder X-Ray Diffractometer (Bruker AXS D8 Advance System, Germany). The observed X-Ray diffractogram of samples were analyzed further to estimate average grain size in the sample by Scherrer's calculation [19].

$$\mathbf{T=K\lambda/ \beta \, Cos \, \theta} \text{ -------------------------------------- } (1)$$

Where, T is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size, K is a dimensionless **shape factor**, with a value close to unity. The shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite, λ is the X-ray wavelength, β is the line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening, in radians. This quantity is also sometimes denoted as $\Delta(2\theta)$, θ is the Bragg angle.

Since the obsorption of light by photocatalyst is the most crucial step in any photocatalysed reaction, and is decided primarily by the band gap energy of material, attempt would also be made to evaluate band gap energy employing a UV spectrometer (UV 2450 Shimadzu).The morphology and size of the titania particles were analyzed by scanning electron microscopy (SEM).

D. Photo-degradation of dyes

In this study by the photo-catalytic degradation of methyl red was investigated. A solution of dye in water: alcohol (3:2 V/V) was prepared and in this solution a suitable quantity of photocatalyst (25g/L) was dispersed. The dispersion was subjected to UV-Visible irradiation for varying duration and after desired irradiation the residual of dye in the solution was determine spectrophotometrically by taken out suitable aliquot of dispersion and removal of photocatalyst by centrifugation. For quantitative estimation of dye concentration, initially calibration curve was obtained and it was utilized to measure the concentration in different unknown sample aliquot obtained at different time. A quantitative estimation of dye concentration spectrometric observation when recorded only at the experimental determines λ max value which is 540 °A [20-22].

III. RESULTS

A. Preparation of TiO_2 and Cu-TiO_2 nanocomposite

Starting with TiO_2 samples of Cu-TiO_2 nanoparticles were prepared. The obtained yield of the product was more than 90% of the expected theoretical yield.

IV. CHARACTERIZATION

A. Phase identification by X-ray diffraction analysis

The obtained X-Ray diffraction patterns of Titania and copper titania are shown in Figures 3.1 and 3.2. The observed pattern of peaks, when compared with the standard JCPDS database, suggested that, in Prapered TiO_2 sample, major peaks at 2θ = 25.5° 37.2, 48.3, and 54.4, which can be indexed to the (101), (004), (200), and (211) crystal facets of anatase TiO_2 (JCPDS File number: 21-1272). Whereas major peaks at 2θ = 26.9° and 28.2° indicate the presence of rutile phase which can indexed to the (110), (121), respectively. In case of Cu-TiO_2 sample, the observed XRD pattern indicates not only a change in the peak intensity, compared to TiO_2, but even the absence of some originally observed TiO_2 peaks [23]. This is, probably, due to the change in the crystallinity and grain fragmentation, when the samples were wet impregnated by copper acetate.

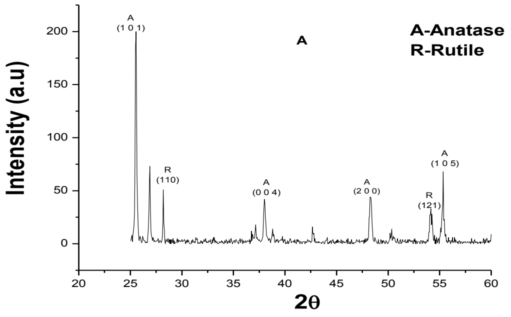

Fig. 3.1 Observed XRD pattern TiO_2

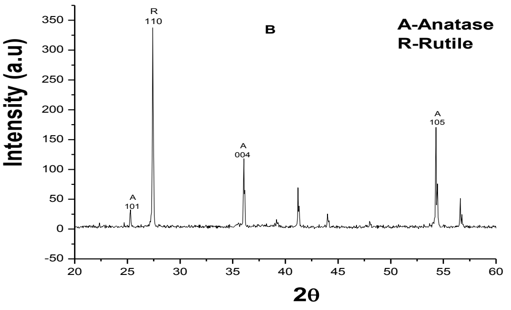

Fig. 3.2 Observed XRD pattern Cu-TiO_2

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B. Determination of Average size of Particles/ Grains in samples

Utilizing the observed X-ray diffraction data of samples, Scherrer's calculations were attempted to know the average size of particles/grains in the samples [19]. Although, Scherrer's calculations are only approximate in nature, but definitely provide a first-hand idea of the average size of the particles/ grains in the samples, which may be quite accurate, provided the size of particles/ grains is below 100 nm. The results of Scherrer's calculations are presented in Table 3.1. The results suggest average size of the particles/ grains in the samples lying in nm range.

Table 3.1:- Average size of particles/grains in the samples of TiO_2 and Cu- TiO_2

Sample	**Particle Size**
TiO2	72
Cu-TiO2	16

C. Scanning Electron Microscopy (SEM)

The morphology of the samples was investigated by scanning electron microscopy and it resumes the most interesting outcomes. 3.3 A and 3.3 B clearly show that both the prepared samples are obtained agglomerate in nanometric dimension. The doping of copper is indicating that the particle size reduce due the penetration of copper in the lattice of titanium dioxide.

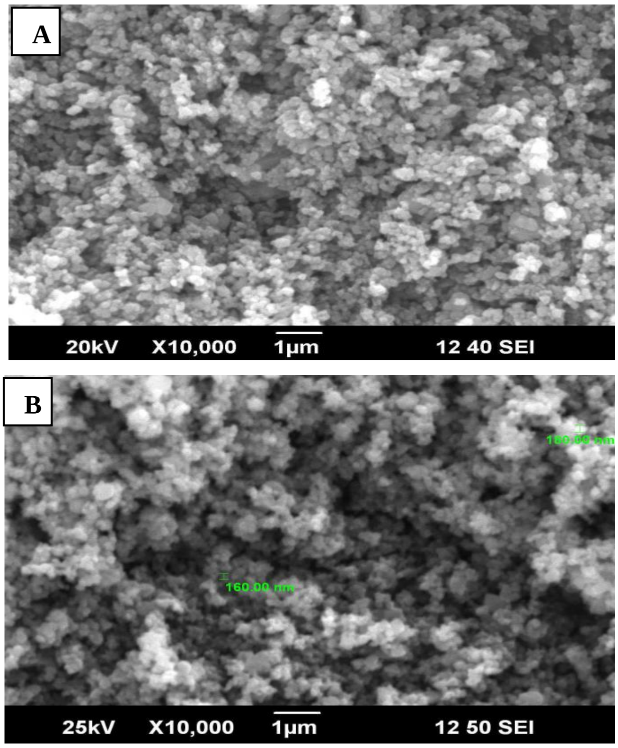


Fig.3.3. SEM image of the (A) TiO_2 (B) Cu-TiO_2

D. Surface Area Analysis (BET)

The specific surface area, pore volume and average pore size of the TiO_2 and Cu-TiO_2 as-prepared photocatalyst were characterized by using the N_2 adsorption technique BET. Table 3.2 summarizes their physical properties. The TiO_2 modified by Copper are fragmentation to some extent during thermal treatment, leading to a marked increase of the BET surface areas and the average pore radius size and decreasing of the pore volume.

Table 3.2:- The specific surface area, pore volume and pore radius of the TiO_2 and Cu-TiO_2

Sample	**Surface area (m^2/g)**	**Pore volume (cm^3/g)**	**Pore radius (nm)**
TiO_2	2.1522	10.132	1.21
Cu-TiO_2	46.685	9.5124	1.64

E. Photo-degradation of Dyes

The photo-catalytic degradation of dye, namely Methyl red in the presence of tio_2 and Cu- TiO_2, as photocatalyst, has been studied. The solutions of dye was prepared in 3:2 (V/V) ratio of water and alcohol. The known amount of photocatalyst 25 g/L was dispersed in the dye solution. The reaction mixture was illuminated under UV – visible light, while kept continuously under agitation, for the different time intervals and different temperature. The residual concentration of dye in the reaction mixture was measured spectrophotometrically. The results obtained for the degradation of Methyl red is shown,in Fig. 3.4 – 3.5.The prominent degradation of Methyl red was found in 3 hour study in the presence of Cu-TiO_2 in comparison to the prepared TiO_2.

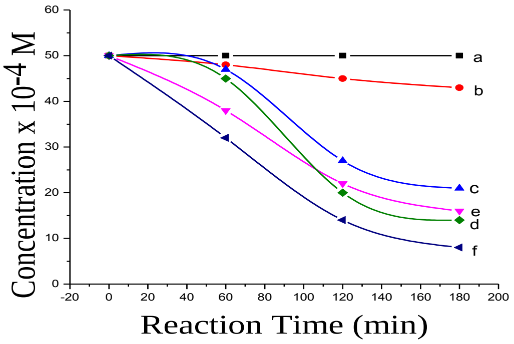


Fig. 3.4 Photodegradation of methyl red at initial concentration $50x10^{-4}$M (a) without photocatalyst at 30°C (b) without photocatalyst at 40°C (c) TiO_2 as photocatalyst at 30°C (d) TiO_2 as photocatalyst at 40°C (e) Cu-TiO_2 as photocatalyst at 30°C (f) Cu-TiO_2 as photocatalyst at 40°C.

F. Effect of Temperature

The effect of system temperature on photocatalysis has not attracted enough attention. But In present research, it is found that the temperature has a great effect on the photodegradation of methyl Red. The photocatalytic efficiency can be increased about 2-3 times if the temperature increased from 30 ℃ to 40 ℃ Because the solar energy include UV light, which can be used to activate the photocatalytic course, which is increase the temperature of photocatalytic system. The experiments showed that Methyl Red cannot be photodegraded if tio_2 or UV light was not used, indicating that Methyl Red cannot be pyrolyzed by heating with the heating temperature which was less than 40 °c and self degraded by absorbing irradiation. Only when TiO_2 and UV light were both used, the Methyl Red was efficiently degraded shown in fig. 3.4-3.5 and 3.6. The obvious decrease of concentration of dye shows that the TiO_2 and Cu- TiO_2 can serve as an effective photocatalyst.

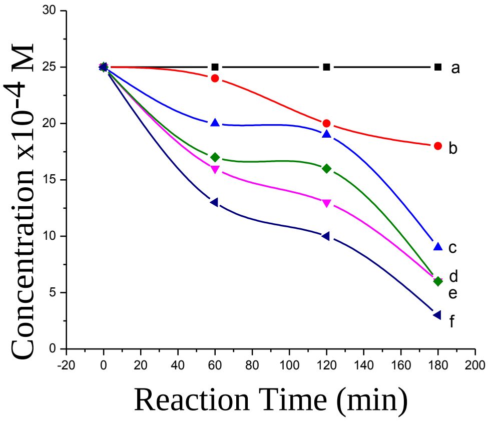


Fig. 3.5 Photodegradation of methyl red at initial concentration $25x10^{-4}$M (a) without photocatalyst at 30°C (b) without photocatalyst at 40°C (c) TiO_2 as photocatalyst at 30°C (d) TiO_2 as photocatalyst at 40°C (e) Cu-TiO_2 as photocatalyst at 30°C (f) Cu-TiO_2 as photocatalyst at 40°C.

G. Effect of concentration of dye

Effect of dye concentration Keeping the catalyst loading concentration constant at 25 g/liter of the dye solution, the effect of varying amounts of the dye was studied on its rate of its degradation (from 50 x 10^{-4} to 25 x 10^{-4} M) as given in Table 3.2 and 3.3. With increasing concentration of MB the rate of degradation was found to decrease. This is because as the number of dye molecules increase, the amount of light (quantum of photons) penetrating the dye solution to reach the catalyst surface is reduced owing to the hindrance in the path of light. Thereby the formation of the reactive hydroxyl and superoxide radicals is also simultaneously reduced. Thus there should be an optimum value maintained for the catalyst and the dye concentration, wherein maximum efficiency of degradation can be achieved.

H. Effect of pH

The photodegradation reaction was also carried out under varying ph conditions from (2 to 7), by adjusting with H_2SO_4 and naoh, with tio$_2$ kept at constant amounts of 25 g/ L of dye solutions (Fig. 3.6). The reaction was found to have low rates at neutral ranges of ph. While at lower cases it was found to increase. This implies that acidic conditions are favourable towards the formation of the reactive intermediates that is hydroxyl radicals is significantly enhanced, which further help in enhancing the reaction rate. On the other hand in neutral medium conditions the formation of reactive intermediates is relatively less favourable and hence less spontaneous.

I. Effect of photocatalyst

It is clear from the results shown in fig.3.4 - 3.5 that both TiO_2 and Cu-TiO_2 are proving as an effective photo-catalyst for the degradation of Methyl Red (MR) dye. However Cu-TiO_2 seems to be more effective as photo-catalyst for the degradation of Methyl Red (MR). The prominent degradation of Methyl red was found in 3 hour study in the presence of Cu- TiO_2 in comparison to the prepaed TiO_2.

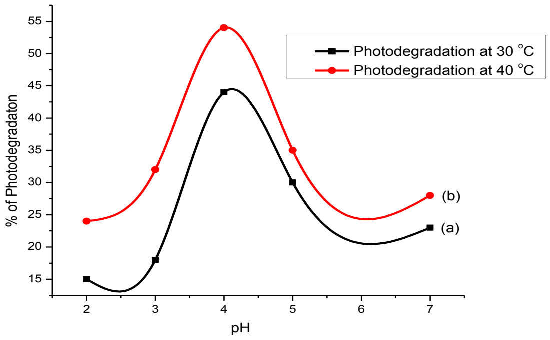


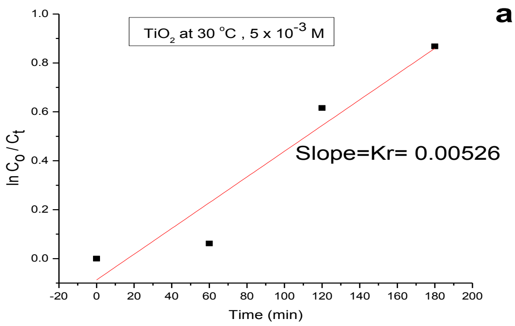
Fig.3.6 Effect of pH (a) Degradation at 30 °C (b) Degradation at 40 °C

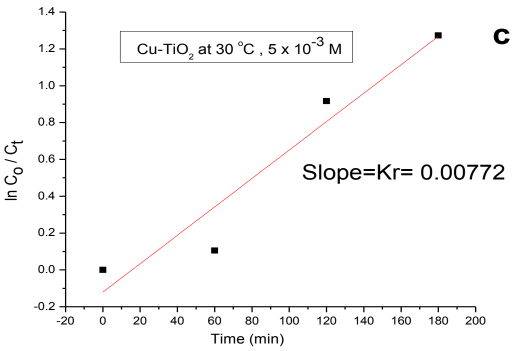
J. Kinetic study

The pseudo-first-order rate constant (k, min^{-1}) for the photodegradation reaction of Methyl Red was determined through the following relation where, k can be calculated from the plot of $\ln(C_o/C_t)$ against time (t), C_o and C_t denote the initial concentration and reaction concentration, respectively.

$$\ln C_o/C_t = k_1t \text{ -----------------------------(2)}$$

In addition, the linear feature of plots of $\ln(C_o/C_t)$ versus time (Fig.3.7 and 3.8) indicates that this photocatalytic degradation reactions follow the pseudo-first-order rate law. The rate constant of the photocatalysis at 30 °c is 0.005260 to 0.01103 min^{-1}.





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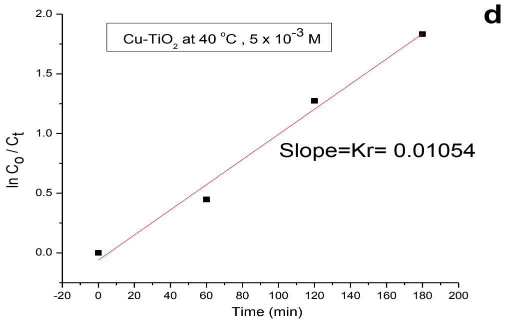
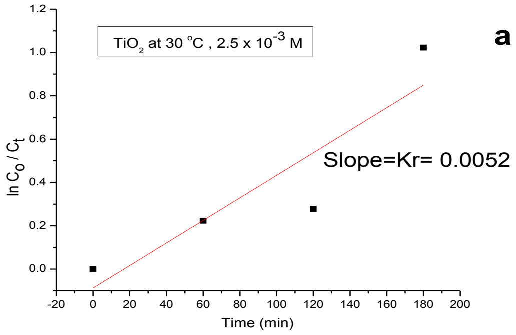
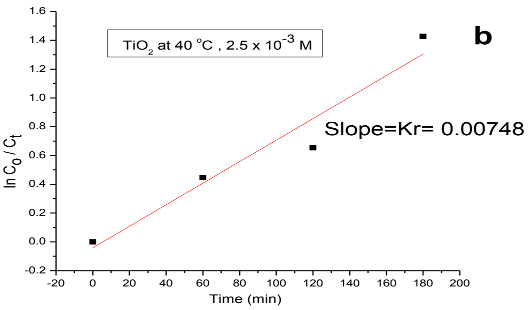
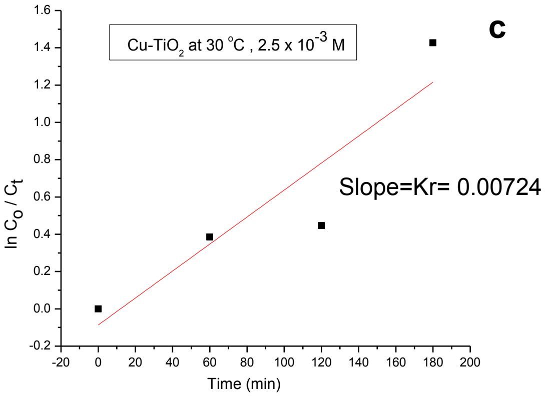


Fig.3.7. The straight line relationship between the ln (C_o/ C_t) and irradiation time (a, b, c and d) indicates photodegradation rate of methyl red (50 x 10^{-4}M) can be approximated by a pseudo first order reaction.







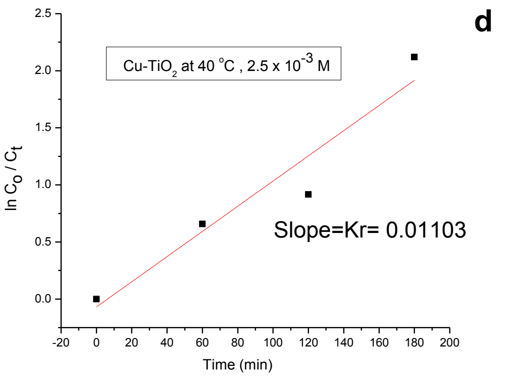


Fig.3.8 the straight line relationship between the ln (C_o/C_t) and irradiation time (a, b, c and d) indicates photodegradation rate of methyl red (25 x 10^{-4}M) can be approximated by a pseudo first order reaction.

K. Thermodynamic Parameter study

In this section an attempt has been made to calculate different activation parameters. For this the reaction has been studied at two different temperatures and with the help of observed rate / rate constant, the energy of activation (ΔE*), specific rate constant (k_r), entropy of

S.No	Metal Oxide Conditions	ΔE* and ΔH*(kjmol^{-1}) x 10^{-3}	Kr (min^1)X 10^{-3}	ΔS*(kjmol^{-1}K^{-1})	ΔG*(kjmol^{-1})x10^2
1	TiO$_2$, 30 ^{o}C, 50 x 10^{-4} M	24.07	5.26	-69.765	18.23
2	TiO$_2$, 40 ^{o}C, 50 x 10^{-4} M	30.23	6.61	-69.463	27.80
3	Cu-TiO$_2$, 30 ^{o}C, 50 x 10^{-4} M	35.33	7.72	-69.154	20.75
4	Cu-TiO$_2$, 40 ^{o}C, 50 x 10^{-4} M	48.23	10.54	-68.535	27.42
5	TiO$_2$, 30 ^{o}C, 25 x 10^{-4} M	23.78	5.2	-69.940	20.98
6	TiO$_2$, 40 ^{o}C, 25 x 10^{-4} M	34.23	7.48	-69.217	27.69
7	Cu-TiO$_2$, 30 ^{o}C, 25 x 10^{-4} M	33.13	7.24	-69.282	20.78
8	Cu-TiO$_2$, 40 ^{o}C, 25 x 10^{-4} M	50.48	11.03	-68.445	27.38

Table 3.7:- Thermodynamic parameters for the photocatalytic degradation of Methyl Red (MR) dye (50x10^{-4} M and 25 x 10^{-4} M) and tio$_2$ and Cu-TiO$_2$(25g/L) under UV light at 30^{o}C and 40 ^{o}C temperature

activation (ΔS^*), enthalpy of activation (ΔH^*), free energy of activation (ΔG^*) and Arrhenius frequency factor (A) have been computed for different reactions. The activation parameters have been calculated with the help of following equations –

$\Delta E^* = \text{value of slope x } 2.303R$

$\log A = \text{Log } kr \text{ (at } 35^0 \text{ C)} + Ea/2.303\,RT$

$\Delta S^* = 2.303\,R(\log A - 13)$

$\Delta G^* = Ea - T\,\Delta S^*$

$\Delta H^* = \Delta G^* + T\,\Delta S^*$

The calculated values of various activation parameters for different redox systems are as follows –

Thermodynamic constants were also evaluated using equilibrium constants changing with temperature. The positive value of ΔG^* indicated the nonspontaneity and the positive values of ΔH^* showed the endothermic nature and negative values of ΔS^* indicated irreversibility of photodegradation of methyl red respectively.

V. CONCLUSION AND DISCUSSION

TiO_2 and Cu-TiO_2 nanocomposites were prepared and used as photo catalyst in the photo-degradation of methyl red. The effective photo-degradation was found in case of methyl red in the presence of Cu- TiO_2 as compared to pure TiO_2 at different conditions. The maximum photo degradation was observed at pH 4. Photodegradation of methyl is following the pseudo first order kinetics. The positive value of ΔG^* indicated the nonspontaneity, the positive values of ΔH^* showed the endothermic nature and negative values of ΔS^* indicated irreversibility of photodegradation of methyl red respectively.

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