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H_2O_2-Assisted Visible Light Activated Photocatalytic Degradation of Aniline and Acetophenone Using Cu_2O

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Photocatalytic degradation of aniline and acetophenone has been studied using Cu_2O as photocatalyst under visible light irradiation. Complete degradation of aniline occurred for 2 h of irradiation and acetophenone degradation to an extent of 90 % occurred for 3 h of irradiation. In both cases, synergetic effect between Cu_2O and H_2O_2 led to faster degradation.

Keywords: Aniline, Acetophenone, Photocatalytic degradation, Synergetic effect, Cu_2O.

INTRODUCTION

Aniline, a common by product of petroleum, coal and other chemical industries such as rubber, polymer, herbicide, fungicide and dyes, occurs as one of the pollutants in ground water wells and surface waters. US Environmental Protection Agency classified aniline as a persistent organic pollutant because of its toxic and recalcitrant nature. Several methods based on adsorption [1], chemical oxidation [2], biological oxidation [3], ozonation [4], reverse osmosis [5], sono-degradation [6], electrochemical oxidation [7], catalytic wet air oxidation [8], Photo-Fenton [9] and combined photo-Fenton & biological oxidation [10] were reported in literature for the removal of aniline. But none of these methods is completely satisfactory because either they generate secondary pollutants or they are energy constrictive making use of UV radiation. In recent times, increased attention is focused on semiconductor mediated photocatalysis for remediation of a wide variety of organic pollutants, because the process is cost effective, yields no hazardous intermediates and amenable for process at ambient temperature. Titanium dioxide has been widely studied as a photocatalyst for degradation of several dyes and other organic pollutants because it can be easily synthesized, low-cost, non photo degradable and chemically inert. Despite these advantages, TiO_2 suffers from some limitations such as wide band gap and rapid recombination rate. To overcome these disadvantages, different approaches have been tried in terms of doping, surface sensitization with more photo absorptive compounds and, fabrication of nano or meso composites with special architectures. Even though these methods succeeded in improving photo catalytic efficiency of TiO_2, they are limited in terms of optimal concentration levels beyond which the dopants themselves act as traps and reduce the photocatalytic efficiency. Alternately, several investigators explored other binary and ternary metal oxide semiconductors that are visible light active namely ZnO, Fe_2O_3, $ZnWO_4$, $Bi_2Mo_3O_{12}$, $Fe_2Mo_3O_{12}$, $BiVO_4$, $Zn_3(VO_4)_2$, $NaBiO_3$, Bi_2WO_6, $Bi_4Ti_3O_{12}$, FeV_3O_8, *etc*. A detailed account of the ternary metal oxide photocatalysts is presented in a recent review [11]. Among the binary metal oxides, Cu_2O is a p-type semiconductor with a band gap of 2.0 to 2.2 eV and easily available. Recently, the authors demonstrated the ability of Cu_2O as a photo catalyst for the degradation mono-, di- and tri-nitro phenols [12] as well as nitrobenzene [13] and some dyes [14]. Present paper describes visible light activated photo-catalytic degradation of aniline and acetopheone using H_2O_2 sensitized Cu_2O.

EXPERIMENTAL

As purchased A.R grade Cu_2O (99 %) was obtained from Sigma Aldrich and A.R grade 99 % aniline and acetophenone were obtained from Merck India Ltd. Phase purity of Cu_2O was ascertained using X-ray diffractometer (PANalytical- X' Pert PRO, Japan) at room temperature with Ni filtered Cu-K_α radiation and a scan rate of 2 °/min. U.V-visible diffuse reflectance spectrum of the sample was obtained using UV-visible spectrophotometer (UV-3600) between 200-800 nm with $BaSO_4$ as reference.

Photocatalytic studies: 100 mg of catalyst powder was added into 100 mL aqueous solution containing 10 ppm aniline/acetophenone. The suspension was magnetically stirred

for 0.5 h in dark. The suspension was then exposed to 400 watts metal halide lamp; 5 mL aliquots were pipetted at periodic time intervals and filtered through 0.45 μ Millipore filters to remove the suspended particles. Extent of degradation was followed by recording the corresponding absorption spectra. All experiments were conducted under ambient conditions. Per cent degradation of pollutant is calculated by using the expression:

$$\text{Degradation } (\%) = \frac{A_0 - A_t}{A_0} \times 100$$

where A_0 and A_t are respectively initial absorbance and absorbance at time't'

RESULTS AND DISCUSSION

X-ray diffraction pattern of Cu_2O is shown in Fig. 1. All the observed peaks could be indexed to cubic Cu_2O of JCPDS File No. 78-2076. Since there are no extra peaks that are not indexed, the sample is considered as phase pure Cu_2O. Fig. 2 shows the UV-visible diffuse reflectance spectrum from which the estimated band gap is obtained as 2 eV.

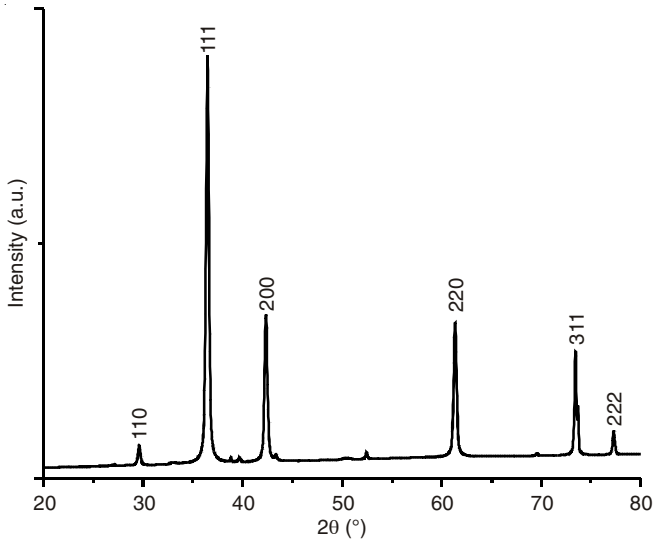

Fig. 1. X-ray diffraction pattern of Cu_2O sample used in this study

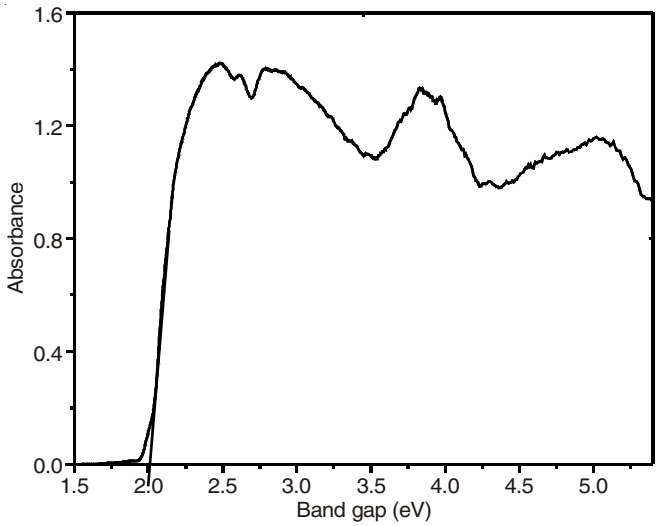

Fig. 2. UVDRS of Cu_2O

Photo catalytic degradation of aniline has been reported with B-doped goethite under UV and visible light irradiation by Liu *et al.* [15], with B-doped MnO under UV radiation by Liao *et al.* [16], with $NaBiO_3$ by Liu and coworkers [17], with Perwinkle shell ash under UV radiation by Aisien *et al.* [18], with TiO_2 by Shahrezaei *et al.* [19], with TiO_2 under UV radiation and by Canle *et al.* [20], with H_2O_2 sensitized $BiVO_4$ under visible light irradiation by Umabala *et al.* [21].

Temporal variation of spectral contours as a function of irradiaton time for aniline, aniline + H_2O_2, aniline + Cu_2O and aniline + Cu_2O + H_2O_2 are shown in Fig. 3. From the figure, it can be seen that aniline shows characteristic absorption at λ_{max} = 230 nm with another small peak at λ_{max} = 280 nm. Aniline does not show any significant photolysis even for irradiation up to 5 h (Fig. 3a). However in presence of H_2O_2, both the peaks get less pronounced, but degradation did not result even after 5 h of irradiation (Fig. 3b). In presence of Cu_2O, aniline shows gradual decrease in intensity with progressive irradiation and after 5 h irradiation, 25 % degradation is noticed (Fig. 3c). In presence of both Cu_2O and H_2O_2 the intensity due to both the peaks got near zero values indicating complete degradation of aniline (Fig. 3d). These results suggest that the observed photo degradation occurs as a consequence of synergetic effect between Cu_2O and H_2O_2 that generates more $^{\bullet}OH$ free radicals which disintegrate the organic molecular structure.

Photo catalytic degradation of acetophenone was reported by Tayade and coworkers [22] using transition metal ion impregnation mesoporous TiO_2 under U.V. irradiation and concluded that both Ag and Ni enhance degradation. Surolia and coworkers [23] reported effect of anions on the photocatlytic degradation of acetophenone over ferric salts/TiO_2 under UV irradiation. Tayade *et al.* [24] reported degradation of acetophenone over anatase and rutile samples separately under UV irradiation. Amarah and Afshar [25] investigated degradation of acetophenone under UV radiation using nano TiO_2 dispersed onto NaX Zeolite. Lewsirisaang *et al.* [26] reported photo catalytic degradation of acetophenone under UV irradiation using TiO_2 powders. Molinari and coworkers [27] reported photocatalytic degradation of acetophenone over Pd-TiO_2 under UV and visible light. Kohtani *et al.* [28] studied photo degradation of acetophenone over coumarine sensitized TiO_2 under visible light. Recently Umabala *et al.* [29] reported visible light active photo catalytic degradation of acetophenone over H_2O_2 sensitized $BiVO_4$. Fig. 4 depicts variation of spectral intensities as a function of irradiation time for acetophenone, acetophenone + H_2O_2, acetophenone + Cu_2O and acetophenone + Cu_2O + H_2O_2.

From the figure, it can be seen that acetophenone exhibits characteristic absorption at λ_{max} =240 nm and undergoes significant photolysis to an extent of 75 % for irradiation of 4 h (Fig. 4a). In presence of H_2O_2, photodegradation to an extent of 51 % is noticed for irradiation 4 h (Fig. 4b). In presence of Cu_2O, 37 % photo degradation of acetophenone is observed (Fig. 4c). However, in presence of both Cu_2O and H_2O_2, 90 % degradation of acetohone is achieved for 3 h of irradiation (Fig. 4c).

The above results indicate that there is a synergetic effect between Cu_2O and H_2O_2 as a result of which degradation is

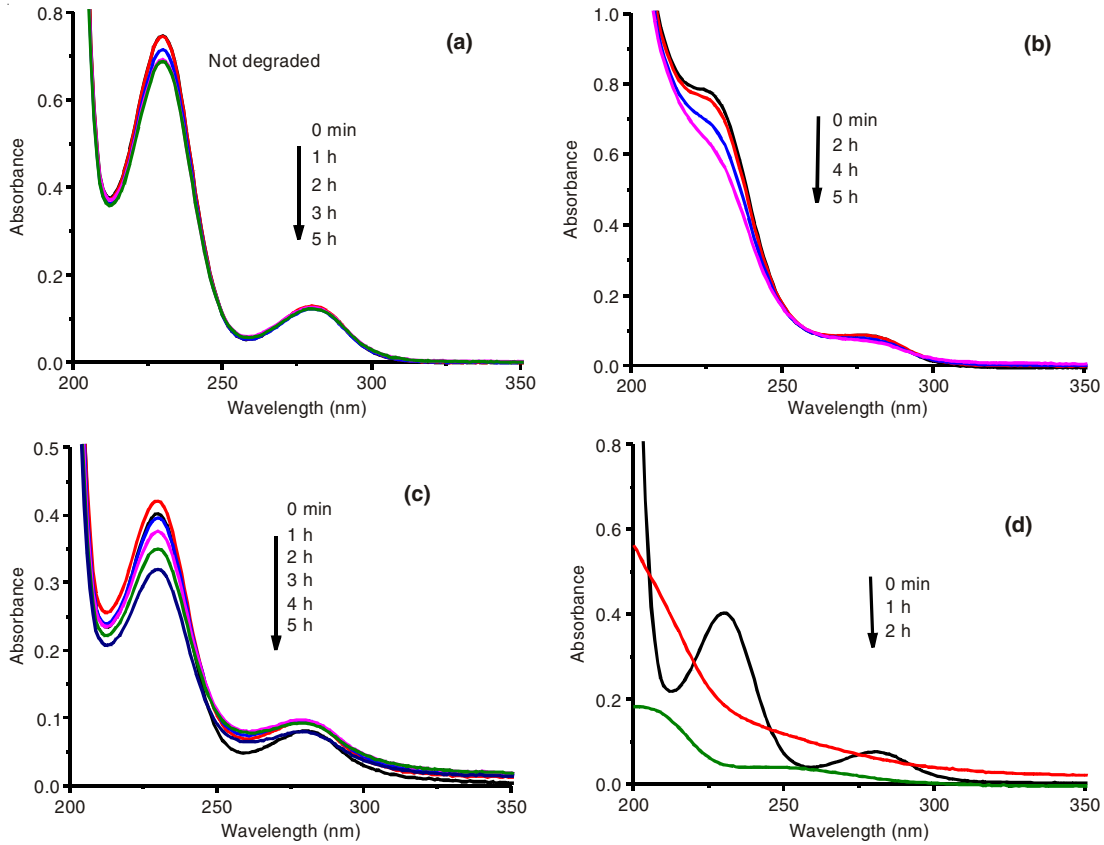

Fig. 3. Variation of spectral intensities as a function of irradiation time for (a) aniline, (b) aniline + H_2O_2, (c) aniline + Cu_2O and (d) aniline + Cu_2O + H_2O_2

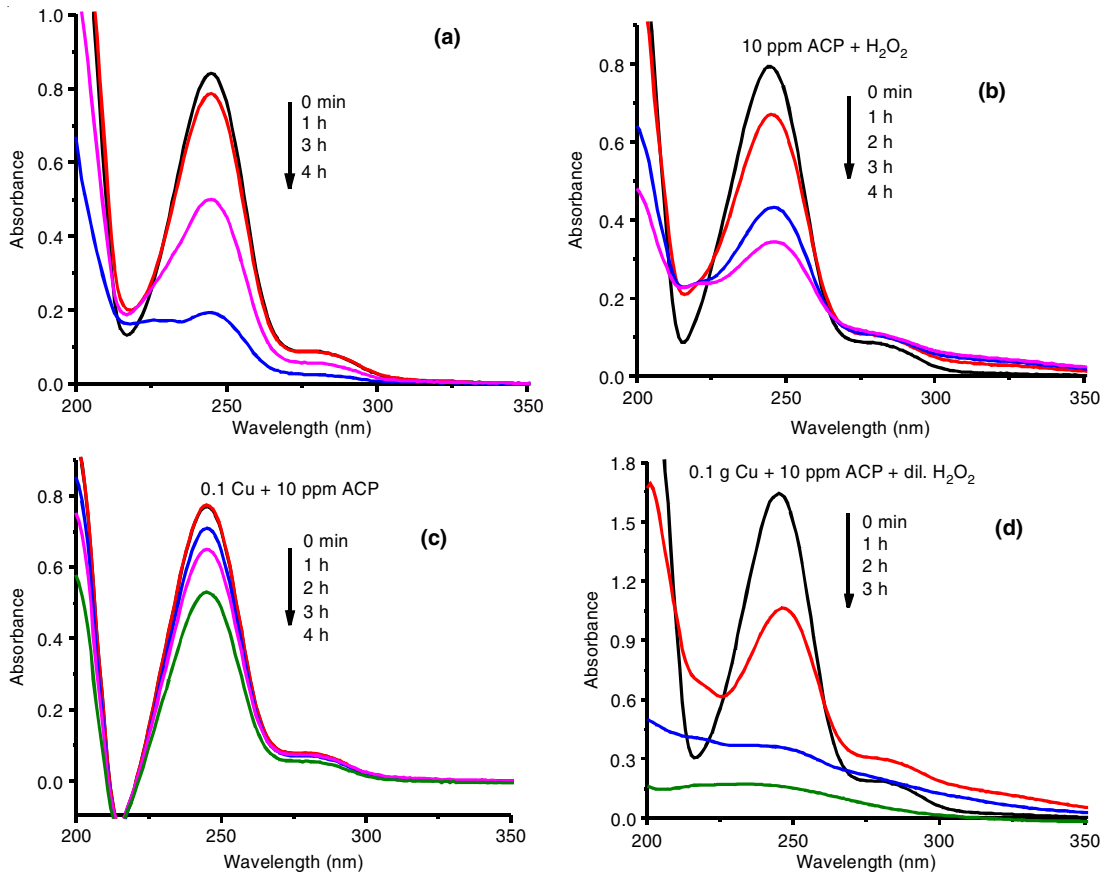

Fig. 4. Time dependent variation of spectral intensities with irradiation time for (a) acetophenone, (b) acetophenone + H_2O_2, (c) acetophenone + Cu_2O and (d) acetophenone + Cu_2O + H_2O_2

enhanced. H_2O_2 is known to be an oxidant, which can react with e^- generated by Cu_2O consequent to absorption of visible light and yield ^-OH ions which subsequently get converted into $^\bullet OH$ free radicals that disintegrate the molecular structure of the pollutant. The possible mechanism involved may be summarized as follows.

$$Cu_2O + h\nu \longrightarrow e^-_{CB}\,(Cu_2O) + h^+_{VB}\,(Cu_2O)$$

$$e^-_{CB}\,(Cu_2O) + H_2O_2 \longrightarrow {}^-OH + {}^\bullet OH$$

$$h^+_{VB}\,(Cu_2O) + {}^-OH \longrightarrow {}^\bullet OH$$

$$\text{Aniline/acetophenone} + {}^\bullet OH \longrightarrow \text{Degradation products}$$

Conclusion

Present study indicates that both aniline and acetophenone can be photocatalytically degraded under visible light irradiation using Cu_2O powdered sample. Complete degradation of aniline occurred for 2 h of irradiation while near complete degradation of acetophenone occurred for 3 h of irradiation. Addition of external oxidant H_2O_2 led to synergetic effect between Cu_2O and H_2O_2.

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