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PHOTOCATALYTIC DEGRADATION OF 2-, 4-AMINO AND CHLORO PHENOLS USING H_2O_2 SENSITIZED Cu_2O AND VISIBLE LIGHT

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ABSTRACT

Photocatalytic degradation of 2-amino phenol, 4-amino phenol, 2-chloro phenol and 4-chloro phenol have been studied under visible light irradiation using Cu_2O as photocatalyst. Complete degradation of 2-amino phenol and 4-amino phenol occurred in 2.0 and 2.5 hrs, respectively. 2-chloro phenol showed only 50% degradation even for irradiation up to 4 hrs while 95% degradation is observed for 4-chlorophenol for 4 hrs of irradiation. In all cases, addition of external oxidant enhanced the rate of degradation and Cu_2O + H_2O_2 showed a synergetic effect. Formation of free radicals which facilitated disintegration of molecular structures of pollutants was ascertained by means of photoluminescence studies using terephthalic acid as probe molecule.

Key words: Cu_2O, Photocatalytic degradation, 2-,4-Amino phenols, 2-,4-Chloro phenols.

INTRODUCTION

Amino phenols are aromatic compounds with -OH and $-NH_2$ groups linked around benzene ring in ortho, meta and para positions. 2-amino phenol (2-AP) is an important intermediate in the synthesis of several dyes, benzoxazoles and agrochemicals. 4-amino phenol (4-AP) is used as precursor or intermediate in many chemical syntheses and also formed in effluents from oil refineries, dyes, lubricants, textiles, rubber and pharmaceutical industries. 4-AP is the primary hydrolytic degradation product of paracetamol, a commonly used antipyretic and analgesic drug. 4-AP is also used in many cosmetic products as well as in hair coloring dyes. Because of their toxic nature, remediation of amino phenols from water resources is highly essential. Similarly, chloro phenols (CPs) are widely used in chemical and wood industries as herbicides, insecticides, fungicides and wood preservatives.

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Among the CPs, 4-chloro phenol (4-CP) is used in the production of dyes, pesticides and drugs. 2-chloro phenol (2-CP) is used in the preparation of phenolic resins, plastics, paints and pesticides. Due to the extensive use, CPs are found in soil, water and environmental organisms. Major sources of 2-CP contamination arise from coal gasification, oil refinery and petrochemical waste water. 4-CP is released into environment as by product of various industries including chlorinated bleaching of paper and chlorination of drinking water and industrial waste water from pharmaceutical and dye industries. CPs cause serious damage to vital organs of human beings. US Environmental Protection Agency (USEPA) has listed five chloro phenols as priority pollutants due to their toxic and carcinogenic nature. Effective remediation of chloro phenols is therefore necessary. Conventional methods used for removal of CPs include biological, chemical and thermal methods of which biological methods require long reaction times while chemical treatments involve precipitation. Adsorption, ion exchange and reverse osmosis require post treatment to remove secondary pollutants. Thermal treatments lead to emission of other hazardous compounds such as dioxins. Advanced oxidation processes, which include Fenton, Photo-Fenton and heterogeneous photocatalytic oxidation seem to be more useful for degradation of pollutants compared to conventional treatment methods. By far, TiO_2 is the longest studied photocatalyst because it is cheap, chemically inert and photo stable. Several methods have been demonstrated to extend the absorption range of TiO_2 from U.V. to visible region. Alternately, several studies relating to heterogeneous photocatalytic degradation are focused on enhancing the photo absorbitivity into visible region of solar spectrum using metal oxides other than TiO_2.[1] Cu_2O is an p-type semiconductor with a band gap in the range of 2.0-2.2 eV and is easily available. Recently, we have reported photocatalytic degradation of rhodamine-B, methyl orange and congo red, nitro phenols, nitro benzene, aniline and acetophenone under visible light irradiation using Cu_2O[2-4]. Present paper describes visible light assisted photocatalytic degradation of 2-, 4-amino and chloro phenols using H_2O_2 sensitized Cu_2O.

EXPERIMENTAL

Materials and characterization

As purchased A.R grade Cu_2O (99%) obtained from Sigma Aldrich is used directly in the photocatalytic studies. Phase purity of Cu_2O is investigated with X-ray diffractometer (PANalytical- X' Pert PRO, Japan) using Nickel filtered Cu-K_α radiation (λ = 1.54059 Å), with a scan rate of 2° min^{-1}.

Photocatalytic studies

100 mg of catalyst powder is added into 100 mL aqueous solution containing 10 ppm

pollutant (2-AP/4-AP/2-CP/4-CP). The suspension is magnetically stirred for 30 minutes in dark. The suspension is then exposed to 400 watts metal halide lamp; 5 mL aliquots are pipetted at periodic time intervals and filtered through 0.45 micron Millipore filters to remove the suspended particles. Extent of degradation is followed by recording the corresponding absorption spectra. All the experiments are conducted under ambient conditions. Percent degradation of pollutant is calculated by using the equation.

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

where A_0 and A_t are respectively initial absorbance and absorbance at time‘t’

Photoluminescence study

50 mg Cu_2O catalyst is added to the beaker containing 100 mL of terpthalic acid (TPA) solution (0.25 mmol L^{-1} in 1 mmol L^{-1} NaOH solution) and 10 µmol H_2O_2. The solution is stirred for 30 min in dark followed by irradiation by 400 w metal halide lamp for 30 min. The reacted solution was centrifuged and the clear solution is used for photoluminescence measurements in a fluorescence spectro flourometer (Flouromax 4) with the excitation wavelength of 315 nm.

RESULTS AND DISCUSSION

X-ray diffraction pattern of as purchased Cu_2O is shown in Fig. 1. All the observed peaks in XRD pattern can be indexed to cubic Cu_2O of JCPDS File No. 78- 2076. As there are no extra peaks, the sample is assumed to be phase pure cubic Cu_2O.

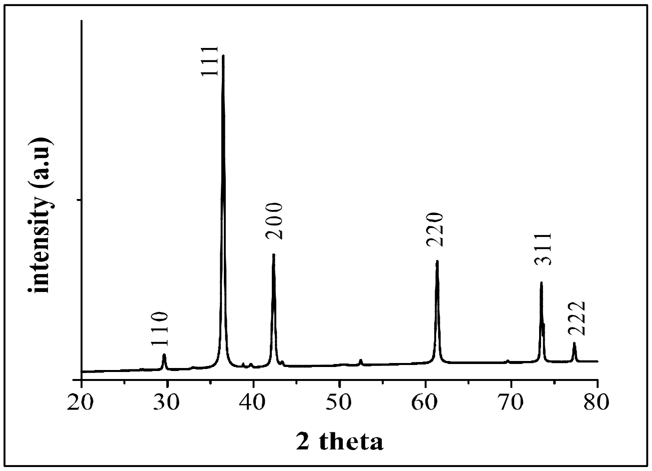

Fig. 1: X-ray diffraction pattern of Cu_2O sample used in this study

Photocatalytic degradation of 2-AP has been reported using TiO_2,[5] Cu_2O[6] under U.V. irradiation and $BiVO_4$[7] with visible light irradiation. Temporal variation of spectral contours of 2-AP, 2-AP + H_2O_2, 2-AP + Cu_2O and 2-AP + Cu_2O + H_2O_2 as a function of irradiation time are shown in Fig. 2. From the figure, it can be seen that 2-AP has a characteristic absorption at λ = 420 nm and it has not undergone any photolysis even after irradiation for 4 hrs (Fig. 2a). In presence of H_2O_2, 2-AP shows photodegradation to an extent of 35% for 4 hrs of irradiation (Fig. 2b). In presence of photocatalyst Cu_2O, 2-AP shows negligible photodegradation even for 4 hrs of irradiation (Fig. 2c). However, in presence of both Cu_2O and H_2O_2, 2-AP undergoes complete degradation for 2 hrs of irradiation (Fig. 2d). These results indicate that there is a synergetic effect between Cu_2O and H_2O_2.

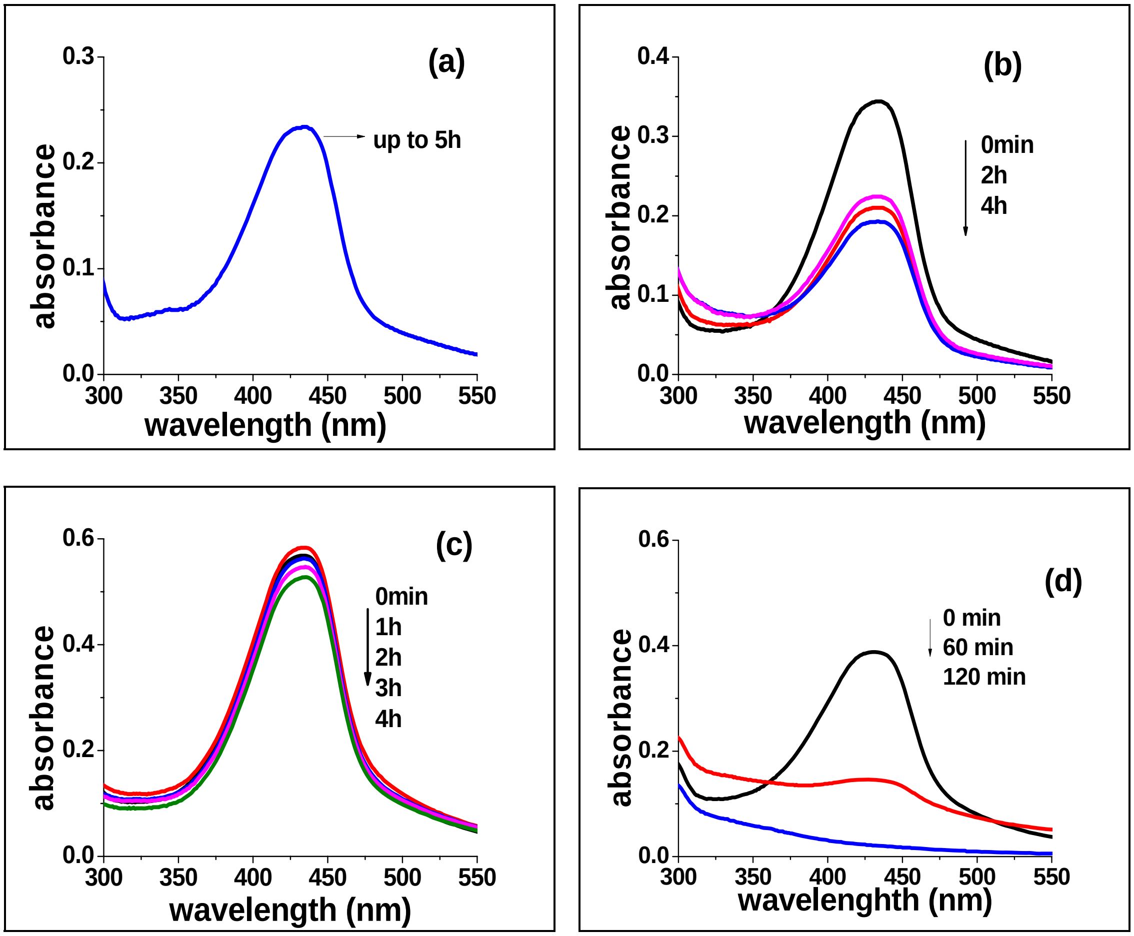

Fig. 2: Time dependent variation of spectral intensities as a function of irradiation time for (a) 2-AP, (b) 2-AP + H_2O_2, (c) 2-AP + Cu_2O and (d) 2-AP + Cu_2O + H_2O_2

Photocatalytic degradation of 4-amino phenol was reported with TiO_2 under U.V. irradiation[8]. Variation of spectral intensities as a function irradiation time for 4-AP, 4- AP + H_2O_2, 4- AP + Cu_2O and 4- AP + Cu_2O + H_2O_2 are shown in Fig. 3. It can be seen from the figure that 4-amino phenol exhibits a characteristic absorption at $\lambda = 470$ nm and undergoes photolysis to an extent of 25.4% for 5 hrs or irradiation (Fig. 3a). Nearly 40% of photodegradation is evident in case of AP in presence of H_2O_2 for 5 hrs of irradiation (Fig. 3b). Photodegradation to an extent of 25% is seen for 4-AP in presence of Cu_2O (Fig. 3c). However, in presence of both Cu_2O and H_2O_2, 4-AP has undergone 100% photodegradation for 2.5 hrs of irradiation (Fig. 3d). These results indicate that Cu_2O and H_2O_2 exert a synergetic effect in the photocatalytic degradation of 4- AP.

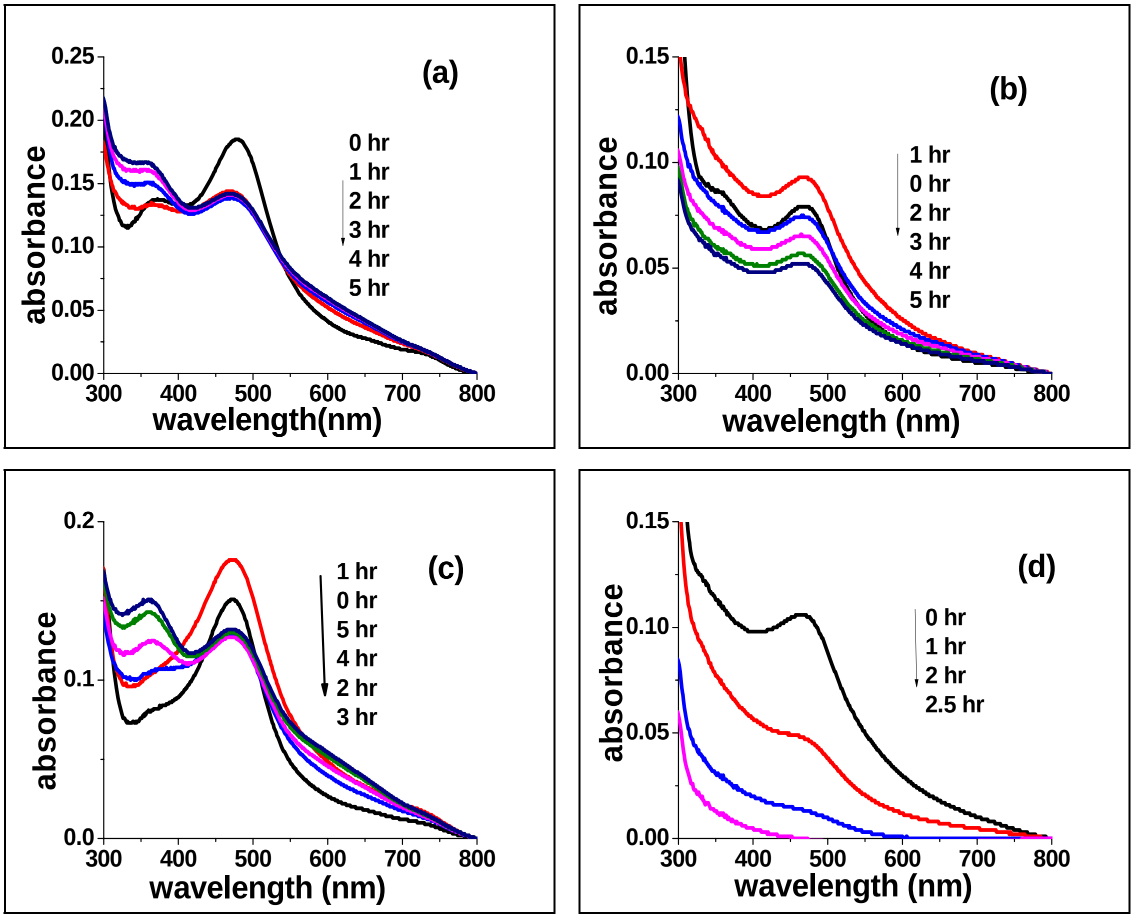

Fig. 3: Variation of spectral intensities as a function of irradiation time for (a) 4-AP, (b) 4-AP + H_2O_2, (c) 4-AP + Cu_2O and (d) 4-AP + Cu_2O + H_2O_2

Photocatalytic degradation of 2-CP has been reported using TiO_2[9], Pt-TiO_2[10] under U.V. irradiation, N-doped TiO_2[11] and chitosan/$CoFe_2O_4$[12] under visible light irradiation. Variation of spectral intensities as a function of irradiation time is shown in Fig. 4 for 2-CP, 2-CP + H_2O_2, 2-CP + Cu_2O as 2-CP + H_2O_2 + Cu_2O. From the figure, it can be seen that 2-CP exhibits characteristic absorption at $\lambda = 270$ nm and shows photolysis to an extent of 30.1% for irradiation of 5 hrs (Fig. 4a). In presence of H_2O_2, 2-CP showed a shift of peak towards lower wave length side (Fig. 4b). In presence of Cu_2O, photodegradation to an extent of 33.8% is noticeable (Fig. 4c). However, in presence of both Cu_2O and H_2O_2, the intensity of the peak is reduced with progressive irradiation and photocatalytic degradation to an extent of 50% is observable (Fig. 4d). These results indicate that Cu_2O + H_2O_2 is more beneficial than either Cu_2O or H_2O_2 for the photodegradation of 2-CP.

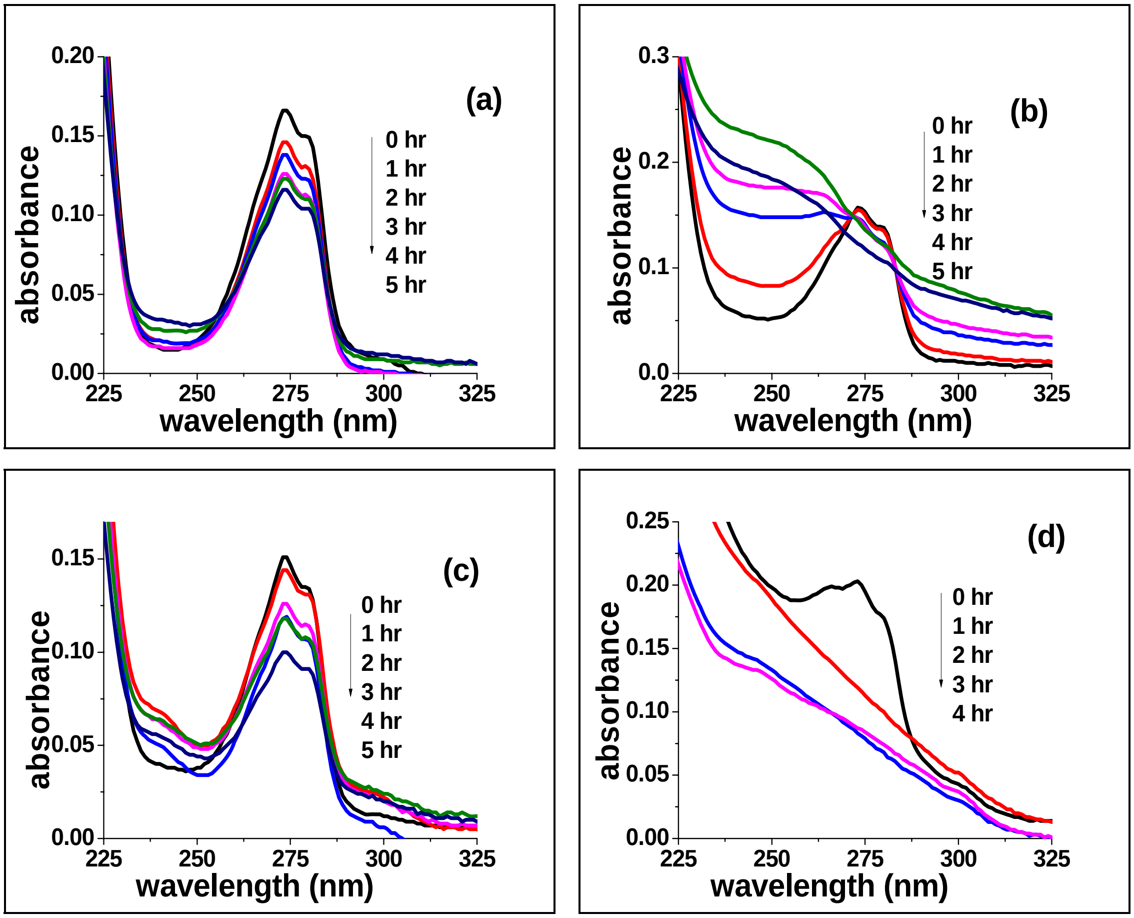

Fig. 4: Variation of spectral intensities as a function of irradiation time for (a) 2-CP, (b) 2-CP + H_2O_2, (c) 2-CP + Cu_2O and (d) 2-CP + Cu_2O + H_2O_2

Photocatalytic degradation of 4-CP has been reported using Au-Ag/TiO_2,[13] Ti-Al-SiO_2,[14] Pb-TiO_2,[15] TiO_2,[16] MgO, CaO, SrO/TiO_2,[17] Mg-ZnO,[18] Co-TiO_2[19] Anatase, Rutile[20], ZnO-TiO_2,[21] TiO_2 + H_2O_2,[22] Cu-AgCl,[23] Fe_3O_4-Cr_2O_3,[24] Mn-doped Zn/Al layered double hydroxides[25] under U.V. irradiation. Photocatalytic degradation of 4-CP under visible light irradiation has been reported using $ZnFe_2O_4$,[26] TiO_2-tungstophophoric acid[27], $LaFeO_3$,[28] $AgIO_3$-AgI/TiO_2,[29] TiO_2-tungstosilic acid[30], Gd, C, N, P doped TiO_2,[31] C/ZnO/CdS nano particles[32], Pt, Cr-TiO_2,[33] W^{6+}-ZnO,[34] AgBr, Au, Pt, Nd/$BiVO_4$,[35] TiO_2-Co-Phthalllocyamine + H_2O_2,[36] Nd^{3+}-TiO_2,[37] Bi_2O_4, Bi_4O_7,[38] TiO_2-CoO/graphene oxide[39], Bi_2O_3-TiO_2[40] and Bi_2WO_6.[41] Temporal variation of spectral contours as a function of irradiation time for 4-CP, 4-CP + H_2O_2, 4-CP + Cu_2O and 4-CP + Cu_2O + H_2O_2 are shown in Fig. 5. From the figure, it can be seen that 4-CP exhibits two absorption peaks- first one at 225 and second at 275 nm. 4-CP shows no photolysis even for irradiation up to 4 hrs (Fig. 5a). In presence of H_2O_2, photodegradation of 4-CP is evident to an extent of 75% (Fig. 5b).

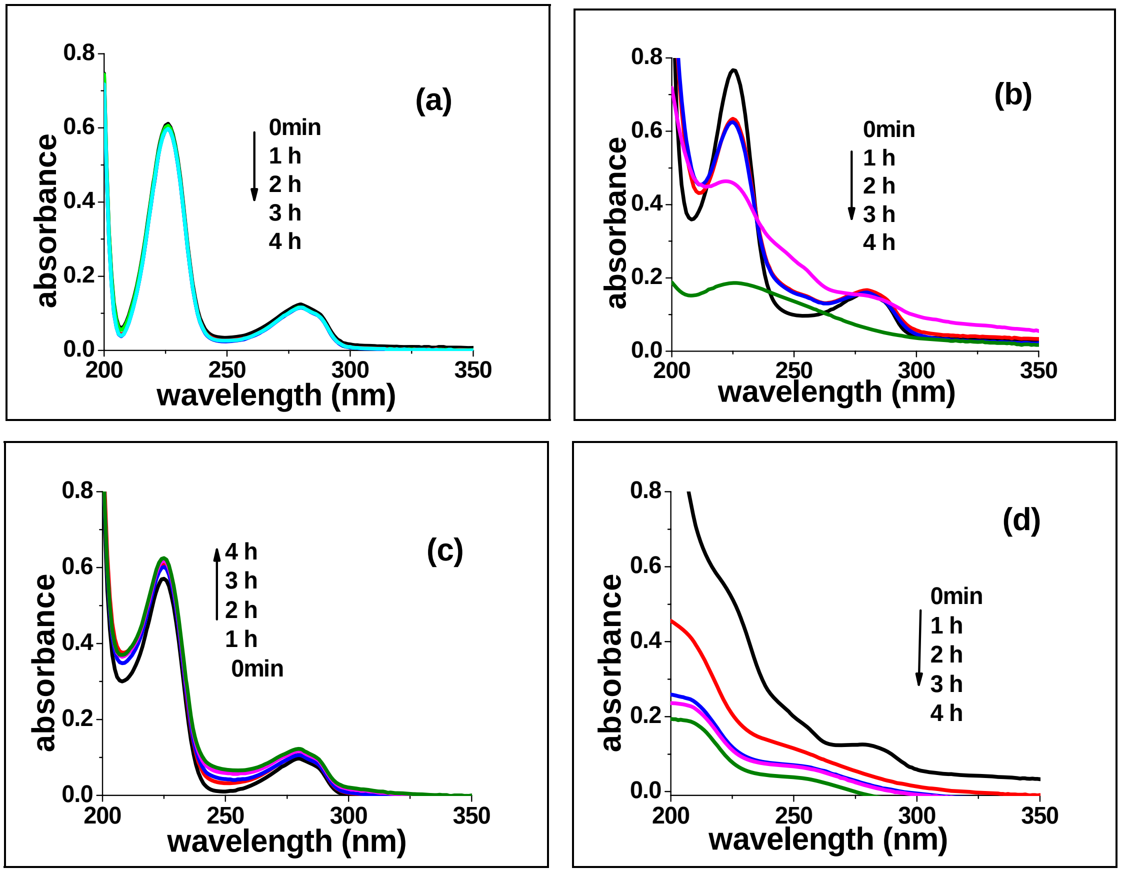

Fig. 5: Temporal variation of spectral contours as a function of irradiation time for (a) 4-CP, (b) 4-CP + H_2O_2, (c) 4-CP + Cu_2O and (d) 4-CP + Cu_2O + H_2O_2

In presence of Cu_2O, there is slight increase in intensity with progressive irradiation and this may be attributed to initial adsorption and subsequent desorption of 4-CP on to the photocatalyst Cu_2O (Fig. 5c). Nevertheless, in presence of Cu_2O and H_2O_2, photo catalytic degradation is very effective to an extent of 95% of peak at 225 nm and 100% of peak at 275 nm (Fig. 5d). These results also indicate that Cu_2O and H_2O_2 together is highly effective in photocatalytic degradation of 4-CP than either Cu_2O or H_2O_2 individually.

In view of a clear synergetic effect observed between Cu_2O and H_2O_2 for the photocatalytic degradation of 2-AP, 4-AP, 2-CP and 4-CP, the mechanism involved may be suggested as indicated below.

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

$$e^-_{CB} + H_2O_2^- \longrightarrow {}^\bullet OH + OH^-$$

$$h^+_{VB} + OH^- \longrightarrow {}^\bullet OH$$

$$^\bullet OH + \text{Chloro/Amino phenol} \longrightarrow \text{Degradation products}$$

Formation of $^\bullet OH$ free radical is ascertained using Terephthalic acid (TPA) as probe molecule. TPA reacts with OH free radicals to form 2-hydroxy terephthalic acid (HTPA) which exhibits a characteristic luminescence peak at $\lambda = 420$ nm. Photoluminescence spectra of Cu_2O + TPA dispersed in 100 ml water in presence and in absence of H_2O_2 prior to and after excitation are shown in Fig. 6.

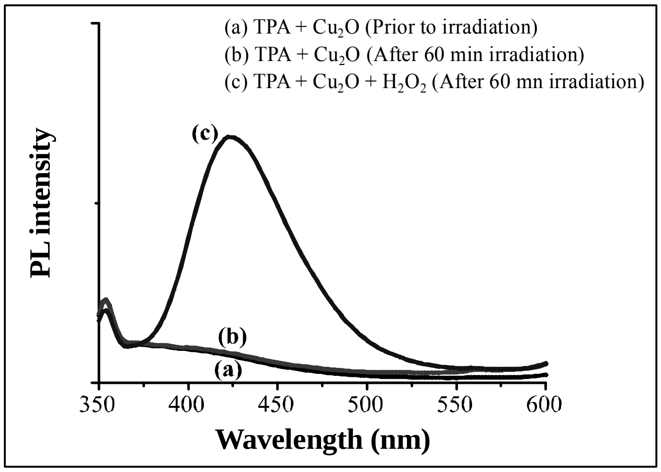

Fig. 6: Photoluminescence spectra of TPA solutions containing Cu_2O in presence and in absence of H_2O_2 before and after irradiation

The intense luminescence peak at $\lambda = 423$ nm for Cu_2O + TPA solution in presence of H_2O_2 after irradiation is a clear indication of the formation of $^{\bullet}OH$ free radicals during irradiation process. It may therefore be surmised that photocatalytic oxidation of amino phenols and chloro phenols can be accomplished under visible light using H_2O_2 sensitized Cu_2O.

CONCLUSION

Photocatalytic degradation of 2- and 4-aminophenols as well as 2- and 4-chlorophenols is achieved under visible light irradiation using Cu_2O as photocatalyst. 2-amino phenol is completely photo degraded in 2 hrs while 4-amino phenol took 2.5 hrs for complete degradation. 2-CP shows only 50% photocatalytic degradation for 4 hrs of irradiation while 4-CP showed near complete photocatalytic degradation for 4 hrs of irradiation. Addition of H_2O_2 enhanced photocatalytic degradation with formation of more $^{\bullet}OH$ free radicals. Presence of $^{\bullet}OH$ free radical formation is ascertained using photoluminescence studies with terephthalic acid as probe molecule.

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