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Visible light activated photocatalytic degradation of mono-, di- and tri - nitrophenols using Cu₂O

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ABSTRACT

Photo catalytic degradation of 4-NP and 2-NP was also achieved over Cu_2O under visible light irradiation for 180 and 150 min respectively in presence of external oxidant H_2O_2 . Photodegradation of 2, 4-dinitrophenol and 2, 4, 6-trinitrophenol occurred in 4 hrs and 5 hrs respectively. Presence of H_2O_2 was found to enhance the rate of degradation in terms of a synergetic effect to generate more 'OH free radicals that help degrade the organic pollutants rapidly. Ease of photocatalytic degradation in the nitrophenols studied has been found to vary in the order 4-nitrophenol > 2-nitrophenol > di-nitrophenol > tri-nitrophenol.

Keywords: Cu_2O , 2-nitrophenol, 4-nitrophenol, 2, 4-dinitrophenol, 2, 4, 6-trinitrophenol, Photocatalytic degradation.

INTRODUCTION

Phenolic compounds are common pollutants in aquatic systems. For instance, nitro phenols (NP) are generally detected in agriculture waste and 4-NP is used in the synthesis of dyes, pesticides, herbicides, explosives and pharmaceuticals. 4-NP is known to be both carcinogenic and mutagenic. Likewise 2, 4-dinitrophenol is used in industries relating to petro chemicals, pesticides, herbicides, dyes, explosives, pharmaceuticals and wood preservatives. It is toxic in nature, and removal of DNP from the industrial effluents is highly essential. 2, 4, 6trinitrophenol is explore under rapid heating. It is resistant to hydrolysis, biodegradation, photolysis and causes dermatitis, skin eruptions and nausea on long exposures. Removal of TNP from ground water is therefore necessary to safeguard human health. Different methods such as solvent extraction, adsorption, membrane separation and chlorination have been reported for removal of phenols. Over the past two to three decades, there has been a growing interest in advanced oxidation process involving semiconductor mediated photo catalysis because the process mineralizes many toxic organic pollutants non selectively at ambient temperature under UV/ visible light irradiation. TiO₂ is the most widely used semiconductor photo catalyst because it is inexpensive, non-toxic, easy to synthesize, photo stable, chemically inert and exhibits good photo catalytic quantum efficiency. However, the wide band gap of 3.2eV associated with TiO₂ allows absorption only in UV region below 380 nm which is < 5% of solar radiation. The process therefore becomes energy constrictive. In order to render TiO_2 into a visible light responsive photocatalyst, three different approaches in terms of (i) doping with transition metal atoms/cations and /or anions, (ii) coupling with a sensitizer, and (iii) composite formation with materials of suitable band potential have been actively pursued. Alternately, attention is also focused on developing other binary and ternary metal oxides to explore effectively the 44% of visible region of solar radiation so as to render the process cost effective and energy conserving green technology [1]. Cu₂O is a p-type semiconductor with a band gap in the range of 2.0-2.2 eV, and it has been reported to be a visible light active photocatalyst for degradation of Methyl orange, Methylene blue and

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Rhodamine-B [2-4]. Besides Degussa P25 (TiO₂), Cu₂O is an important photocatalyst because it is in expensive, readily available, low in toxicity with environmental acceptability, possesses good absorption in the visible region and shows high adsorption for molecular oxygen. The present paper describes H_2O_2 assisted visible light induced photocatalytic degradation of mono nitrophenols (MNP) 2- and 4 – nitro phenols, 2, 4 –dinitrophenol (DNP) and 2, 4, 6-trinitrophenol (TNP) using Cu₂O under visible light irradiation.

MATERIALS AND METHODS

Materials used:

As purchased A.R grade Cu_2O (99% Sigma Aldrich), 2-nitrophenol, 4-nitrophenol were obtained (Central drug house), 2, 4- dinitrophenol GR (Molychem), 2, 4, 6-trinitrophenol AR (Merck) are used directly in the photocatalytic studies.

Characterization Techniques:

Phase purity of Cu₂O was investigated with X-ray diffractometer (PANalytical- X' Pert PRO, Japan) at room temperature, using Nickel filtered Cu-K_{α} radiation (λ = 1.54059 Å), with a scan rate of 2° min⁻¹. Micro structural investigation of the sample was performed on the powdered sample using SEM (JEOL-JSM-6610LV, Tokyo, Japan).UV–visible diffuse reflectance spectrum (UVDRS) of the sample was obtained with dry pressed disk samples using Shimadzu UV-visible spectrophotometer (UV-3600) between 200 to 800 nm range. Spectral grade BaSO₄ was taken as reference in the UV-DRS.

Photocatalytic Studies:

100 mg of catalyst powder was added into 100 ml aqueous solution containing 10 ppm 2-NP/ 4-NP/2, 4-DNP/2, 4, 6-TNP. The suspension was magnetically stirred for 30 minutes in dark. The suspension was then exposed to 400 watts metal halide lamp; 5ml aliquots were pipetted at periodic time intervals and filtered through 0.45 micron Millipore filters to remove the suspended powder. Extent of degradation was followed by recording the corresponding absorption spectra. All the experiments were conducted under ambient conditions. Percent degradation of pollutant is calculated by using the expression.

% degradation = $(A_0 - A_t)/A_0 \times 100$

where A₀ and A_t are respectively initial absorbance and absorbance at time't'

RESULTS AND DISCUSSION

X-ray diffraction (XRD) pattern of Cu_2O powder used in the present study is shown in Fig.1. All the observed diffraction peaks could be indexed to cubic Cu_2O phase reported in JCPDS file number 78- 2076. Since there are no extra peaks relating to possible impurities such as CuO or Cu, the sample is ascertained to be phase pure Cu_2O . The calculated lattice parameter of a= 4.2699 A° agrees well with reported value of 4.267 A°.



Fig. 1. X-ray diffraction pattern of Cu₂O sample used in this study

Scanning electron micrograph of the sample is shown in Fig. 2. SEM image indicates particles of size in μ m region with no characteristic morphology or texture. UV-visible diffuse reflectance spectrum of Cu₂O is given in Fig.3. The spectrum indicates Cu₂O absorption range in the visible region from 400 nm to 600 nm. Band gap computed from the spectrum comes to 2.0 eV which is in agreement with earlier reports on Cu₂O.



Photocatalytic degradation of 4-Nitrophenol (4-NP) has been reported under UV irradiation using ZnO/TiO₂ with oxygen bubbling [5], TiO₂ impregnated with different transition metal ions [6], TiO₂ dispersed over active carbon, ZSM-5, SiO₂ and rice husk [7], Ag-TiO₂ particles [8], ZnO nano flakes [9], TiO₂+H₂O₂ [10], ZnO particles [11], Cu-TiO₂ nano particles [12], and $M_xNb_xTiO_{1-2x}O_2=x/2$ where M= Cr, Fe, x= 0.01 – 0.2 [13]. Degradation of 4-NP has also been reported under visible light using Cu₂O/TiO₂ hetero junction [14], Ag/Cu₂O hybrid [15], Cu₂O electrodeposited on indium tin oxide substrate [16], Cu core-Cu₂O shell [17], Cu₂O/NiFe₂O₄ [18], Cu₂O-TiO₂ composite [19], TiO₂+Cu-porphyrin + H₂O₂ [20], N, S. co-doped TiO₂ [21], TiO₂- Zn phthalocyanin [22], CuCr₂O₄ + H₂O₂ [23], Au, Pt/TiO₂ [24], g-C₃N₄ [25], Zn₃(VO₄) ₂ [26], Fe₃O₄- N-doped TiO₂ [27], TiO₂-Sn porphyrin nano particles [30], and BiVO₄ + H₂O₂ [31].

Time dependant spectral intensity variations as a function of irradiation time for 4-NP, 4-NP + H_2O_2 , 4-NP + Cu_2O , and 4-NP+ Cu_2O + H_2O_2 are depicted in Fig. 4. From the figure it may be noticed that 4-NP has characteristic absorption at λ max = 320 nm along with another less intense peak at λ = 410 nm which are attributed to protonated and deprotonted forms of 4-NP respectively. 4-NP shows very minute photolysis even after 180 min of irradiation (Fig. 4a). Addition of H_2O_2 showed a very little effect on the intensity of the peak at λ max = 320 nm while the peak at λ max = 410 nm showed considerable decrease for irradiation of 180 min (Fig. 4b). Degradation rate of deprotonted form of 4-NP is much faster compared to that of protonated form in both of the above cases. With Cu_2O , 4-NP showed a slight lowering in intensity for the peak at λ max = 310 nm with a simultaneous increase in the intensity of peak at λ max = 410 nm indicating preferential transformation of protonated to deprotonated form (Fig. 4c). However, in presence of both Cu_2O and H_2O_2 , 4-NP shows rapid decrease in absorption intensity with progressive irradiation and complete degradation is achieved for 120 min of irradiation (Fig. 4d) suggesting a synergetic effect due to Cu_2O and H_2O_2 .



 $\label{eq:Fig. 4. Temporal variation of spectral intensities as a function of irradiation time for (a) 4-NP, (b) 4-NP+H_2O_2, (c) 4-NP+Cu_2O and (d) 4-NP+Cu_2O+H_2O_2 \\ NP+Cu_2O+H_2O_2 \\ \end{tabular}$

Photocatalytic degradation of 2-Nitrophenol (2–NP) has been reported over TiO₂ [32], Ag/TiO₂ [33], V₂O₅-ZnO [34] under UV irradiation and with BiVO₄ + H₂O₂ under visible light irradiation [31]. Time dependent spectral intensity variations as a function of irradiation time for 2-NP aqueous solution, 2-NP+H₂O₂, 2-NP+Cu₂O, and 2-NP+Cu₂O+H₂O₂ are shown in Fig. 5. From the figure, it can be seen that 2-NP exhibits characteristic absorption peaks at $\lambda = 275$ nm and 350 nm. Progressive irradiation causes photolysis of 2-NP to an extent of 42% for 180 min of irradiation (Fig. 5a). In presence of H₂O₂, 2-NP shows decrease in peak intensity corresponding to 42% degradation for the peak at $\lambda = 350$ nm (Fig. 5b). In presence of Cu₂O, 2-NP shows a gradual decrease in peak intensity at $\lambda = 275$ nm with simultaneous appearance of a new peak centered at $\lambda = 410$ nm indicating some transformation (Fig. 5c). However, in presence of both Cu₂O and H₂O₂, complete degradation of 2-NP is achieved for 150 min of irradiation (Fig. 5d) indicating a synergetic effect between Cu₂O and H₂O₂.



Fig. 5. U.V-visible absorption spectra of (a) 2-NP, (b) 2-NP + H_2O_2 , (c) 2-NP + Cu_2O and (d) 2-NP + H_2O_2 + Cu_2O as a function of irradiation time

Remediation of DNP has been reported in terms of photocatalytic degradation over TiO₂ [35-40], carbon nanotubes-TiO₂ composite [41], Bi₂O₃/Bi₂MoO₆ [42], V₂O₅-ZnO [43], Fe₃O₄/Al₂O₃/TiO₂ nanocomposite [44], N, In- codoped TiO₂ nano composite [45], Ag doped BiVO₄ [46], photo, photo-Fenton, solar Fenton catalytic oxidation [47, 48] and BiVO₄ [49]. Fig. 6 depicts temporal variation of spectral contours as a function of irradiation time for DNP, DNP+H₂O₂, DNP+Cu₂O and DNP+Cu₂O+H₂O₂. It can be seen from Fig. 6a that DNP shows characteristic absorption at λ max = 350 nm and undergoes very little photolysis up to ~ 14% for 4 hrs of irradiation. Addition of H₂O₂ led to a photodegradation of 18% of DNP as seen from Fig. 6b for the same irradiation time. In presence of Cu₂O, DNP showed very little photodegradation (Fig. 6c) where as in presence of both Cu₂O and H₂O₂ complete degradation of DNP occurred for irradiation of 4 hrs (Fig. 6d). In the absence of any new peaks arising simultaneously in the entire U.V-visible region under investigation, complete decrease in intensity at λ max = 350 nm may be ascribed to complete photodegradation of DNP.



Fig. 6. Temporal variation of spectral intensities as a function of irradiation time for (a) DNP, (b) DNP + H_2O_2 , (c) DNP + Cu_2O and (d) DNP + H_2O_2 + Cu_2O

Remediation of TNP has been reported in terms of photo-electrochemical [50], catalytic [51], wet air oxidation [52], vacuum ultra violet [53], Fenton and Photo Fenton [47], and photocatalytic degradation over TiO₂ [54, 55, 35], carbon nanotubes/NiFe₂O₄ [56] and BiVO₄ [49]. UV-visible absorption spectra of TNP, TNP+H₂O₂, TNP+Cu₂O and TNP+Cu₂O+H₂O₂ as a function of irradiation time are shown in Fig. 7. From the figure, it is apparent that TNP shows a maximum absorption at $\lambda = 350$ nm. Irradiation up to 5 hrs did not cause any measurable photolysis of TNP (Fig. 7a). In presence of H₂O₂, TNP showed considerable degradation up to 35% for 5 hrs of irradiation (Fig 7b). Photocatalytic degradation of TNP over Cu₂O did not show measurable degradation of TNP as seen from Fig. 7c. However, TNP in presence of both Cu₂O and H₂O₂ has undergone progressive degradation as evidenced by the lowering in intensity at λ max = 350 nm and irradiation of 5 hrs led to complete degradation (Fig. 7d).



Fig. 7. U.V-visible absorption spectra of (a) TNP, (b) TNP + H_2O_2 , (c) TNP + Cu_2O and (d) TNP + H_2O_2 + Cu_2O as a function of irradiation time

Based on the experimental data presented above, the photo degradation mechanism for 4-NP and 2-NP may be suggested as follows:

 $\begin{array}{l} Cu_2O + h\upsilon \rightarrow e^-{}_{CB}\left(Cu_2O\right) + h^+{}_{VB}\left(Cu_2O\right) \\ e^-{}_{CB}\left(Cu_2O\right) + H_2O_2 \rightarrow {}^{\cdot}OH + {}^{-}OH \\ h^+{}_{VB}\left(Cu_2O\right) + {}^{-}OH \rightarrow {}^{\cdot}OH \\ MNP/DNP/TNP + {}^{\cdot}OH \rightarrow Degradation \ products \end{array}$

Our results show that 2-nitro phenol, 4-nitro phenol, 2, 4-dinitrophenol and 2, 4, 6-trinitrophenol can be successfully degraded by H_2O_2 assisted Cu_2O under visible light and the addition of H_2O_2 augmented rate of degradation. Ease of photocatalytic degradation in the nitrophenols studied has been found to vary in the order 4-nitrophenol > 2-nitrophenol > di-nitrophenol > tri-nitrophenol.

CONCLUSION

 Cu_2O has been found to be an effective visible light photo catalyst for the degradation of 2-nitrophenol, 4nitrophenol, 2, 4-dinitrophenol and 2, 4, 6-trinitrophenol. Degradation of 4-NP and 2-NP occurred for 120 and 180 min of irradiation respectively. Degradation of 2, 4-dinitrophenol and 2, 4, 6-trinitrophenols occurred in 4 hrs and 5 hrs respectively. Presence of H_2O_2 showed synergetic effect on the degradation of nitro phenols over Cu_2O .

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