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VISIBLE LIGHT ACTIVATED PHOTOCATALYTIC DEGRADATION OF NITROBENZENE USING Cu_2O

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ABSTRACT

Photo catalytical degradation of nitro benzene has been studied under visible light irradiation in presence of as purchased Cu_2O sample. XRD pattern of Cu_2O indicated that Cu_2O is monophasic and cubic. Complete degradation of nitro benzene was observed for 180 min of irradiation in presence of Cu_2O .

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INTRODUCTION

Nitrobenzene (NB) even at low concentrations is a high risk to human health, Industrial discharges with higher than 2mg NB /L have been declared as hazardous by U.S. Environmental Protection agency (USEPA). NB is widely used in the manufacture of dyes, explosives and pesticides and waste water effluents from these industries therefore require more effective pretreatment methods for remediation of NB. Presence of $-\text{NO}_2$ a strong electron affinity makes nitrobenzene more restricted to chemical and biological oxidation. Degradation of nitrobenzene has been reported interms adsorption (Dai and Zhao, 2014), ozonation (Beltran et al., 1998) Fenton, U.V. Fenton, super critical oxidation (Latifoglu and Gurol, 2003, Rodriguez et al., 2000 and Arslan-Alaton and Ferry, 2002) photochemical reduction (Makarova et al., 2000) reductive degradation (Mu et al., 2004) and chemical reduction with Sn/HCl (Evers et al., 1991). However, none of these methods is satisfactory as they either generate secondary pollution due to phase transfer, or non economical to treat large volumes of effluents. During the past three to four decades, there has been a growing interest in the advanced oxidation processes (AOPs) such as Fenton, Photo Fenton and semiconductor mediated heterogeneous photocatalysis because AOPs help mineralize many toxic organic pollutants completely and non selectively at ambient temperature. Among

the various AOPs heterogeneous photocatalysis has been studied extensively for the degradation of many dyes as model

compounds. TiO_2 is widely used as a semiconductor photocatalyst because it is inexpensive, easy to synthesize, non photo degradable, chemically and biochemically inert. But the wide band gap of 3.2 eV associated with anatase form of TiO_2 allows absorption of radiation in UV region below 380 nm which is available only to an extent of 5% only. Hence, to transform TiO_2 into a visible light active photocatalyst, three different approaches have been demonstrated in literature – (i) doping/co-doping/tri-doping of TiO_2 with transition metal atoms, cations and anions, (ii) treating with a suitable sensitizer of higher absorption coefficient, and (iii) formation of nano composites with suitable materials to yield high surface to volume ratio. Alternately, several binary metal oxides such as ZnO , Fe_2O_3 and ternary metal oxides like ZnWO_4 , $\text{Zn}_3(\text{VO}_4)_2$, Bi_2MoO_6 , $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ have also been explored to enhance the absorption range of solar radiation from U.V. region to visible region so as to make the process energy efficient and environmentally acceptable (Prasada Rao et al., 2015). Among the many binary metal oxides that have been investigated, Cu_2O has been reported as a visible light active photocatalyst for degradation of some dyes (Zhang et al., 2010, Madina et al., 2012 and Narasimha Murthy et al., 2015). Cu_2O is a p-type semiconductor with a band gap in the range of 2.0-2.2 eV. Cu_2O is inexpensive, abundantly available, and possesses good range of absorption in the visible region. Present study describes visible light activated photocatalytic degradation of nitrobenzene using Cu_2O .

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MATERIAL AND METHODS

Materials and Characterization

As purchased A.R grade Cu₂O (99%) and A.R grade Nitrobenzene (99%) obtained from Sigma Aldrich are used directly in the photocatalytic studies. 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 ($\lambda = 1.54059 \text{ \AA}$), with a scan rate of 2° min^{-1} .

Photocatalytic Studies

100 mg of catalyst powder was added into 100 ml aqueous solution containing 10 ppm NB. 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 particles. 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.

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

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

RESULTS AND DISCUSSION

As recorded X-ray diffraction (XRD) pattern of Cu₂O powder used in the present study is shown in Fig.1. All the experimentally observed diffraction peaks are indexed to cubic Cu₂O phase of JCPDS file number 78- 2076. In the absence of unindexed peaks, the sample is considered to be pure monoclinic cubic form of Cu₂O.

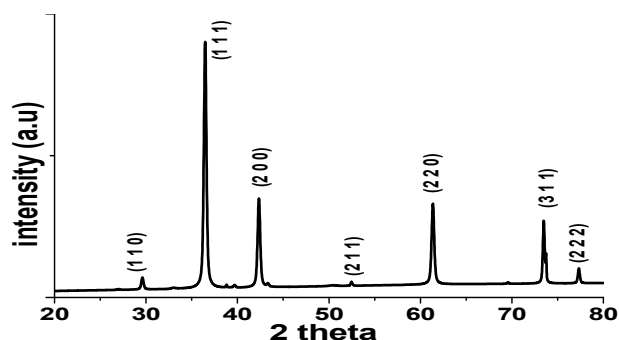
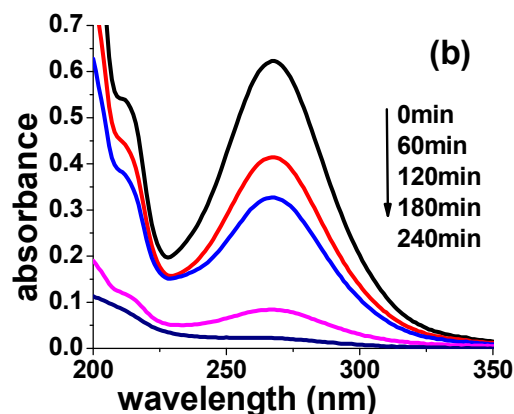
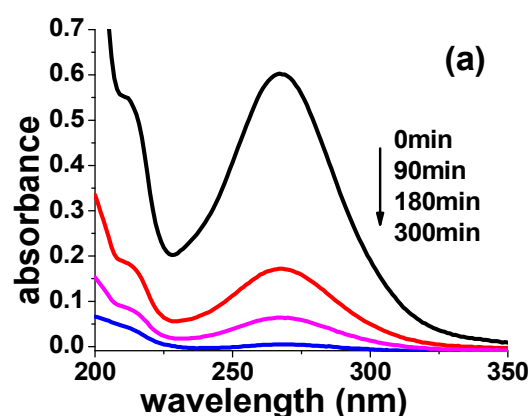


Fig. 1 X-ray diffraction pattern of Cu₂O sample used in this study.

Photocatalytic degradation of NB was reported under sunlight by Dhanajaya *et al.*, 2003 using TiO₂, and Byrppa *et al.*, 2004 using activated carbon/TiO₂ composites under sunlight. Praveen and Rakesh, 2015 reported 59% degradation of NB in 240 min using Fe, Co, Ni, Cu and Ag containing titanosilicates and concluded that Ag⁺ ions show pronounced enhancement in photocatalytic activity. 75% degradation of NB in 240 min was reported by Wang *et al.*, 2010 using H₃PW₁₂O₄₀ as photocatalyst under sunlight. Aliyu *et al.*, 2015 reported 87% degradation of NB in 120 min of visible light irradiation over microwave synthesized coupled Cu/ZnO nano composites. Degradation of NB under U.V irradiation was reported by Whang *et al.*, 2012 using TiO₂ coating on quartz tube. Their study indicated 90% degradation of NB at pH=4 for 180 min of

irradiation under air bubbling. Reynoso-Soto *et al.*, 2013 reported 97% degradation of NB in presence of 0.5 atomic percent of Zn in TiO₂ for 120 min of U.V irradiation. Aliyu *et al.*, 2014 reported 70% removal of NB in 120 min under U.V irradiation over coupled grafted casseva/ZnO. Jo *et al.*, 2014 reported enhanced degradation of NB over graphitic carbon/TiO₂ composite under U.V irradiation for 240 min of irradiation. Nitoi *et al.*, 2015 reported UV-Visible photocatalytic degradation of NB using heavy metal doped titania at pH=4 for 240 min of irradiation. Recently, effective visible light photocatalytic degradation of NB has been reported over H₂O₂ sensitized BiVO₄ from this department (Umabala *et al.*, 2015). Temporal variation of spectral contours as a function of irradiation time for aqueous solutions of NB, NB+Cu₂O are shown in Fig 2. From the figure, it can be seen that NB shows considerable photolysis with progressive radiation as evidenced by a simultaneous decrease in intensity of characteristic absorption peak at $\lambda_{\text{max}} = 260 \text{ nm}$ with irradiation time and complete degradation occurred for 300 min of irradiation (Fig 2a). In presence of 10 mg of Cu₂O, however, there is a rapid decrease in intensity with irradiation time increased and complete degradation occurred for 240 min (Fig. 2b). In order to assess the optimal amount of catalyst needed for the degradation of 10 ppm NB spectra are recorded for NB aqueous solutions with 20 and 30 mg of Cu₂O as a function of irradiation time. The time dependent spectral variations for NB with 20 mg and 30 mg catalyst are shown in Fig 2c and 2d.



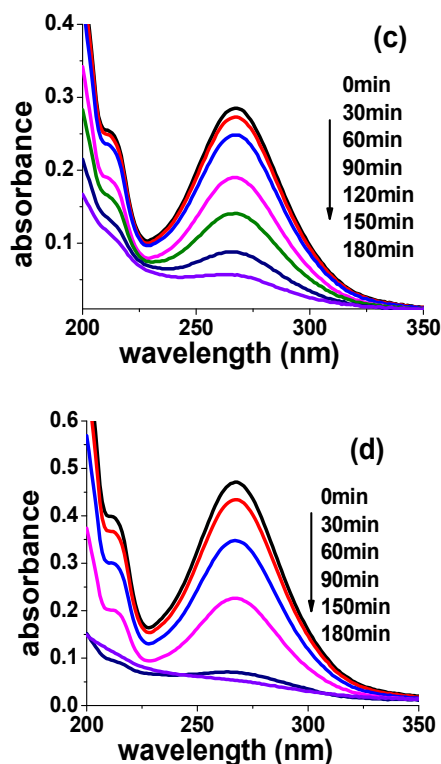
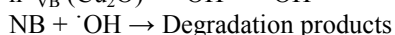
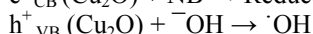
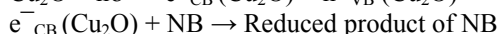
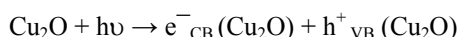


Fig. 2 Temporal variation of spectral contours as a function of irradiation time for (a) NB, (b) NB+10 mg Cu₂O, (c) NB+20 mg Cu₂O, (d) NB+30 mg Cu₂O.

From the figure it is clear that the degradation time of 10 ppm NB with 20 mg Cu₂O is 180 min, While with with 30 mg Cu₂O, is also 180 min. The possible mechanism involved in the photocatalytic degradation is suggested below:



Our results indicate that nitrobenzene can be effectively degraded photocatalytically in the visible light in the presence of Cu₂O, as photo catalyst.

CONCLUSION

Cu₂O has been shown to be an effective visible light photo catalyst for the degradation of nitrobenzene. Complete degradation of 10 ppm nitrobenzene occurred for 180 min of irradiation.

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