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Synthesis of nanosize CuO for environmental clean up

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ABSTRACT

The photocatalytic degradation ofCongo red dye using nano size CuO was studied in presence of natural sunlight. The effect of pH, amount of catalyst loading and presence of sunlight on the degradation of dye was studied. CuO prepared by co-precipitation method using two different starting materialswere characterized by XRD and IR.

The rate of photodegradation was monitored by UV – Visible spectrophotometer. The degradation products were analyzed by qualitative analysis and COD measurements. Recovery and reusability of the photocatalyst was also studied. A tentative mechanism of the photocatalytic process has been assigned.

Keywords: COD, Congo red dye, Co-precipitation, CuO,Photodegradation

I. INTRODUCTION

The release of waste water generated by textile, dyeing and pharmaceutical industry without treatment into water streams is very dangerous, since most of the dyes are carcinogenic in nature and pose a serious threat to the environment[1]. Various methods like coagulation and adsorption merely transfer dye from water to solid. Advanced oxidation processes (AOPs) have been found to be an alternative method for the complete degradation of organic contaminants.Several works have been done on heterogeneous semiconductor photocatalysis using various semiconductors such as TiO_2, ZnS, CdS, Fe_2O_3, ZnO, CeO_2etc[2-4] .

CuO is attractive as a selective solar absorber since it has high solar absorbency and a low thermal emittance. It is a promosing semiconductor for solar cell fabrication due to its suitable optical properties[5]. CuO is readily available and non-toxic and this makes it more attractive for different applications[6]. The photodegradation of Congo red dye has been investigated in presence of ZnO under visible light irradiation by Siva Kumar et al[7]and others[8].

The present work involves synthesis of CuOfrom two different starting materialsscrap copper wires and $CuCl_2$ by co-precipitation method and subsequent characterization by XRD and FTIR methods. The photocatalyticdegradation of Congo red an azo dye with prepared CuO as photocatalyst using natural sunlight in aqueous solution has been investigated under different conditions. Recovery and reusability of the photocatalyst was also studied.

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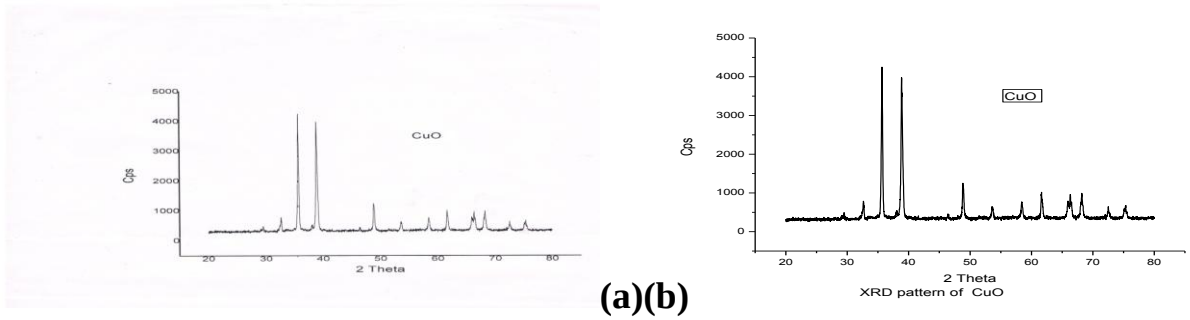
II. EXPERIMENTAL

CuO was prepared by co-precipitation method as described by Borker et al[4]. The starting materials used in this study were pieces of scrap copper wire and $CuCl_2.2H_2O$ respectively. In this process Cu wires were cut into pieces and dissolved using aqua- regia to obtain a clear solution. To this a solution of 10% AR Grade NaOH solution was added with constant stirring till greenish precipitate was formed and subjected to oxidation by dropwise addition of 30% H_2O_2 with continuous stirring. The precipitate was filtered, washed with distilled water and dried at 100°C. It was then heated to 400 ^{0} C for 30 minutes. Subsequently, the precipitate was crushed to obtain black colouredCuO powder. CuO was also prepared from $CuCl_2$ in similar manner.

The diffraction patterns were recorded on Rigaku X-ray diffractometer using Cu K α radiation, filtered through Ni absorber, at a scanning rate of 0.1°/min. The average particle size was estimated by using Debye – Scherrer formula: $D = 0.9\lambda/ \beta \cos \theta$, where λ is wavelength of X-ray (1.5405 ^{0}A), β is FWHM (full width at half max), θ is diffraction angle and D is particle diameter. The infrared spectra of synthesized CuO were recorded as KBr pellets using Infrared spectrophotometer (model SHIMADZU – 8101).

Photocatalytic degradation of Congo reddye was studied using prepared CuO samples in presence of sunlight. 100 ml of the 10^{-5} M dye solution along with 150 mg of prepared photocatalyst was kept in sunlight between 10:00 to 2:00 pm. The degradation rate was monitored by measuring absorbance of the dye solutionat maximum wavelength after every 30 min using UV-visible spectrophotometer (SPECTRO 119). The reaction was carried out at various experimental conditions like change in pH, with different amount ofphotocatalyst and with and without sunlight. The pH was measured with pH meter. The pH of the solution was adjusted by using previously standardized 1N HCl and 1N NaOH. The degradation products were analyzed by COD method and qualitative analysis. Recovery and reusability of the photocatalyst samples were also calculated.

III. RESULTS AND DISCUSSION



(a)(b)

Fig. 1 XRD pattern of (a) CuO from wire (b) from $CuCl_2$

The formation of CuO was checked by recording X- ray powder diffractogram of the samples.Fig.1 shows the XRD pattern of CuOprepared from (a) scrap copper wire and (b) $CuCl_2$.Well developed peaks corresponding to

2θ values 35.64, 38.88 and 48.92 were obtained which are in good agreement with JCPDS, CuO file No. 5-661.The size of the CuO particles were in the range 28-40 nm.

FTIR spectra exhibit peak at 528cm^{-1} which can be attributed to the vibration of Cu-O and additional peak at 1384 cm^{-1} due to $Cu^{+2} - O^{2-}$ stretching, confirming the formation of pure CuOnanopowders in both the samples.

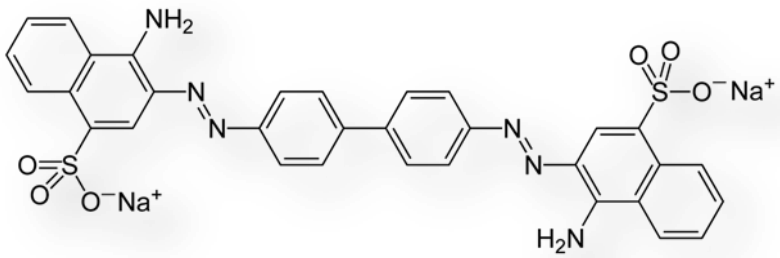


Fig. 2 Structure of Congo red dye

Photocatalytic degradation of Congo red dye was carried out using prepared samples. Congo red dye has absorption in visible region at λ_{max} 497nm in water. Measuring the absorbance of the solution at this wavelength monitors the progress of photocatalytic degradation. The reaction was studied for various experimental conditions like amount of catalyst, without using catalyst and with catalyst, only dye and different pH.

The dye is unable to degrade in absence of sunlight and photocatalyst.The optimum amount of catalyst was found to be 150 mg for the degradation of 100 ml of 10^{-5} M Congo red dye solution as shown in Fig 3.

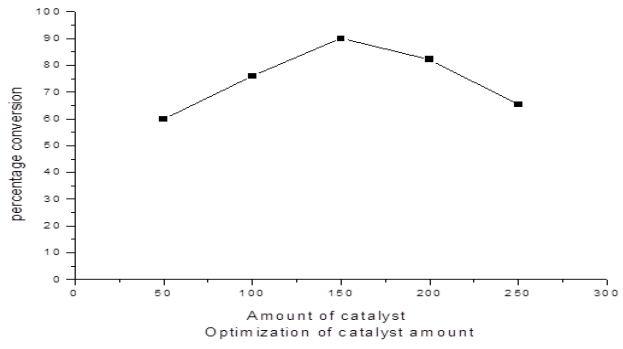


Fig. 3 Optimization of catalyst amount

The rate of dye degradation increased with the amount of photocatalyst which may be attributed to the increase in the exposed surface area of the semiconductor. But after a certain limit (150 mg), if the amount of photocatalyst is increased further, there will be a saturation point [4].

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Under solar irradiation, along with catalyst the dye is degraded completely within 180 minutes time interval. Fig. 4 shows photodegradation of Congo red dye over CuO. Decrease in absorbance indicates that the degradation products are colourless. Thus the photocatalytic degradation provides an efficient way to mineralize the dye. It was observed that CuO is a good photocatalyst for the degradation of Congo red dye. Due to low band gap value (1.7eV)CuO absorb large portion of visible light and thus show maximum photocatalytic efficiency.

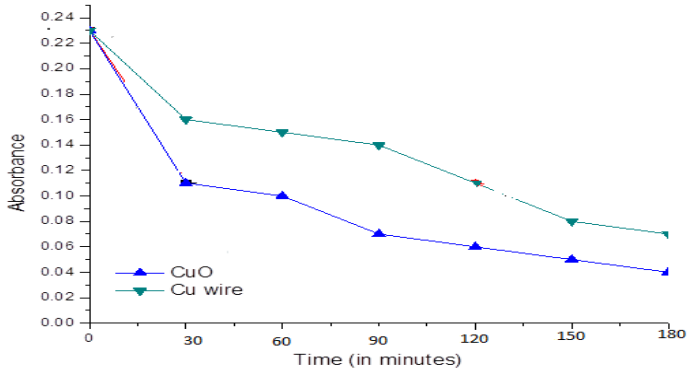

Fig. 4 Photocatalyticdegradation of Congo red dye over CuO

Dye degradation was studied at different pH conditions, which is one of the important factors. It has been observed that degradation of dye is faster in alkaline pH, ie at pH 10. In alkaline medium, there is greater probability for the formation of hydroxyl radical ($OH^{\cdot}$), which can act as an oxidant, thus increasing the rate of photodegradation of the dye[5]. At higher pH less time is required for dye degradation whereas dye removal efficiency is minimum at acidic pH range.

Analysis of the degradation productwas done by COD and qualitative methods. 90% decrease in COD was observed after degradation process, which indicates the existence of minerals.The formation of CO_2, SO_4^{2-}, NO_3^- and NH_4^+ was identified. pH of the solution remained same before and after degradation.

3.1 Reusability Studies

The solution resulting from the photocatalytic degradation of the dye was filtered, washed and the photocatalyst was dried. The dried catalyst sample was heated at 100^0C for 2 h and again employed for second cycle to degrade the same dye. It is important to mention here that the ratio of catalyst and dye was same as that used for 1st cycle. It was observed that catalyst in 2nd cycle was able to degrade the dye more rapidly as compared to that of 1st cycle. Decrease in concentration of dye for 2nd cycle is much more than that of the 1st cycle as shown in Fig. 5. The result can be attributed to the passivation of surface states and in non- radiating recombination centers. The surface of photocatalyst is being passivated as a result of these chemical reactions; therefore there is a lesser probability for the electron hole recombination. As a result more electron and holes will participate in degradation of dye and dye will degrade to more extent [9].

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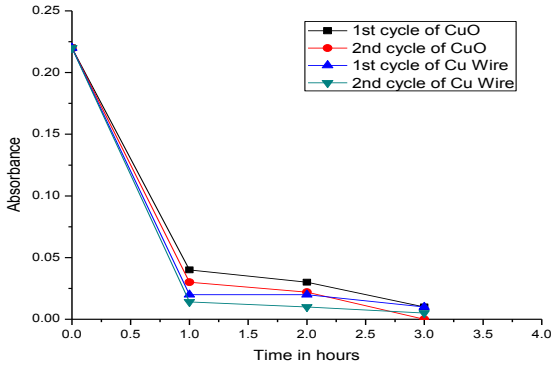

Fig. 5 Reusability study over CuO for 2cycles

3.2 Mechanism

Many investigators have suggested various mechanisms for the degradation of dye pollutants [4,10]. On exposure to solar radiation, the semiconductor (SC) will be excited by light to give SC*. This excited state will provide an electron (e^-) in the conduction band leaving a hole in the valence band. This electron is then trapped by molecular O_2 forming O_2^- ions. The valence band hole generates hydroxyl radical ($OH^\cdot$) from hydroxyl ions, which can easily attack the adsorbed dye, thus leading finally to their complete mineralization. Scheme 1 suggests one of these mechanisms.

$$SC + hv \rightarrow SC^*$$

$$SC^* \rightarrow e^-_{CB} + h^+_{VB}$$

$$e^-_{CB} + O_2 \rightarrow O_2^-$$

$$O_2^- + H_2O \rightarrow 2OH^- + 2OH^\cdot + O_2$$

$$h^+_{VB} + OH^- \rightarrow OH^\cdot$$

$$OH^\cdot + \text{Dye} \ldots\ldots\ldots\ldots \rightarrow \text{Degraded product } (CO_2, NH_4^+, NO_3^-, SO_4^{-2})$$

Scheme 1

IV CONCLUSION

Theco-precipitation method has been used for the synthesis of CuO using two different starting materials scrap copper wire and $CuCl_2$. XRD and IR methods confirmed the formation of oxides. Particle size of the samples was in the range of 28-40 nm. It was found that Congo red dye can be degraded efficiently using nano size CuOphotocatalyst with sunlight. The dye degrades to a colorless solution after a period of 180 min irradiation time. Decrease in COD value indicates the mineralization of the dye.The mechanism involves the formation of $OH^\cdot$radical, which is an active oxidizing species for the degradation of dye. The catalyst can be easily recovered and reused for several applications, lowering further more treatment cost. Thus photocatalysis with the oxidephotocatalystobtained from waste would be possible application for pollution control using solar energy

which is a renewable energy form, cost effective, completely free and which can be used directly to oxidize or degrade the dye chemicals.

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