Photocatalytical degradation of Methyl Orange using laboratory prepared Copper Oxide photocatalyst

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Abstract: Copper oxide materials have been successfully synthesized by the chemical precipitation method using copper nitrate, sodium hydroxide and sodium lauryl sulphate. As prepared materials were characterized by using X-ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR). The XRD data revealed that as prepared CuO is crystalline in nature. The particle size of the material was found to be approximately 10 nm indicating nano-sized particle. Photocatalytic efficiency of CuO nanoparticle was then studied. In this study, methyl orange (MO) was used as model dye pollutant. The MO degradation rate using CuO photocatalyst was studied at different pH condition, varying time of Ultra Voiler (UV) irradiation, variation of catalyst dose. Results revealed that the optimum pH was found to be 3 and optimum time was found to be150 min using optimum dose of 0.05g under UV light irradiation in presence of H_2O_2 in MO dye solution. The rate constant of MO degradation was found to be 0.0099 min^{-1} indicating good rate of reaction which was in agreement with literature value 0.0089 min^{-1}.

Introduction

Environmental safety has become one of the most serious concerns for the scientific community because of rapid increase of organic pollutants used in agriculture and various industries which cause adverse effects on the soil, air and water bodies[1].In order to remove the organic and inorganic pollutants from waste water different methods have been used such as coagulation/flocculation, membrane separation or elimination by activated carbon adsorption, biodegradation, chemical and photochemical degradation[2]. In recent years, an enormous interest has been devoted to photocatalysis using oxide semiconductor owing to its potential applications to both environmental applications and organic synthesis. Metal oxide nanoparticles have got special attention in the field of photocatalytic activity, sensing, optoelectronics, catalysis and solar cells due metal elements are able to form a large diversity of to their unique physical and chemical properties. These metal oxides can adopt a vast number of structural geometries within an electronic structure that can exhibit metallic, semiconductor or insulator character[3].

Copper and their oxides are, one of the prominent materials which were widely studied on the basic as well as applied research community due to theirexcellent catalytic, optical, electrical and thermal properties. It also exhibits physical properties such as high temperature superconductivity, electron correction effects and spin dynamics. The copper oxide (CuO) is a p-type semiconductor and has the low band gap energy of 1.2 eV. Hence, CuO is good promising candidates for dye degradation and for waste water treatment because of its photocatalytic property[4-5]. In present study, CuO has been used to degrade dye from aqueous solution. A number of methods that have been adopted to synthesize CuO nanoparticles such as sol- gel[6], precipitation[7], solid state reaction[8], sono-chemical[9], microwave irradiation[10-12], plasma[12] and thermal decomposition[13]. Among them, simple

aqueous precipitation methods have been employed in this study for the preparation of CuO photocatalyst.

Methyl orange (MO) as a model pollutant

Methyl orange is commonly used industrial dye. It is categorized as an anionic azo-dye due to the presence of three nitrogen atom attached to the benzene ring[14]. The chemical composition of methyl orange is $C_{14}H_{14}N_3NaO_3S$. The molecular structure is shown in Fig. 1.
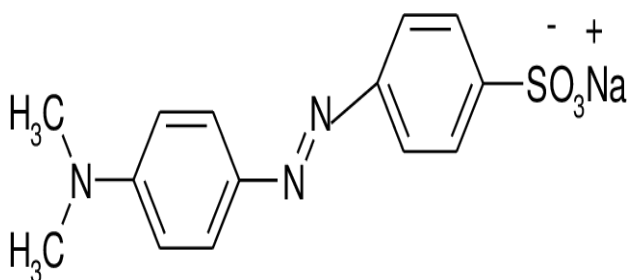

Figure 1: Chemical structure of methyl orange.

When MO is exposed to water it forms non-biodegradable toxic component. Its toxic effect may result from its accidental ingestion by human. Due to its toxic nature it has adverse effect on aquatic lives. It causes eye and skin irritation, nausea, vomiting and diarrhea. So it is considered as one of the awful organic pollutant among azo dyes. Hence, in this study, MO has been used as model dye pollutant to study the photocatalytical degradation efficiency of CuO nanoparticles.

Materials and methods
Reagents

All the reagents obtained were analar grade and solutions were prepared in distilled water.

Copper (II) nitrate trihydrate $Cu(NO_3)_2.3H_2O$ (AR), Sodium hydroxide NaOH (LR), Lauryl sodium sulphate NaCl, H_2SO_4 (LR) were purchased from SD fine, India. Dehydrated Alcohol (C_2H_5OH) was bought from Bengal Chemicals and Pharmaceutical Ltd, India. AR grade methyl orange was purchased from Glaxo smith kline Ph armaceuticals Limited, Mumbai.

Synthesis of CuO nanoparticles

The 20 mL of 0.1 M NaOH solution was taken in beaker. The 4 mL of lauryl sodium sulphate (SDS) was added to it. Then (0.1 M) $Cu(NO_3)_2.3H_2O$ solution was added drop wisely from the burette. During addition, stirring was done continuously with the help of magnetic stirrer. Here, Lauryl sodium sulphate (SDS) was used as capping agent. Then copper hydroxide was formed which was filtered and washed with distilled water and finally with the dehydrated ethyl alcohol. Then the precipitate was calcined at 500ºC for 6 hours[15]. Thus, CuO has been prepared. The phase state of as prepared CuO was studied by using XRD (Rigaku X-Ray diffractometer using monochoromatized Cu Kα{λ=1.54º}) and surface functionality was investigated by FT-IR spectroscopic methods.

Photocatalytic activity of the CuO nanoparticles

To evaluate the photocatalytic activity of as prepared CuO, MO has been used as the representative pollutant. The photo degradation experiments were carried out under the following conditions: The 0.05 g of as prepared CuO were added into a 100 mL aqueous MO dye solution with the initial concentration of 0.9×10^{-5} M at the room temperature, acidic pH, followed by the addition of 1.5 mL of 50% H_2O_2. The resultant suspension was stirred using a magnetic stirrer for 1 hour in dark to establish an adsorption- desorption equilibrium. The concentration of the residual dye was measure d using UV-visible Spectrophotometer at 350 nm wavelength. The photocatalytic activities were examined by measuring the absorbance at every 30 min. The absorbance was measured till more than 80% degradation of the dyes resulted.

Similarly, other experiments were carried out by varying the dose of CuO such as 0.025g 0.25g, 0.1g and 0.3g. In the same way opti,mum pH of the solution were also investigated. The % degradation of MO using CuO photocatalyst was also calculated by using the formula (equation 1)

% Degradation = C_0-C/C_0×100 ………………(1)

Where, C_0 is the initial concentration of MO, C is the final concentration of MO.

Reaction kinetics was also investigated. The pseudo-first order rate constant (k) is calculated using Langmuir – Hinshelwood model (equation 2):

$$\ln (C_0/C) = k \quad \text{……………………………(2)}$$

Where, k, denoted the apparent reaction rate constant,
C_0 is the initial concentration, and
C is the concentration at the reaction time (t).

Results

Characterization of CuO

XRD

The XRD pattern of as prepared CuO is shown in Fig. 2. In Fig. 2, the diffraction peaks were well defined and one can observe sharp diffraction peaks at 35°, 39°, 49°, 53°, 58°, 62° and 68° at 2θ which are assigned for CuO according to JCPDS card No 89-5899. The sharp diffraction peaks are the indication of crystalline nature of the material.
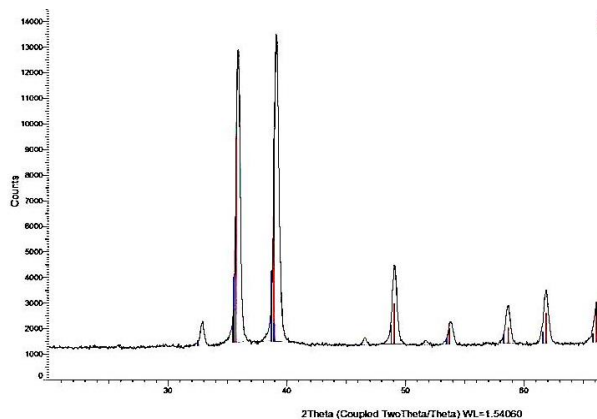

Figure 2: XRD pattern of as prepared CuO material.

The average crystalline size was also calculated from the most intense peaks using Debye-Scherer's equation (eqn 3)

$$D = K\lambda/ \beta Cos\theta \quad \text{……………………………(3)}$$

where, K is the shape factor for spherical particles which value is equal to 0.9. Similarly, λ is the wavelength of X-ray radiation which is equal to 0.15406 nm. Whereas β is the full width at half maximum and θ is Bragg's angle.

Here, D indicates the average particles size. The particle size was found to be 10 nm. Hence, as prepared CuO was found to be nano in size. The XRD pattern and crystalline size are quite analogous with reported value[16].

Fourier Transformation Infrared [FT-IR]

The FT-IR spectrum was obtained which is shown in Fig. 3. The weak and broad band around 3387-3600 cm^{-1} and 1606 cm^{-1} were observed which indicates the stretching band of hydroxyl groups. Similarly, weak vibration band at 1600 cm^{-1} could be seen which indicates the presence of little water absorbed on the surface of the metal oxide. A peak around the 1111 cm^{-1} was found which broadcast the stretching band of C-H vibration. It can also be observed a band at around 600 cm^{-1} which is assigned for Cu-O stretching band. These bands are in agreement with bands reported in the literature[16].
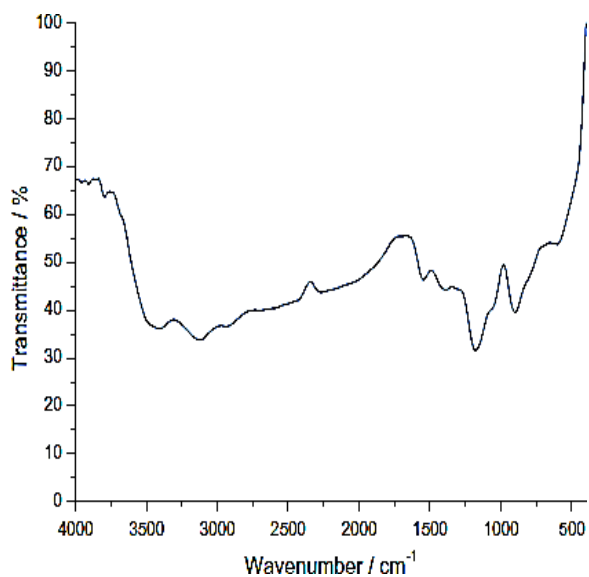

Figure 3: IR-spectra of CuO.

Spectrophotometric method for the determination of methyl orange (MO)

The determination of the methyl orange solution was obtained by using the spectrophotometer. The λ_{max} was obtained at 465 nm wavelength. The calibration curve was prepared to determine equilibrium concentration of MO after photocatalytical degradation. The efficiency of photocatalyst was investigated where the effect of pH,

effect of catalyst dose, time of degradation were also studied. The results revealed were collected.

Effect of pH on the photocatalytic activity of CuO photocatalyst for the degradation of MO

The effect of pH on photocatalytic degradation of MO in the presence of 0.05 g CuO nanoparticle under UV-irradiation was investigated at pH 3, 4, 6 and 9. The results are presented in Fig. 4.
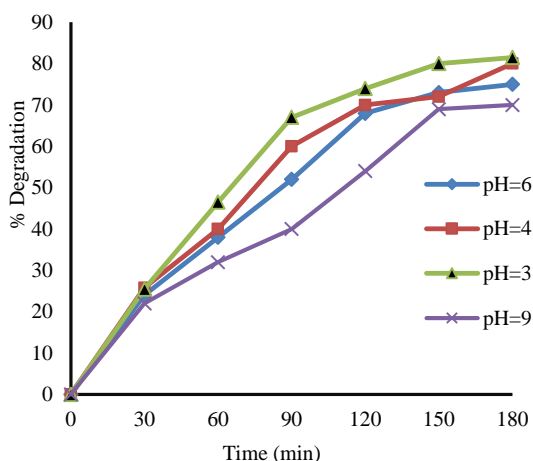
Figure 4: Percentage degradation of MO using 0.05 g of CuO photocatalyst at different pH as a function of time (min) of UV light irradiation.

The nature of curve shows that at all pH degradation increases in similar pattern upto 30 minutes. However, the curve seems to be different after 60 minutes. When pH increases from pH 4 to 9 the degradation % gradually decreases which was obvious in the curves (Fig. 4).

The curves clearly display the high degradation % at pH 3. In acidic condition, there are positively charged protons at the surface of CuO which attracts negatively charged sulphonate groups of MO. Hence, at acidic conditions, the interactions between a positively charged catalyst surface and negatively charged dyes favor electrostatic attraction. But when the solution pH went up from 4 to 9, attraction tendency decreased. It may be due to high OH^- group at the surface which showed repulsion between negatively charged sulphonate groups of MO and OH^- group at the surface of catalyst. When MO dye attracts towards surface of catalyst, then degradation of MO takes place. Hence, further experiments were carried out at pH 3.

A study on photocatalytical activity of CuO by varying catalyst dose
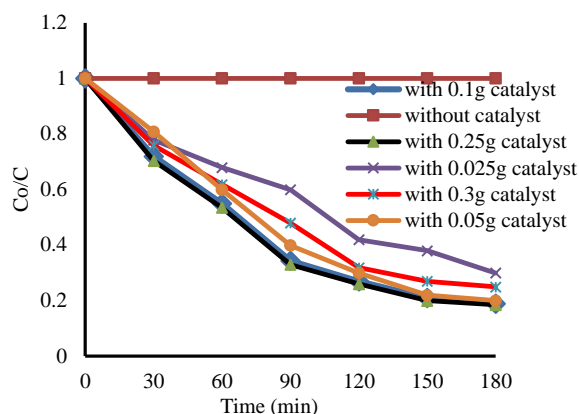
Figure 5: A plot of Co/C as a function of time (min) in photocatalytic degradation of MO using different dose of CuO catalyst under UV light in presence of H_2O_2.

Fig. 5 shows the plot of photocatalytical degradation of MO at pH 3 under UV light in the presence of H_2O_2 by the use of different dose of CuO photocatalyst. A straight line curve could be seen in plot which shows there is no MO degradation without using catalyst. When the less amount of the catalyst (0.025g) has been used, some degradation of the dye could be seen. The further degradation could be clearly perceived in graph with 0.05g and 0.25g photocatalyst. However, when the dose of the catalyst was further increased to 0.3g, the degradation was found to be decreased. This declined degradation may be due to the large amount of catalyst. In general, the increase in the catalyst amount actually increases the number of active sites on the photocatalyst surface thus causing an increase in the formation of number of •OH radicals which can take part in actual discoloration of dye solution. Here, H_2O_2 acts as oxidant which also provide more •OH radicals and helps in dye degradation. However, beyond certain limit of the catalyst amount, the solution becomes turbid and thus blocks UV radiation to enter into reaction flask and therefore percentage degradation starts decreasing. Here, 0.025g of the catalyst was found to be insufficient for the photocatalytic degradation of the dye so that the percentage degradation is less whereas 0.3g of the catalyst is excess which causes turbidity and possibility of agglomeration of nano catalyst which hinders the UV light radiation to reach at the bottom. Hence, the photocatalytic degradation of the

dye was found to be reduced. Here 0.05 and 0.25 g catalyst dose showed good results. Then, further apparent constants were evaluated to find the rate of reaction.

The apparent rate constant using different dose of CuO under UV light in presence of H_2O_2 was calculated and the results were presented in Fig. 6.
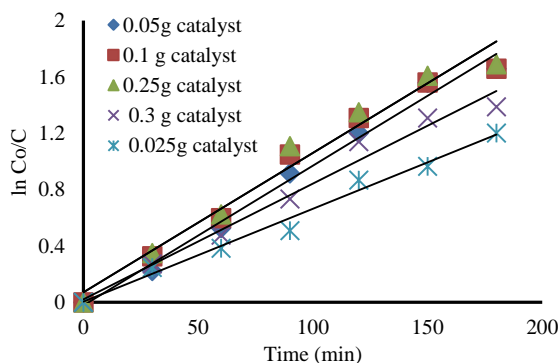

Figure 6: A plot of ln C_0/C as a function of radiation time (min) to determine apparent rate constant K.

Figure 6 shows a graph of ln C_0/C as a function of time in minute. In the graph, straight lines were observed for catalyst dose 0.025, 0.05, 0.25, 0.3 g. The rate constant K of all straight curves were evaluated using slope of respective curve. The value of rate constant of all the cases is presented in Table 1 which leads to the rate of reaction. The results revealed that the rate constant 0.0099 min^{-1} in case of using 0.05 g of photocatalyst leads to good photocatalyst reaction. It is in agreement with literature value[17]. But, the rate of reaction is lowered at high catalyst dose of 0.3 g. Similarly, the rate of reaction was also found to be lowered at low dose of the catalyst (0.025g). Hence, the optimum CuO dose was found to be 0.05g at pH 3 under UV light using H_2O_2.

Table 1: Rate constant calculated for different CuO catalyst dose.

Dose (in g)	Rate constant K (min^{-1})
0.05	0.0099
0.1	0.0097
0.25	0.0099
0.3	0.0082
0.025	0.0066

Determination of optimum time of irradiation

The optimum time for degradation of MO dye was also evaluated at optimum pH 3 and optimum catalyst dose of 0.05 g CuO under UV light in presence of H_2O_2. The result is presented in Fig. 7. A curve shows that there is sharp increase in degradation % upto 90 min, however after 120 minutes curve was observed to be plateau indicating constancy. Hence, the optimum time for the degradation of MO was established to be 150 minute.
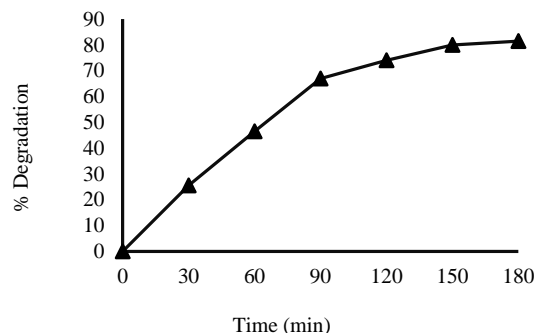

Figure 7: Percent Degradation as a function time (min) of UV light irradiation using 0.05g of CuO catalyst dose at pH 3in presence of H_2O_2

Possible reaction mechanism of photo degradation of MO using over CuO photocatalyst

Possible photocatalytic processes is shown in Fig. 8. As can be seen in Fig. 8, when CuO photocatalyst in contact with the organic pollutants, was illuminated with UV light, reaction system absorbs light quanta hμ. As a result, electrons are promoted from its valence band to the conduction band and electron-hole pair will be generated.

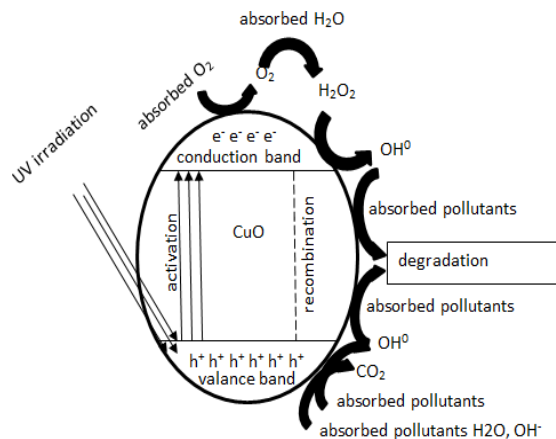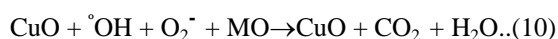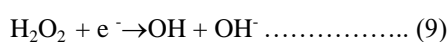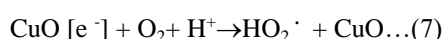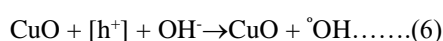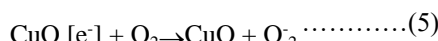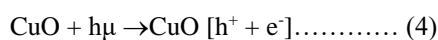**Figure 8: Possible pathways followed during the MO degradation.**

The charge species OH•, H⁺ and •O₂⁻ will be formed and diffused rapidly towards the catalyst CuO surface where oxidation-reduction reactions may occur. Then the excited photoelectrons will be formed which may react with adsorbed oxygen molecules O_2 to form electronically active superoxide anion radicals (O_2^-). On the other hand, photo-induced holes in the valence band may oxidize OH^- leading to the formation of hydroxyl radical species ($OH^°$). The valence band (h^+) potential is positive enough to generate hydroxyl radical ($^•OH$) from water that adsorbed at the surface on CuO and the conduction band (e^-) potential is negative enough to reduce adsorbed molecular oxygen leading to peroxide radicals as shown in the following equations (4-10):

$CuO + h\mu \rightarrow CuO [h^+ + e^-]$............ (4)

$CuO [e^-] + O_2 \rightarrow CuO + O_2^-$ ....(5)

$CuO + [h^+] + OH^- \rightarrow CuO + ^°OH$.......(6)

$CuO [e^-] + O_2 + H^+ \rightarrow HO_2^· + CuO$...(7)

$HO_2^· + H^+ \rightarrow H_2O_2$ ....(8)

$H_2O_2 + e^- \rightarrow OH + OH^-$ ....(9)

$CuO + ^°OH + O_2^- + MO \rightarrow CuO + CO_2 + H_2O$..(10)

Here, hydroxyl radical is a powerful oxidizing agent which may attack the organic matter (R) present at or near the surface of CuO. It is capable to degrade toxic and bio resistant compounds into harmless species. The products of photodegradation may reduce to purely mineralized compounds and then CO_2 will be released.
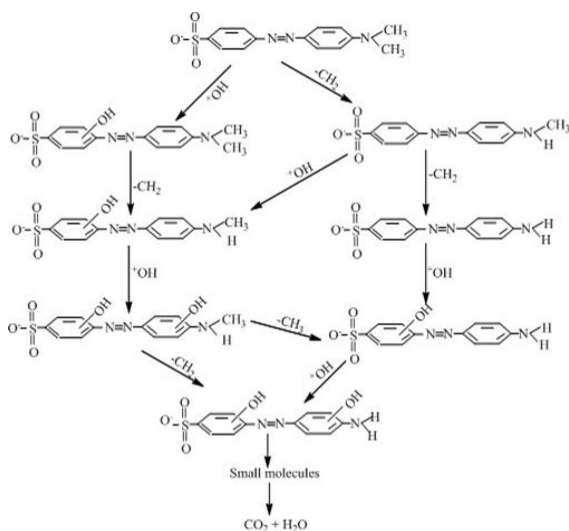

Figure 9: Possible pathways followed during MO degradation.

Figure 9 shows the degradation pattern of MO using CuO photocatalyst[18].

As can be seen in Fig. 9, there are mainly two branches of reactions namely branch I and branch II. Each branch consists of different steps which are described as follows:

Branch I: It consists of following steps:

Step a. Hydroxyl radical released in the system, was absorbed by MO (N,N- dimethylaminoazobenzene-4-sulphonic acid) and (N,N-dimethylaminoazo benzene-1-hydroxy-4-sulphonic acid) was formed.

Step b. Then methylene group departs and N-methylaminoazobenzene-1- hydroxy-4-sulphonic acid was formed.

Step c. Again, another hydroxyl radical gets attached to the benzene ring giving the compound of N-methylamino-1-hydroxyazobenzene-1-hydroxy-4- sulphonic acid.

Step d. Then, another methylene group departs leaving amino-1- hydroxyazobenzene-1-hydroxy-4-sulphonic acid. Thus formed compound degraded into small molecules and finally break down into CO_2 and H_2O as a byproduct.

Branch 2: Similarly, it also consists of following steps:

Step a. Methylene group departs from MO (N,N-dimethylaminoazobenzene-4- sulphonic acid) then it results in the formation of N-methylaminoazobenzene- 4-sulphonic acid.

Step b. Then, from the above formed compound N-methylaminoazobenzene- 4-sulphonic acid, either it absorb OH• radical and follows branch 1 again or if it releases CH_2 it gives aminoazobenzene sulphonic acid.

Step c. It further reacts with reactive OH• and produces aminoazo-1- hydroxybenzene sulphonic acid.

Step d. The above formed compound again reacts with the reactive OH• to give amino-1-hydroxyazobenzene-1-hydroxy-4-sulphonic acid. Thus formed compound degraded into small molecules and finally break down into CO_2 and H_2O as a byproduct.

Discussion

From the study, it has been summarized that Copper oxide (CuO) can be synthesized by simple precipitation method. The XRD pattern of as prepared CuO showed the sharp peaks at 35º, 39º, 49º, 58º, 62º and 68º at 2θ for CuO indicating the crystalline nature. FTIR spectra showed a band at around 600 cm^{-1} which was assigned for Cu-O stretching band.

The photocatalytic activity of CuO was evaluated by the photocatalytical degradation of MO. Without catalyst, photolytic degradation of MO was not effective but a pronounced effect was exhibited when catalyst was used. The 0.05g of catalyst was found to be sufficient for 81% degradation of MO dye. The 81% of the photocatalytic degradation was reached within 150 min. The rate constant (K) for methyl orange using 0.05g CuO catalyst was found to be 0.0099 min^{-1} demonstrating decent rate of reaction.

Acknowledgement

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