Synthesis and Characterization of Copper Oxide Composite and Study of Composite mediated Photo-oxidative Degradation of Methylene Blue Under Visible Light

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ABSTRACT. Copper oxide composite was prepared from copper(II) acetate. Characterization of composite was performed by Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), FT-IR Spectroscopy and X-ray diffractometry. According to the findings of SEM the particle size was within the range from 450 nm to 550 nm. Band gap energy was determined by reflectance measurement and value was found to be 4.21 eV. From the result of EDS, it appears that the composite contains only Cu and O atoms. Result of XRD confirms that the composite contains CuO, Cu$_2$O and metallic Cu. FTIR spectrum of composite supports the presence of Cu$_2$O. Adsorptive and catalytic properties of composite were studied using Methylene blue as adsorbent. Photo-oxidative degradation of MB was investigated in the suspension of composite in separate experiments at different pH ranging from 2.5 to 5.5 under visible light. Low pH range from 2.5 to 3.5 is most effective for degradation. This was explained by proposing a cyclic mechanism which suggests the conversion of Cu$_2^{2+}$ to Cu$^{2+}$ and vice versa. 95.5% of MB was found to degrade when 5×10$^{-5}$ M solution of MB was irradiated for three hours in 100 mL suspension of composite having concentration 1gL$^{-1}$ at pH 2.5.

1. INTRODUCTION

The use of solar energy for the destruction of pollutants is drawing the attention of scientists. The growing interests among the researchers to find an efficient and economic method to degrade the nonbiodegradable organic pollutants lead them to use solar light in presence of photocatalysts. TiO$_2$, ZnO mediated photodegradation of organic pollutants is well studied but the process is very inefficient in presence of artificial visible light or even in solar light due to the wide band gap of these semiconductor oxides [1-4]. Fenton reactions [5] have shown to be useful in the degradation of organic pollutants where Fe$^{II}$ is oxidized to Fe$^{III}$ producing very efficient oxidant OH• radicals which leads to photooxidative degradation of pollutants. Another efficient photocatalyst is copper(I) oxide the band gap energy of which is 2.17eV [6] but it is thermally unstable and is easily converted to copper (II) oxide. A sophisticated instrument is required to synthesis Cu$_2$O. On the other hand literature value of band gap energy of copper(II) oxide is 1.7eV which is a p type semiconductor and is inefficient photocatalyst. Oxidation reaction involving Cu$^+/Cu^{II}$ have been studied by many researchers. In presence of aerobic oxygen this redox couple can produce H$_2$O$_2$ which breaks down to OH• radicals under suitable conditions. The presence of Cu$_2$O in the composite may give Fenton like reaction Cu$^+ + H_2O_2 = Cu^{2+} + OH^- + OH•$ in which H$_2$O$_2$ may act both as oxidizing and reducing agents resulting the conversion of Cu$_2^{2+}$ to Cu$^{2+}$ [7] and producing OH• radicals. However, there is a tremendous paucity of information about the use of Copper oxide composites as photocatalyst.

The present objectives are to prepare copper oxide composite by simple method and to use the composite as mediator of degradation of MB and finally to apply the cyclic conversion of Cu$^{I}$ to Cu$^{II}$ and vice versa to explain the experimental results.
2. EXPERIMENTAL

2.1. Preparation of copper oxide composite

In a 500 mL beaker equipped with a magnetic stirrer, 6.25 g of copper(II) sulfate pentahydrate was dissolved in 125 mL of water with continuous stirring at 40°-50°C. 15 mL of 50% ammonia solution was added to it in warm condition until the color of the solution turns to intense blue color of copper ammonium complex. During the addition of ammonia, the precipitate of light blue copper(II) hydroxide was formed which was dissolved with further addition of ammonia solution. 2.0 g of sodium hydroxide pellets was added to the deep blue solution and the mixture was stirred about 30 minutes at 55°-65°C. A light blue precipitate of copper(II) hydroxide was reappeared during this time. The mixture was allowed to cool at room temperature and the precipitate was filtered using a Buchner Funnel. The blue precipitate was repeatedly washed with warm water and dried. Copper(II) hydroxide was dissolved in 25 mL of 10% acetic acid with continuous stirring in a 250 mL beaker. When the solution was nearly to dry under warm condition, it was dried on filter paper and was grounded using a mortar. Prepared Copper(II) acetate was calcined at 200°C for about 2 hours.

2.2. Characterization of prepared composite

Prepared composite was characterized by different techniques. Scanning Electron Microscopy (JSM-6490, JEOL, Center of Advanced Research Science, University of Dhaka), Energy Dispersive X-Ray Spectrometer (Center of Advanced Research Science, University of Dhaka), Fourier Transform Infrared Spectrophotometer (SHIMADZU, Department of Chemistry, University of Dhaka), X-ray diffractometer (Department of Chemistry, Tohoku University, Japan) and Reflectance measurement (UV-1800 PC, UV-visible Spectrophotometer, SHIMADZU) were used to study morphology, particle size, stoichiometry, identification of functional groups, crystallinity and band gap energy of the prepared composite.

2.3. Adsorptive and photocatalytic properties of composites

10.0 mL of Methylene blue solution was added to 90.0 mL suspension of copper oxide composite in a 100 ml beaker. The desired pH of the suspension was adjusted using either 1.0M or 0.1M HCl. Suspension was placed on magnetic stirrer in the lamp house in absence of light. After proper mixing about 2.0 mL of suspension was taken in a semi-micro test tube to analyze and to determine the initial concentration. This was done in a shortest possible time. After an hour (equilibrium time) 2.0 mL of suspension was collected in a test tube and was then centrifuged for 30 minutes. The centrifugates was analyzed by UV-visible Spectrophotometer and absorbance was measured at $\lambda_{\text{max}}$ of Methylene blue using the reference of deionized water the pH of which is same as suspension. Amount adsorbed was calculated. Experiments are carried out in ambient temperature. To study the photocatalytic activity of composite the suspension was irradiated by visible light and the light source was placed in a closed lamp house covered with black cloth. The interior walls of the house were covered with aluminium foil to prevent the loss of light by absorption. Before the irradiation the suspension was stirred by magnetic stirrer for an hour to achieve the equilibrium of adsorption in dark. During photodegradation suspension was collected at different time intervals in different test tubes and were centrifuged for 30 minutes and were analyzed as before to determine the absorbance at different time intervals.
3. RESULTS AND DISCUSSION

3.1. SEM image of composite

Fig. 1. SEM image of composite at 25000 and 50000 magnification.

The SEM images of composite show particle size (diameter) in the range of 540.9 nm to 467.38 nm at 50000 magnification. The images also show that the particles are mostly hexagonal and spherical. The earlier investigators obtained the morphology of the tenorite nanoparticles which suggests rod shape structure [8].

3.2. EDS spectrum of composite

EDS spectrum (Figure 2) of composite shows peaks of Cu and O supporting the purity of the compound. The ZAF standerdless method was used to know the abundance of atoms in the sample. Data shows the abundance of Cu and O atoms are 71.74 and 28.26 percent respectively. Percentage of abundance of atoms indicates that the sample may be composed of Copper(I) oxide (Cu$_2$O) and Copper(II) oxide (CuO).

Fig. 2. EDS spectrum of composite.
3.3. **FTIR spectrum of composite**

Fig. 3. shows the FT-IR spectrum of composite. Strong peak corresponding to 650 cm\(^{-1}\) confirms the formation of pure Cu\(_2\)O [9]. A weak band at around 2300 cm\(^{-1}\) may be due to the vibrations of atmospheric CO\(_2\). The adsorption band corresponding to 3310 cm\(^{-1}\) was attributed to the presence of H-O-H bond.

![Fig. 3. FTIR spectrum of composite.](image)

3.4. **XRD pattern of composite**

The XRD pattern of composite (Fig. 4.) shows a series of characteristic peaks. The XRD peaks at 2\(\theta\) values of 29.584\(^\circ\), 36.416\(^\circ\) and 43.336\(^\circ\) correspond to the crystal planes of (110), (111) and (200) of crystalline Cu\(_2\)O (JCPDS file no. 05-0667).[10] The peaks at 35.505\(^\circ\) and 38.672\(^\circ\) can be attributed to the Miller indexes of (-111), (200) confirming the presence of CuO according to JCPDS file no. 05-0661 [11]. Two peaks appearing at 42.363\(^\circ\) and 50.416\(^\circ\) can be indexed to the (111) and (200) crystal planes of metallic copper (JCPDS file no. 04-0836) [12].

![Fig. 4. XRD pattern of composite.](image)
3.5. Band gap energy of composite

![Graph showing reflectance as a function of wavelength.]

**Fig. 5.** Measurement of reflectance as a function of wavelength.

In the fig. 5, the best fit point corresponds to 295 nm which gives band gap energy of composite to be 4.21 eV.

3.6. Adsorption of MB in the suspension of composite

![Graph showing amount adsorbed vs. pH.]

**Fig. 6(a).** Amount of MB adsorbed on composite at different pH.

![Graph showing spectrum of MB after adsorption.]

**Fig. 6(a).** Spectrum of MB after adsorption for an hour at different pH.

Adsorption of MB in the suspension of 0.10g composite was investigated at the equilibrium time. The equilibrium time was found to be an hour by earlier experiment. The experiment was repeated by varying the pH of the suspension. The graph 6(a) shows the variation of amount adsorbed vs. pH, suggesting that the amount of adsorption decreases with increasing pH of suspension. The observed facts may be explained with the help of solubility of Cu₂O. In acidic medium Cu₂O dissolve giving Cu²⁺ ions which remain in the bulk leaving the surface negatively charged. The surface will acquire lesser negative charge as the pH of the suspension increases. Since MB remains as cation in aqueous media, it will be easily adsorbed on the negative surface and adsorption will increase with decreasing pH. Cationic Methylene blue adsorbed mainly via electrostatic force of attraction on the negatively charged surface.
3.7. Photo-oxidative degradation of MB in the suspension of composite

Photo-oxidative removal of MB was investigated by irradiating the suspension under artificial visible light at room temperature with continuous stirring in a closed chamber at constant pH. Change of absorbance was measured at different time intervals.

![Graph showing % Removal vs. Time (min) at different pH](image)

**Fig. 7(a).** Comparison of removal of MB at different pH in the suspension.

![Graph showing % Removal vs. Initial pH](image)

**Fig. 7(b).** Removal of MB at different pH in the suspension of composite.

The experiment was repeated under different pH within the range 2.5 to 5.5. The results are shown in figure 7(a). The decrease of removal of MB with increasing pH of suspension has been shown in the figure 7(b). Sharp decrease was found after pH 4. This is expected from the result of adsorption. This can be explained by the following mechanism.

In the presence of light, following reactions may occur under acidic condition [7];

\[
\text{Cu}_2\text{O} + \text{H}_2\text{O}^+ = \text{Cu}_2^{2+} (\text{aq})
\]

\[
\text{Cu}_2^{2+} + \text{O}_2 + 2\text{H}^+ = 2\text{Cu}^{2+} + \text{H}_2\text{O}_2
\]

\[
2\text{Cu}^{2+} + 2\text{H}_2\text{O}_2 = \text{Cu}_2^{2+} + 2\text{HO}_2^- + 2\text{H}^+
\]

\[
\text{Cu}_2^{2+} + \text{H}_2\text{O}_2 = 2\text{Cu}^{2+} + \text{OH}^- + \text{OH}^-\cdot
\]

\[
\text{MB} + \text{OH}^-\cdot \rightarrow \text{Degradate Products}
\]

\[
\text{MB} + \text{HO}_2^-\cdot \rightarrow \text{Degradate Products}
\]

H\(_2\)O\(_2\) may act both as oxidizing and reducing agent. Reactions 3 and 4 show the production and consumption of cuprous ions suggesting that as soon as Cu\(_2^{2+}\) ions diffuse in the bulk, reaction starts following cyclic path. Production and consumption of cuprous ions (by step 3 and 4) by H\(_2\)O\(_2\) produce powerful oxidants OH\(^-\) and HO\(_2\)\(^-\) which immediately react with MB to degrade this into smaller fragments. The mechanism shows that the degradation follows cyclic process. The above processes are pH dependent. At lower pH reactions 1 and 2 will be faster than higher pH and as a result all processes will be faster in lower pH. It is expected that the photo-oxidative degradation will be maximum in the lowest pH and vice versa.

The present results can be compared with the results of J. Bandara, J. Kiwi who investigated the degradation of nitrophenols in the suspension of CuO aerogel [7] (80% Cu\(^{1+}\) + 15% Cu\(^{11+}\) + 5% Cu\(^{6+}\)) by irradiation under solar simulator. They found that the pH 2.5 was the most favorable condition for degradation. They also suggested the above cyclic mechanism involving Cu ions.
support of the proposed mechanism for the present degradation, the tests for Cu\(^{2+}\) and H\(_2\)O\(_2\) were performed. In the centrifugate of suspension of different pH, the drop of potassium ferrocyanide was added. In the centrifugate of pH 2.5, large amount of colored precipitates were formed indicating the presence of Cu\(^{2+}\) ions. The intensity of color decreases with increasing pH suggesting that pH 2.5 is most favorable condition for Cu\(^{2+}\) ions to form. In another portion of centrifugate, one drop of potassium permanganate was added and was wormed. The color of the permanganate was fully disappeared for the centrifugate of pH 2.5, 3.5 and 4.5, supporting the presence of H\(_2\)O\(_2\). However the test of Cu\(^{2+}\) and H\(_2\)O\(_2\) did not give positive results where pH was beyond 5.5. The above qualitative tests confirm that the low pH (pH 2.5 – 4.0) is the favorable condition for the production of Cu\(^{2+}\) ions and H\(_2\)O\(_2\).

4. CONCLUSION

Copper oxide composite was prepared from copper acetate and characterized by SEM, EDS, FTIR, XRD and band gap energy is measured by reflectance measurement in UV-visible spectrophotometer. The results of characterization show that the composite is composed of Cu(I), Cu(II) and metallic copper of which Cu(I) was predominant. Adsorption of MB in suspension was investigated at room temperature. The adsorption was due to electrostatic force of attraction since MB remains as cation in the suspension and surface becomes negatively charged due to dissolution of Cu\(_{2}^{2+}\) ion from Cu\(_2\)O. Adsorption was found to increase with decreasing pH. Copper oxide composite mediated photo-oxidative degradation was performed in presence of visible light at different pH ranging from 2.5 to 5.5. When 5×10\(^{-5}\) M solution of MB was irradiated in 100 mL suspension of composite of concentration 1gL\(^{-1}\) at pH 2.5 for three hours in visible light 95.5% was found to degrade. The removal was found to be pH dependent. Lower is the pH of the suspension, higher is the removal. The photooxidative degradation of MB proceeds through a mechanism involving series of reactions producing H\(_2\)O\(_2\), OH• and HO\(_2\)• radicals as intermediates. H\(_2\)O\(_2\) acts both as oxidizing and reducing agent for Cu\(_{2}^{2+}\) and Cu\(^{2+}\) ion respectively which play vital role to produce antioxidant species.

References