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Synthesis and Characterization of New Heterogeneous Catalysts Via Pre-templating of Schiff base Cu (II) Complexes for Efficient Photo Degradation of Methylene Blue

Laila H. Abdel-Rahman[1,*], *Khaled M. H. Mohammed*[1,2], *Mohamed R. Shehata*[3], *Ebtehal Abdel-Hameed Ahmed*[1] *and Ayman Nafady*[1]

[1]Chemistry Department, Faculty of Science, Sohag University, 82524 Sohag, Egypt
[2]School of Chemistry, University of Southampton, Southampton, SO17 1BJ, UK
[3]Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt

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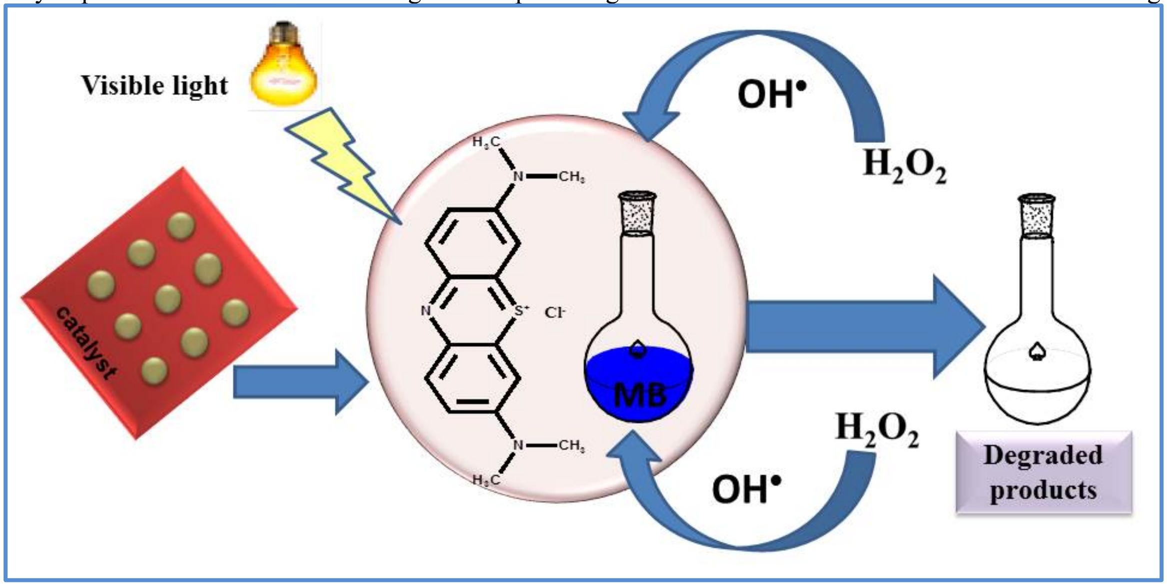
Abstract: In this study, two copper Schiff base complexes (CuHL and CuH_2L) were successfully anchored to functionalized graphene oxide (FGO) to afford C1 and C2 heterogeneous catalysts. The physicochemical and microscopic properties of the prepared complexes were characterized via different analytical techniques such as IR, UV-Vis, X-ray and SEM, which all attested to the formation of the desired complexes. Additionally, the photocatalytic efficiency of both C1 and C2 catalysts was evaluated by the photodegradation of methylene blue (MB) in the presence of H_2O_2 as an oxidizing agent under visible light. The kinetics of the photocatalytic reaction were monitored in terms of pH, catalyst dosage and MB concentration. The results revealed that at optimum conditions that combined 5 mg of the catalyst, pH= 10 and 6.25×10^{-3} M of MB the photocatalytic process was first order with degradation percentage of 72.4 % for C1 and 91.2 % for C2 in visible light.



Keywords: Schiff bases, Cu(II) complexes, heterogeneous catalysis, photocatalytic degradation.

1 Introduction

Over the past decades, removal of the organic dyes that have different colors, low biodegradability and high toxicity is one of the most challenging tasks in modern society [1-4]. Notably, over 100,000 organic dyes are used worldwide in the manufactures [5]. Temperature, turbidity, pH, alkalinity, acidity and color are all affected by the discharge of primary constituents of pollutants in wastewater into water sources from textile and other industries [6]. The release of these colored wastewaters into ecosystems generates major environmental issues such as aesthetic pollution and eutrophication, as well as the formation of harmful by-

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[*] Corresponding author E-mail: Laila.abdelrahman@science.sohag.edu.eg

products via oxidation, hydrolysis, or other chemical processes in the effluent phase [7, 8]. Thus, it is necessary to develop efficient catalysts that can effectively decompose organic dyes and easy to prepare and operate [9]. Schiff base complexes with ligands containing N, O and other donor atoms play a significant role in applied chemistry as they are chemically stable, biologically active [10], and are applicable in different fields such as oxidation catalysis [11], electrochemistry [12], etc. In this regard, several recent studies have reported the synthesis of novel Schiff base complexes for the purpose of degrading the hazardous colors created during dying and textile production processes [13-16].

Separation, recycling and inadequate stability is considered as the main problem of homogeneous transition metal complexes as catalysts. Because of the long catalytic lifetime, thermal stability, facile separation, easy recyclability, and good selectivity [17]. One of the most effective and important methods of heterogenization is anchoring the homogeneous catalyst on a solid support with a high surface area [18]. Several solid materials have been utilized for heterogenization including, carbonaceous materials, organic polymers, clays, metal organic frameworks, mesoporous silica. etc. [19, 20].

GO is considered as one of the most important solid supports in heterogeneous catalysis. This is due to its high surface area and the presence of epoxides and hydroxyl groups, which enable the binding of active sites. Fortunately, by further chemical modification or functionalization, oxygenated groups can greatly expand the structural/chemical diversity of GO, providing an effective way to tailor the physical and chemical properties of GO to expected extents [21].

In the present work, we report the synthesis of two Cu(II) heterogeneous catalysts (C1 and C2 complexes) obtained via pre-templating of Schiff base ligands, namely HL and H2L and investigating their ability in the photodegradation of MB as a model for the organic pollutants.

2 Experimental

Materials

All chemicals and solvents were of reagent grade. Salicylaldehyde, 2-aminopyridine $Cu(OAc)_2.H_2O$, 2-hydroxy-1-naphthaldhyde is purchased from Sigma Aldrich company. 2,3-diaminopyridine is of Merck company. 3-aminopropyltriethoxysilane (3-APTES), triethylamine (Et_3N), graphite powder, sulfuric acid, potassium permanganate, hydrogen peroxide, hydrochloric acid, methylene blue and toluene were commercially available and used without purification.

Characterization techniques

IR spectra were registered in a range of 400-4000 cm^{-1} with a resolution of 4 cm^{-1} on (FT-IR Alpha Bruker with Platinum -Ate with KBr pellets). Bruker D8 Advance using monochromatic Cu-kα radiation (k = 1.5406 Å) was used to perform X-ray powder diffraction analysis. SEM analysis was conducted on QUANTA FEG250 at National Research Center, Egypt. The UV spectra of the degradation process were recorded on PG spectrophotometer model T+80 at 298 K. The photocatalytic ability was monitored on Jasco V-530 UV/Vis spectrophotometer.

Synthesis of Schiff base ligands and complexes

Synthesis of HL Schiff base and its Cu(II) complex

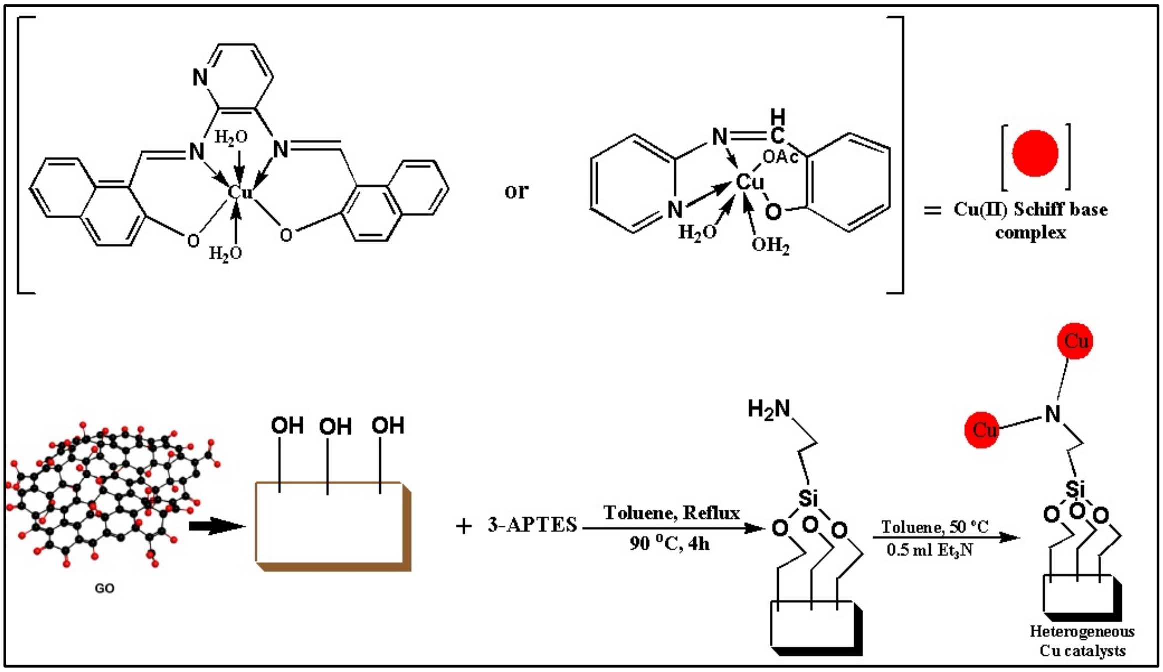
The Schiff base ligand was prepared via the condensation of 2- aminopyridine (0.01 mol, 0.193 ml) and (0.01 mol, 0.941) of pure salicylaldehyde in 20 ml of absolute ethanol. The resulting mixture stirred at room temperature for 4 h. The obtained precipitate was filtered off, washed several times with ethanol and diethyl ether and dried in vacuum. Cu(II) imine complex prepared in 20 ml EtOH (1 mmol, 0.170 g) of $CuCl_2.2H_2O$ added to (1 mmol, 0.198 g) of the free ligand. The mixture was stirred and refluxed at 60˚C for 2h. The solid product was filtered, washed with ethanol and dried under vacuum. The purity of the prepared complex was examined by TLC. The prepared compounds were characterized and listed in supplementary data.

Synthesis of H2L Schiff base and its Cu(II) complex

Schiff base ligand by mixing 0.545 g of 2, 3-diaminopyridine (5 mmol) with 1.72 g of 2-hydroxy-1-naphthaldhyde (10 mmol) in 30 mL ethanol with continuous stirring and reflux for half an hour at 50 ºC with the addition of drops of piperidine as a catalyst till the formation of yellow precipitate [22]. The precipitate was then filtered, washed and dried in vacuo over anhydrous $CaCl_2$. CuH2L complex was prepared by mixing 2.08 g of the H2L Schiff base (5 mmol) with the hydrate metal salt $Cu(CH_3COO)_2.H_2O$ (0.99 g, 5 mmol) in 20 ml ethanol. The reaction mixture was allowed to be stirred for 3 h at room temperature. The solid precipitate of the metal complex was separated, filtered, washed with ethanol, left for drying in vacuo under anhydrous $CaCl_2$. The prepared complex was characterized with different techniques. The results were listed in supplementary data.

Synthesis of Cupper complexes anchored GO

GO was synthesized using modified hummer method [23]. The obtained GO was subjected to surface modification of GO by chemical grafting. Then 0.5 g of GO was refluxed at 90°C for 4 h with 7ml of (3-APTES) dissolved in 15 ml dry toluene. The solid product was filtered and washed with toluene several times and dried overnight at room temperature [24]. The desired C1 and C2 catalysts were prepared by immobilization of the as-prepared Cu(II) Schiff base complexes on the modified graphene oxide by adding 0.1 g of the later in 10 ml toluene to a solution of Cu(II) complex (0.1 g) in 10 ml toluene and



Scheme 1: Schematic representation of GO-CuL catalysts.

0.5 ml of Et_3N [25]. The mixture was stirred and refluxed at 50°C for 5 h as seen in **scheme 1**. The resulting precipitate was filtered, washed with toluene and left to dry.

Photocatalytic degradation of MB

30 ml of methylene blue (MB) at 6.25×10^{-3} M and 5 mg of the catalyst was taken and put in the dark for 30 minutes. Then, a tungsten lamp (100 W) was directed to the mixture [26]. 1 ml of H_2O_2 (30%) was added in a closed system. 2 ml of the supernatant withdrawn from the mixture every 10 minutes and scaned by UV-Vis spectrometer at 652 nm of MB. The efficiency of degradation of MB dye was calculated from the following relation: % degradation = $\frac{(Ao-At)\times 100}{Ao}$

3 Results and Discussion

IR spectra

The spectrum of graphene oxide showed abroad band at 3376 cm^{-1} which attributed to the stretching mode of O-H bonds [27] and confirming the presence of many hydroxyl groups on the surface of graphene oxide. Also, GO exhibited a set of characteristic bands at 2797, 1709, 1612, 1222 and 1034 cm^{-1} due to the stretching mode of –CH, C=O, C=C, C-O and C-O-C moieties, respectively [28]. In comparison, the spectrum of functionalized GO exhibited an obvious decrease in the intensities of the bands and displayed some new bands at 3346 and 1559 cm^{-1} which indicated the presence of NH_2 groups. Also, two bands at 2867 and 2924 cm^{-1} confirming the aliphatic C-H bands [29]. In addition, peaks at 1310 and 1006 cm^{-1} demonstrate the presence of C-N and Si-O-C bonds, respectively; confirming successful functionalization of graphene oxide with the amino propyl group [30]. After immobilization of the complex on the solid support, the imine band was found at 1609 and 1602 cm^{-1} for C1 and C2 complexes, respectively. Also, a complete disappearance of the band corresponding to (N-H). This confirmed the successful immobilization of the prepared complexes on the surface of the modified GO. The IR data were presented in **Fig.1**.

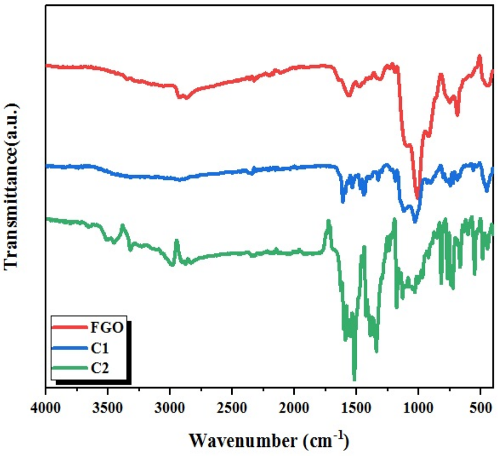


Fig.1: IR spectra of the prepared compounds.

Molecular electronic spectra.

In order to investigate the chemical changes brought on by the loading of the Schiff base complexes, we have also used UV-Vis spectroscopy to study the GO and C1 and C2 catalysts. GO exhibited two characteristic bands at 238 and 284 nm π→π* transitions of C=C bonding and n→π* for the transitions of C=O group, respectively. The immobilization of the prepared Schiff base complexes leads to significant changes and shifts. C1 exhibited two bands at 240, 294 which corresponding to π→π*, n→π* and another two bands at 361 and 415 nm which represent LMCT and d-d, respectively. On the other hand, C2 showed two bands at 327 and 350 nm referred to π→π* and n→π* transitions. Also, there are two broad bands at the range 400-500 nm and 600-700 nm which assigned to LMCT and d-d transitions, respectively. The resulting shift in the spectra can be attributed to the conjunction between the complex and the surface of GO [31].

SEM and XRD analyses.

Scanning electron microscope (SEM) **Fig.2** describes the microstructure and morphology of the samples. The SEM images of GO show crumbled-layered structure and have a smooth surface. Heavy wrinkled flakes are observed in GO layers and edges referring to the Cu complexes immobilized on the GO.

The XRD of GO revealed that upon oxidation of graphite the basal reflection peak is appeared at 2θ = 13˚, the characteristic peak of graphene oxide. The pattern revealed a greater interlayer spacing of graphene oxide between the layers due to oxygen functional groups [32]. The modification process of GO resulted in a significant decrease of the peak at 13˚to a large extent due to exfoliation of GO layers and appearance of a broad peak at 22˚ due to the presence of amorphous silica [33]. After immobilization, it has been found that the broad peak decreased to a large extent which confirmed a successful immobilization and formation of the catalysts. The results are presented in **Fig.3**.

Photocatalytic activity

The photocatalytic activity was investigated under visible light before and after immobilization of the complexes. This can be detected by the decrease in the absorbance of MB by time. In presence of the Schiff base complexes, CuHL was found to have a slight activity towards the degradation of MB **Fig. 3a**. This may be returned to the nature of the Schiff base ligand. In contrast, there is no activity observed for CuH2L before immobilization on modified graphene oxide **Fig. 3b**. The effect of the immobilized Schiff base complexes was

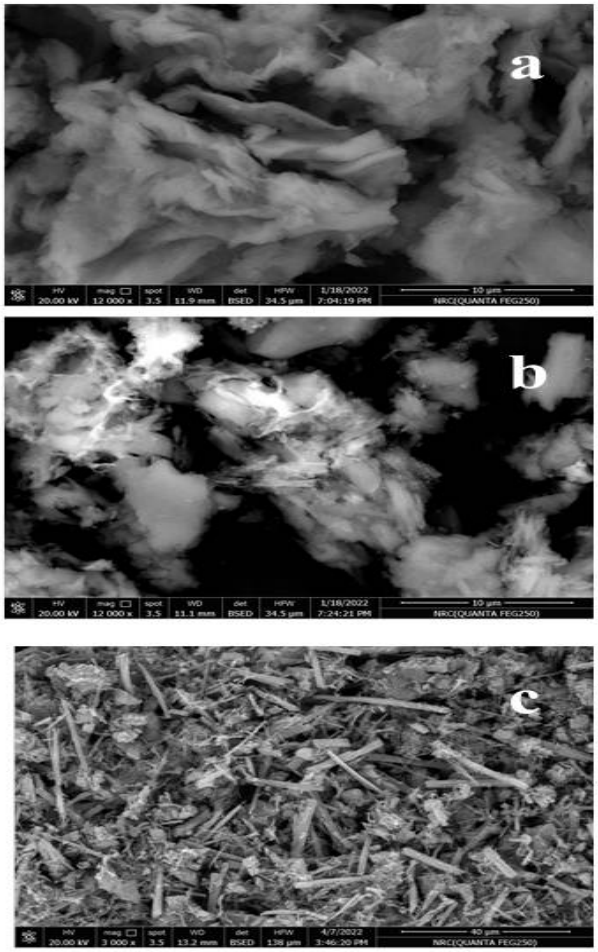


Fig. 2: SEM images of a) GO b) C1 and c) C2.

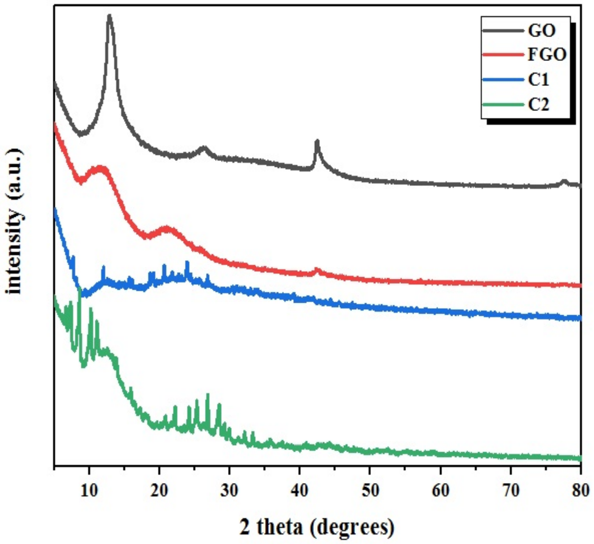


Fig. 3: XRD patterns of GO, FGO, C1 and C2.

clearly detected by the reduction in the absorption intensity of MB **Fig. 4**. To study the kinetics of the photodegradation process in presence of C1 and C2 catalysts, the experimental data were subjected to the following equation **[**34, 35**]**:

$$\ln (C_t/C_o) = -k_{app}t \text{ or } \ln (A_t/A_o) = -k_{app}t \qquad \textbf{(2)}$$

Where, where C_o and C_t are concentration at the beginning and at time, t is the irradiation time. A_t is the absorbance at time t, A_o is the initial absorbance, k is the apparent rate constant and t is the reaction time. From the calculated data, the rate of the reaction was found to be 1.48×10^{-2} min^{-1} with a percent of degradation 72.4% for C1 and 1.6×10^{-2} min^{-1} with a percent of degradation 91.15 % for C2.

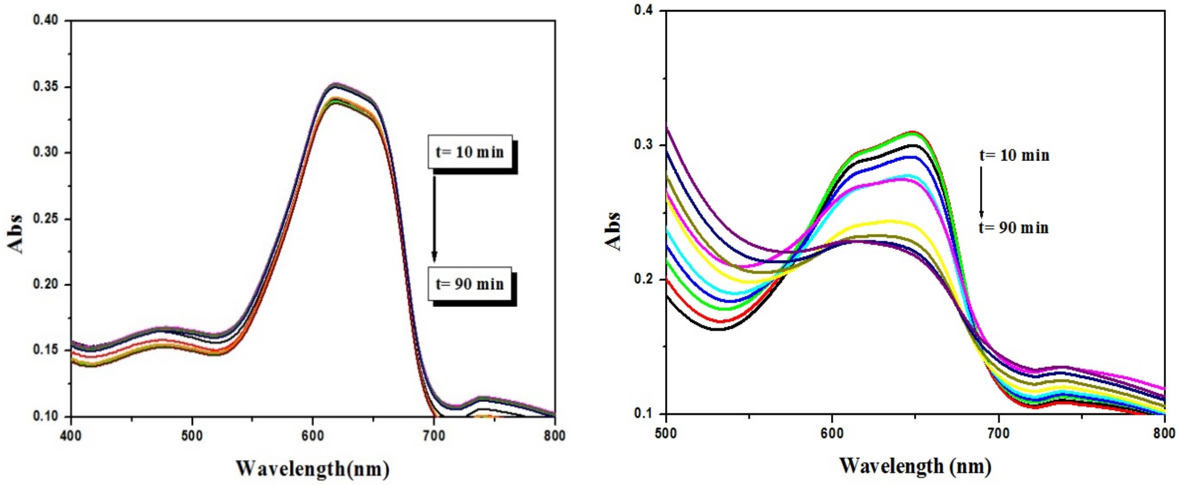


Fig. 3: Photodegradation of MB dye for a) CuHL and b) CuH2L Schiff base complexes under visible light, [complex]= 5 mg , [MB]= 6.25×10^{-3} M.

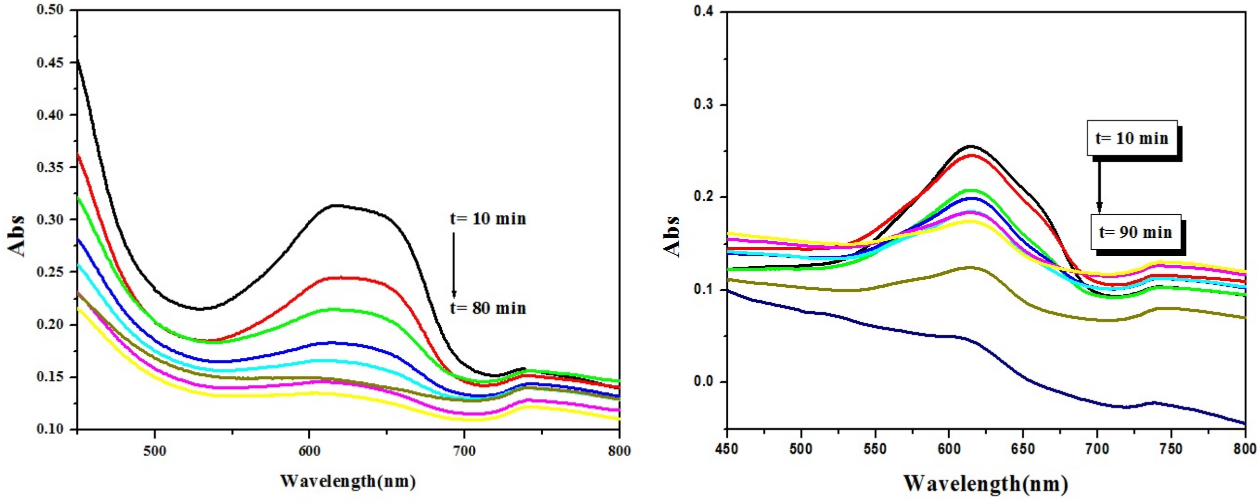
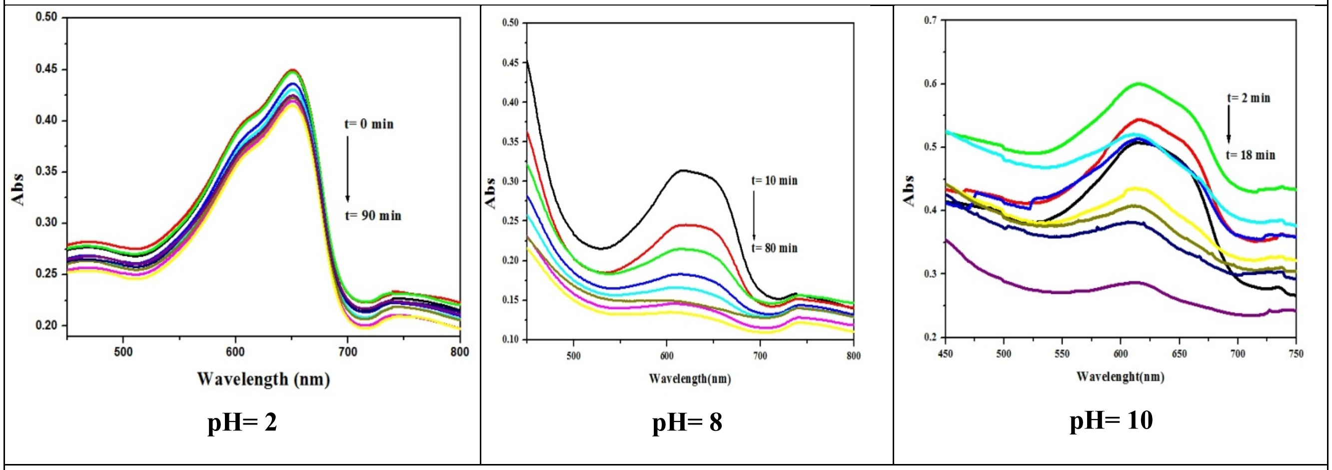


Fig. 4: Photodegradation of MB dye for C1 and C2 Schiff base complexes under visible light and optimum conditions, [complex]= 5 mg, [MB]= 6.25×10^{-3} M.

Effect of pH on degradation of MB

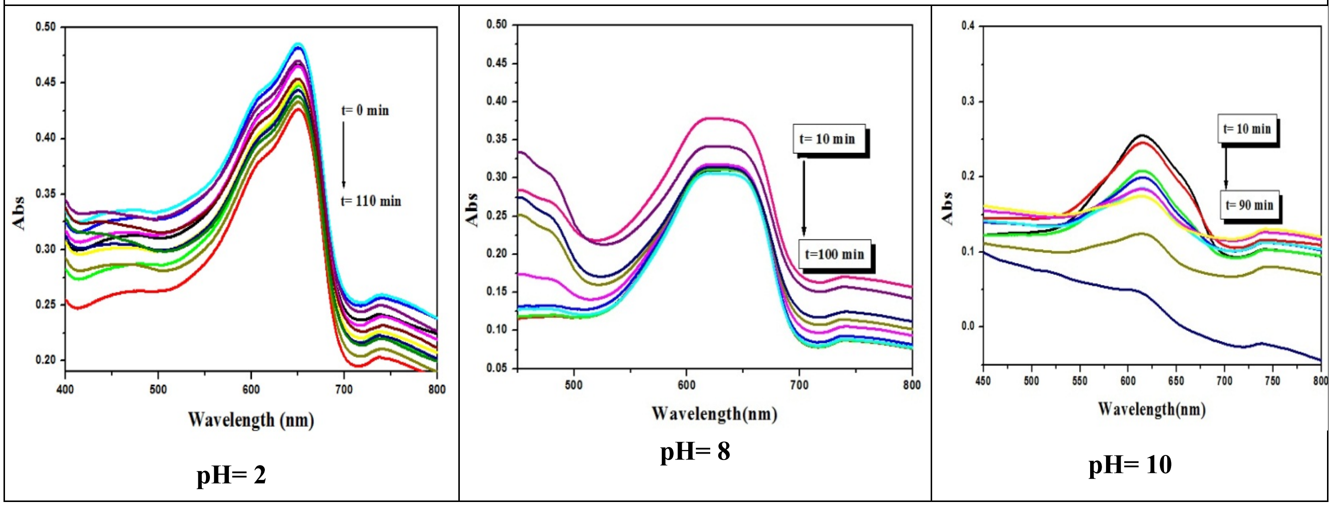
As the pH influences the rate of dye degradation, it was necessary to study the effect of its variation on the reaction. This includes investigating the behavior of the prepared catalysts in three different pH values towards the degradation of MB see **Fig. 5**. Firstly, For C1 catalyst, it has been found that by increasing the pH from 2 to 8, the percent of degradation increased from 6.9 % to 72.4 %, respectively. In addition, the time consumed for the catalytic process decreases. Upon increasing the pH to 10, we found that the percent of degradation decreased to 53.4 %. This can be explained by the fact that when the pH increases, the surface of the catalyst has a higher adsorption of MB which inhibits the penetration of light. In case of C2 catalyst, the basic medium enhances the degradation process and decreasing the reaction time. The percent of degradation displayed the following order: pH 10 > pH 8 > pH 2. This may be due to the effect of basic medium which activating the generation of excess $OH^{\cdot}$ radicals which have a significant role on the degradation of MB **[**36-40**]**.

1. **C1 catalyst**



pH= 2 **pH= 8** **pH= 10**

2. **C2 catalyst**

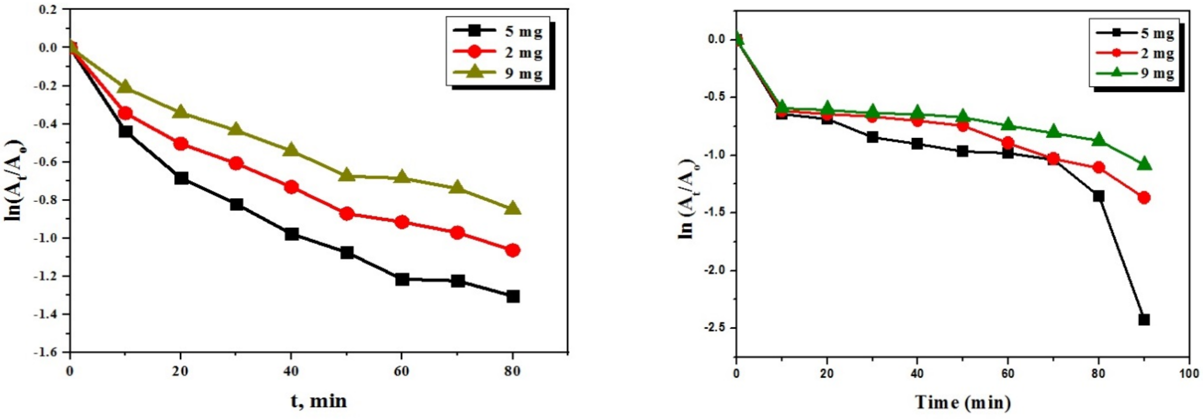


pH= 2 **pH= 8** **pH= 10**

Fig. 5: Photodegradation of MB dye for anchored Schiff base complexes a) C1 and b) C2 catalysts at different pH, [complex]= 5 mg, [MB]= 6.25×10^{-3} M under visible light.

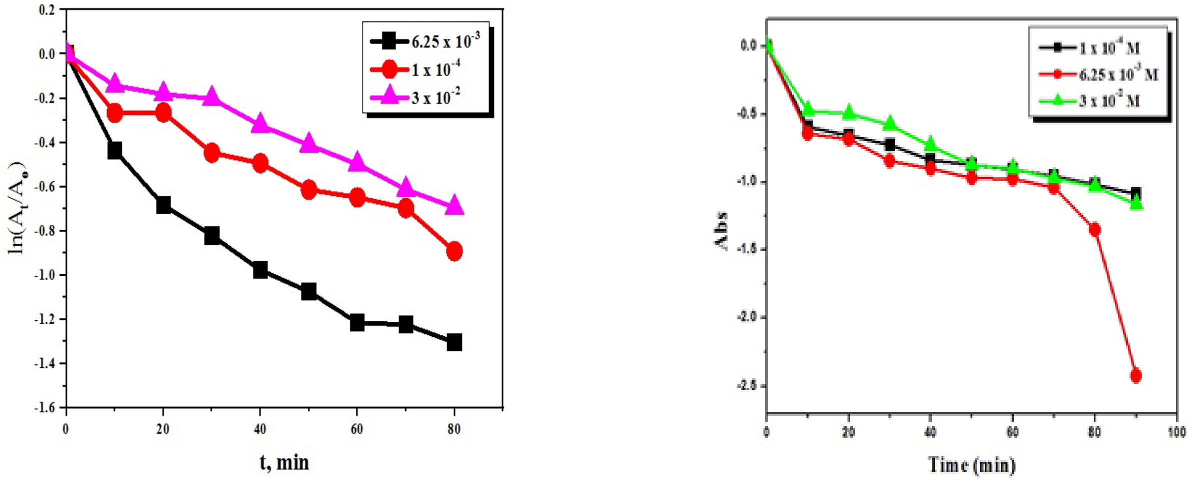
Effect of catalyst dosage and MB concentration

The influence of the catalyst dosage on the photodegradation of MB was investigated by varying the amount of catalyst in the range 2 to 9 mg to detect the optimum value. For performing these studies, the concentration of MB was kept constant at 6.25×10^{-3} M. **Fig. 6a** and **b** shows that the degradation activity increased by increasing the amount of catalyst from 2 to 5 mg. Upon increasing the amount of the catalyst above 5 mg, it shows reduction in the degradation efficiency. This can be discussed on the basis that MB molecules available are not sufficient for adsorption with the number of the prepared catalysts. So the additional particles didn't participate in the photodegradation process **[**41**]**. In addition, the higher amounts of the catalysts lead to the aggregation of the particles on the surface and decrease the interfacial area between the reaction mixture. Also, above the optimum dose, the additional amount causes turbidity and hinders the penetration of the light to the solution. On the other hand, the effect of MB concentration is an important parameter that affects the photodegradation activity. For evaluating the optimum conditions, three different concentrations of MB (1×10^{-4}, 6.25×10^{-3} and 3×10^{-2} M) were prepared and used for the reaction at constant catalyst amount (5 mg) and pH: 10. The catalytic activity of the prepared complexes displayed an increase by increasing the concentration of MB up to 6.25×10^{-3} M. After that, there is a decrease in their activity as shown in **Fig. 7a** and **b**. This could be returned to the availability of the active sites for dye molecules to be adsorbed on the surface of the photocatalyst leading to the increase in its activity of degradation. At higher concentration, the MB particles are also increased on the surface which adsorb light and prevent it to reach the surface of the catalyst which causes a decrease in the activity **[**42**]**.



(a) **(b)**

Fig. 6: Photodegradation of MB dye for anchored Schiff base complexes a) C1 and b) C2 at different amounts of catalyst, [MB]= 6.25×10^{-3} M under visible light at pH:10.



(a) **(b)**

Fig. 7: Photodegradation of MB dye for anchored Schiff base complexes a) C1 and b) C2 at different concentrations of MB, [catalyst]= 5 mg under visible light at pH:10.

4 Conclusion

In this work, we have successfully prepared two heterogeneous catalysts C1 and C2 via anchoring Cu(II) Schiff base complexes on the surface of GO. The structure and morphology of the prepared catalysts were characterized using IR, UV-Vis, XRD and SEM which revealed well loading of Cu(II) complexes on the surface of the solid support. The developed heterogeneous catalysts were found to be highly active towards the degradation of MB under visible light in presence of H_2O_2 as an oxidant. The obtained data explained that C1 is less active than C2 with percent of degradation of 72.4% and 91.15 %, respectively. The effect of the main reaction parameters such as pH, amount of catalyst and concentration of MB were studied in details. We found that a complete degradation process in case of C1 catalyst was obtained at pH= 8, 5 mg catalyst and 6.25×10^{-3} M of MB. The same concentration and amount of catalyst was sufficient for giving a complete degradation in case of C2 but at pH=10.

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