Degradation of methylene blue using synthesized $CuO/MgO/Fe_3O_4$ nanocomposite by sol-gel method

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ABSTRACT

In this work $CuO/MgO/Fe_3O_4$ nanocomposite was synthesized by the sol-gel pyrolysis method. Characterization of the samples was performed by the X-ray diffraction (XRD) and Fourier transform infrared spectrometry (FTIR). The photocatalytic activity of $CuO/MgO/Fe_3O_4$, evaluated using the photodegradation of methylene Blue (MB) as a probe reaction under the irradiation of Xenon light. The dye photodecolorization process was studied considering the influence of experimental parameters such as catalyst concentration, $CuO/MgO/Fe_3O_4$ ratio and pH on methylene blue adsorption rate. The maximum photocatalytic activity of the CuO/MgO photocatalyst was observed to be calcined at 450°C for 3 h (the molar ratio of Cu to Mg was 1:2) due to the sample with good crystallization and high surface area. The complete photodecolorization of a 1×10^{-5} mol L^{-1} methylene blue solution, at pH =10 and room temperature was achieved in less than 20 min. Experimental results show that $CuO:MgO:Fe_3O_4$ (30:50:20) nanoparticles possess high photocatalytic activity at compression of universal catalysts.
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KEYWORDS

$MgO/CuO/Fe_3O_4$ nanocomposite;
Photocatalytic activity;
Degradation;
Methylene blue;
Sol-gel.

INTRODUCTION

Nowadays, the growing population has led to the increase mainly contamination of surface and ground water. Organic dyes used in textile and food industries are their important sources of the environmental contaminations due to their non-bio degradability and high toxicity to aquatic creatures and carcinogenic effects on humans. Malachite green (MG) (Color Index No.42000), also called basic green 4 or victoria green B, having IUPAC name 4-[(4-dimethylaminophenyl)-phenyl-methyl]-N,N-dimethylaniline with chemical formula $C_{23}H_{25}N_2Cl$, is a green crystal powder with a metallic luster, highly soluble in water and ethanol with blue-green solutions[1]. Methylene blue (MB) (Color Index No. 52015) is a heterocyclic aromatic chemical compound having IUPAC name 3,7-bis(dimethylamino) phenothiazin-5-ium chloride with the molecular formula $C_{16}H_{18}N_3SCl$. It has many uses in a range of different fields, such as biology and chemistry. At room temperature it appears as a solid, odorless, dark green powder that yields a blue solution when dissolved in water. The international Nonproprietary Name (INN) of MB is methylthionium chloride. It is a highly toxic chemical

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primarily used as a dye as like as MG[2–4]. In order to decrease damage caused by organic dye pollution to environment and humans, the use of photocatalyst to degrade organic compounds in contaminated air or water or to convert them into harmless chemicals has been extensively studied. In this manner, metal oxide nanoparticles such as ZnO[5], TiO_2[6], etc.[7–9] has been widely used to degrade non-biodegradable dyes by photocatalytical routes. Therefore, the researches focused on increasing degradation rate of pollutants by combining inorganic materials with conductive polymers to realize synergetic and complementary behaviors between the polymer and inorganic materials[10–13]. Many conducting polymers are known as good hole conducting materials[14,15]. These conductive polymers act as a stabilizer or surface capping agents when combined with metals or semiconductor nanoparticles[16–19]. ZnO is a wide band gap semiconductor (3.37 eV) with a 60 meV exciton binding energy, which permits laser emission at room temperature[20]. This large band gap is suitable for the use of ZnO to collect high-energy photons (UV light)[21]. Due to these properties, it has a potential for wide range of optical and electronic applications such as photovoltaic devices, solar cells, transducers, etc.[22–24]. Conducting polyaniline (PANI) is one of the promising polymers studied polymer due to high conductivity, simple synthesis procedure, good environmental stability[25,26] and a large variety applications such as in electro-chromic devices, light emitting diodes, corrosion protecting paint and electrostatic discharge protection[27–29].

In the present work, $CuO/MgO/Fe_3O_4$ nanocomposite was synthesized by the sol-gel pyrolysis method and photooxidation of MB is chosen as a reaction model. The preparation of CuO/MgO adopted a sol-gel method in the presence of as prepared Fe_3O_4 nanoparticles. The $MgO/ZnO/Fe_3O_4$ nanocomposite prepared, were characterized by X-ray diffraction (XRD) and Fourier transform infrared spectrometry (FTIR), and UV–Vis spectrophotometry.

EXPERIMENTAL

Preparation of Fe_3O_4

At first step the Fe_3O_4 nanoparticleswere prepared by chemical co-precipitation procedure. Ferrous chloride (2.0 g), ferric chloride (5.2 g), and hydrochloric acid (12 mol L^{-1}, 0.85 mL) were dissolved in 25 mL pure deionized water. The mixture was added dropwise into 250 mL NaOH solution (1.5 mol L^{-1}) under vigorous stirring with nitrogen gas passing continuously through the solution during the reaction. After the reaction, the obtained MNPs precipitate was separated from the reaction medium under the magnetic field, and rinsed with 200 mL pure deionized water four times. Then, the product was oven dried at 80 °C.

Synthesis of CuO/MgO nanocomposite

For synthesis CuO/MgO, first, 50 mL of 0.02 mol L^{-1} copper acetate solution including 10 g L^{-1} polyvinyl pyrrolidone (PVP) as structure director additive was sonicated for 30 min and then, enough volume of sodium hydroxide (0.3 mol L^{-1}) was slowly added. In this step, nano-structured Cu hydroxide was formed. Subsequently the mixture was additionally sonicated for 30 min, then filtered and washed with distilled water and ethanol for three times. The final obtained precipitate was dehydrated at 320 °C in a furnace for 2 h. At dehydration phase, nanostructured CuO was formed. The nanoparticles were sonicated in ethanol for 30 min to eliminate agglomeration. At final step, the mixture was filtered and dried at 110°C. The final product was obtained in powder form.

For synthesis of CuO/MgO nanocomposite, a 50 mL aliquot containing magnesium acetate solution (0.04 mol L^{-1}) and 2 g of CuO nanopowder and PVP (10g L^{-1}) was sonicated for 30 min and then, 7.5 mL of NaOH solution (0.3 mol L^{-1}) was slowly added. In this step, nanostructured magnesium hydroxide was formed. At the end of the process of adding NaOH solution, the mixture was additionally sonicated for 30 min. To form the CuO/MgO nanocomposite, the obtained precipitate was dehydrated at 450°C in a furnace for 3h. The CuO/MgO nanocomposite was sonicated in ethanol for 30 min to eliminate agglomeration and then dried at 110°C. The final product was obtained in nanopowder form.

Preparation of $CuO/MgO/Fe_3O_4$ catalyst

$CuO/MgO/Fe_3O_4$ catalyst was obtained by mixing CuO/MgO nanocomposite and Fe_3O_4 nanoparticles at different proportions in an aqueous suspension and this was continuously tired for 2 h. After this, the mixture was filtered and dried at room temperature.

Photocatalytic experiments

The photocatalytic degradation experiments have

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been conducted using a designed glass photoreactor that cooled by water circulation (Figure 1). The reaction vessel (100 mL) was made of borosilicate glass andthe quartz was a double-walled, with inlet and outlet tubes for cooling. The inlet tube extends down the annular space and ensures the upward flow of coolant from the bottom of the well upward to the outlet. The reactor bottom is flat to allow the use of a magnetic stirrer. The radiation source was a 450 W medium-pressure mercury-vapour lamp. Methylene blue was used as a model pollutant to evaluate the photocatalytic activity of the prepared catalysts. Each of CuO/MgO and CuO/MgO/Fe₃O₄ catalysts (0.1 g) was suspended in a solution of MB (100 mL, $1×10^{-5}$ mol L^{-1}) at natural pH. Prior to the irradiation, the solution magnetically stirred for 30 min to ensure an adsorption/desorption equilibrium in the dark.
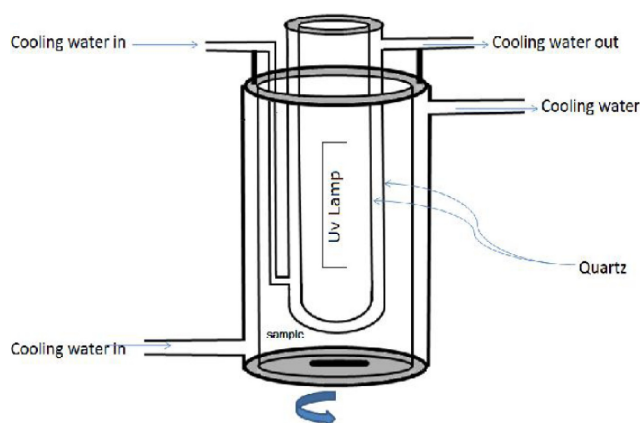

Figure 1 : Photochemical experimental setup

The photodegradation was initiated by a UV lamp in room temperature. Aliquot amount samples (5mL) were taken at equal times (20 min) and Centrifuged (2000 rpm, 2 min). The degradation of MB was monitored by measuring the absorbance at λ=664nm as a function of irradiation time with a UV−Vis spectrophotometer (GBC–Cintra6). In this study, the photocatalytic degradation was calculated as the following formulae: Amount degraded MB=C/C_0, where C_0 and C are the initial and final concentrations of MB at t = 0 and t.

RESULTS AND DISCUSSION

Characterization of synthesized catalysts

The synthesized catalysts were characterized by XRD and FTIR. XRD analysis of CuO/MgO/Fe₃O₄ catalyst (Figure 2) exhibit only patterns assigned to the well crystalline hexagonal phase of CuO, MgO and a small peak at 2θ=43 that can correspond to Fe₃O₄.

The FT-IR spectrum of MB is given in Figure 3a. Figures 3b and c give FT-IR spectra of CuO/MgO, CuO/Fe₃O₄ photocatalyst. FT-IR spectrum in Figure 3b shows the characteristic peaks of MB in the region of 1000–1700 cm⁻¹. This indicates the adsorption of MB on the CuO/MgO/Fe₃O₄ catalyst. The FTIR spectrum of CuO/MgO/Fe₃O₄ photocatalyst after the complete degradation is shown in Figure 3d. Comparison of Figures 3b
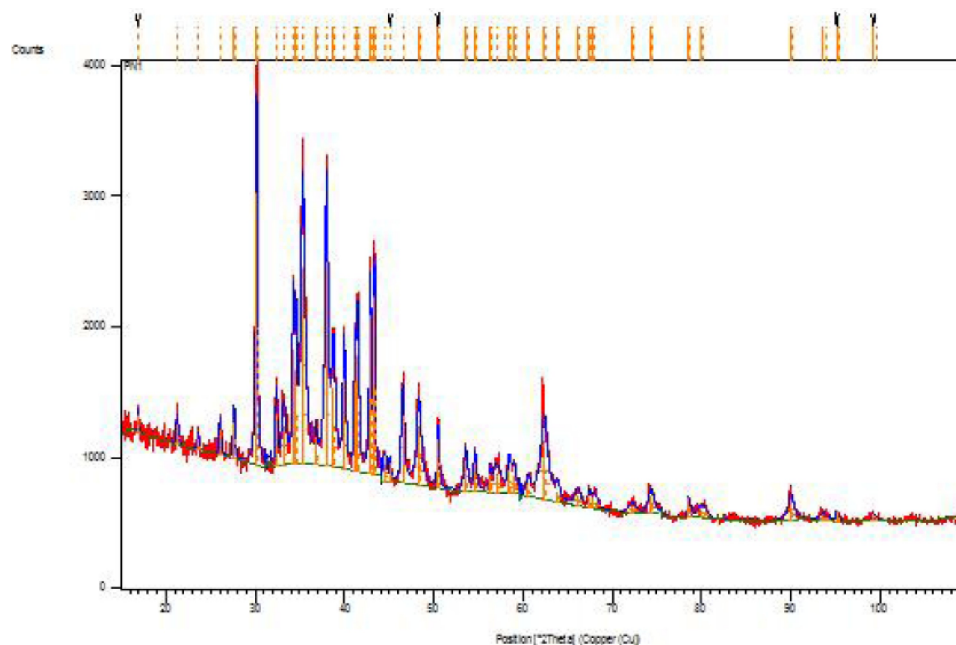

Figure 2 : X-ray diffraction patterns of CuO:MgO:Fe₃O₄ (30:50:20)

and c reveals that the characteristic peaks of MB on the absorption spectra of CuO/MgO/Fe$_3$O$_4$ present in Figure 3b disappeared and the spectrum in Figure 3d is similar to the spectrum of the catalyst given in Figure 3b. This reveals that the dye molecules, adsorbed on Fe$_3$O$_4$ are being transferred to the CuO/MgO present in the pores where they are degraded on irradiation.

Photodecolorization process

Influence of catalyst composition

The photocatalytic efficiency of 100mg of CuO/MgO/Fe$_3$O$_4$ materials on the decolorization of a 1×10^{-5} mol L^{-1} MB solution was tested during 120min (Figure 4). In the presence of the CuO, only 80 min were needed for the complete MB decolorization. Optimum result in the absence of Fe$_3$O$_4$ was obtained using CuO/MgO and the decolorization time was reduced to 70 min. The minimum time (20min) for the complete MB decolorization was achieved using the Fe$_3$O$_4$/CuO/MgO. Analyzing these results it is possible to say that

the complete photodecolorization occurs in less than 20 min, nearly 60min faster than the CuO photoassisted process and showed the highest photoactivity among all as-prepared samples.

Figure 5 shows the mechanistic scheme of the charge separation and photocatalytic reaction for CuO/MgO/Fe$_3$O$_4$ photocatalyst. As illustrated in this scheme, the photo-generated electrons inject into the conduction band of catalyst from that of the excited CuO/MgO/Fe$_3$O$_4$ photocatalyst. Also, the transfer of photo-generated gap also occurs from the catalyst to the valence band of CuO/MgO/Fe$_3$O$_4$ similarly. Such an efficient charge separation increases the lifetime of the charge carriers and enhances the efficiency of the interfacial charge transfer to adsorbed substrates. Thus, the photocatalytic properties increase because the possibilities of recombination between photo-generated electron and hole are reduced through facilitating their separation. As well known, the spherical catalysts powders with small size present a superior activity due to the large
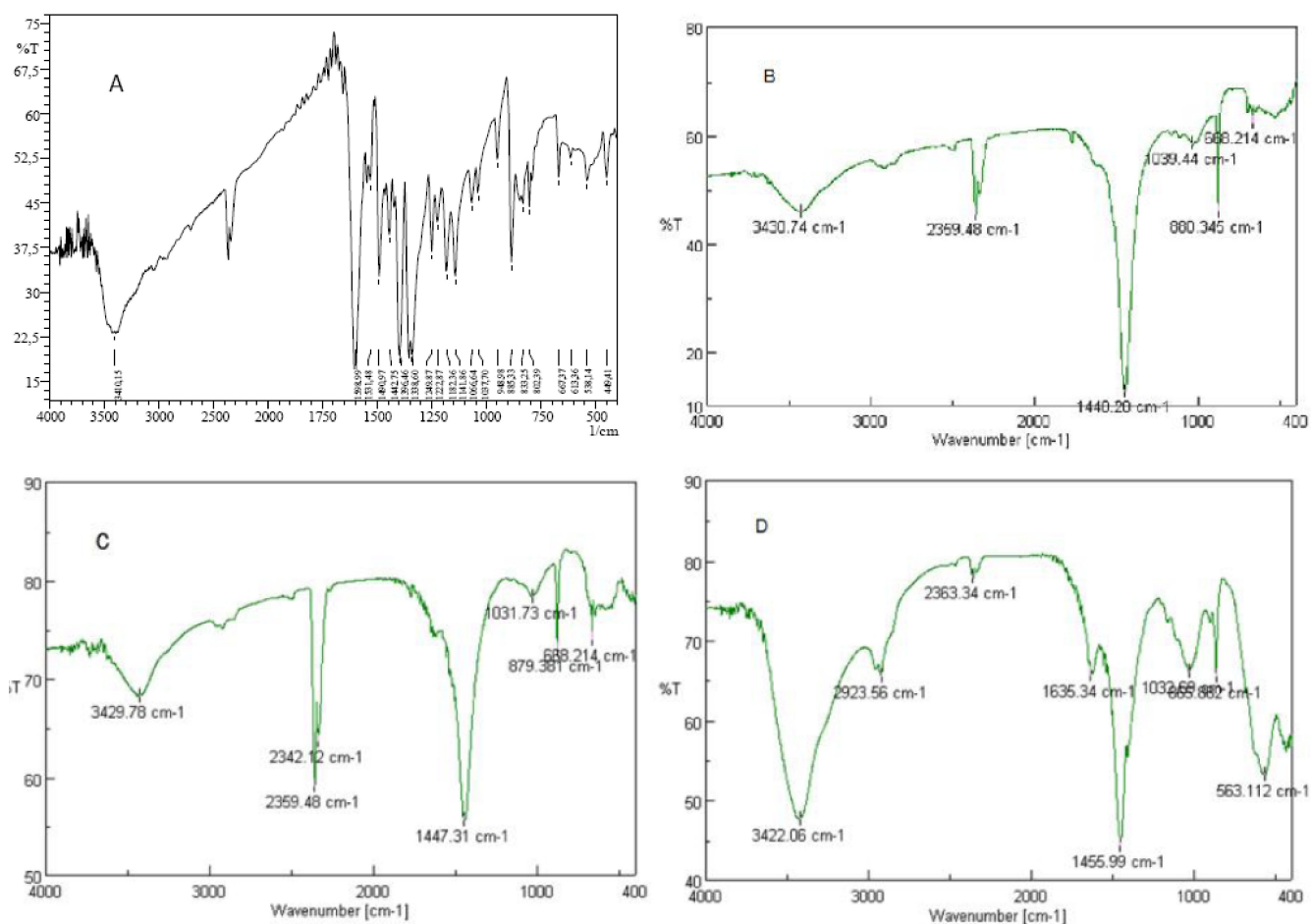

Figure 3 : FTIR spectra of the MB before degradation (a) and after the its complete degradation at presence of MgO/CuO (b), CuO/Fe$_3$O$_4$ (c) and Fe$_3$O$_4$/CuO/MgO (d)

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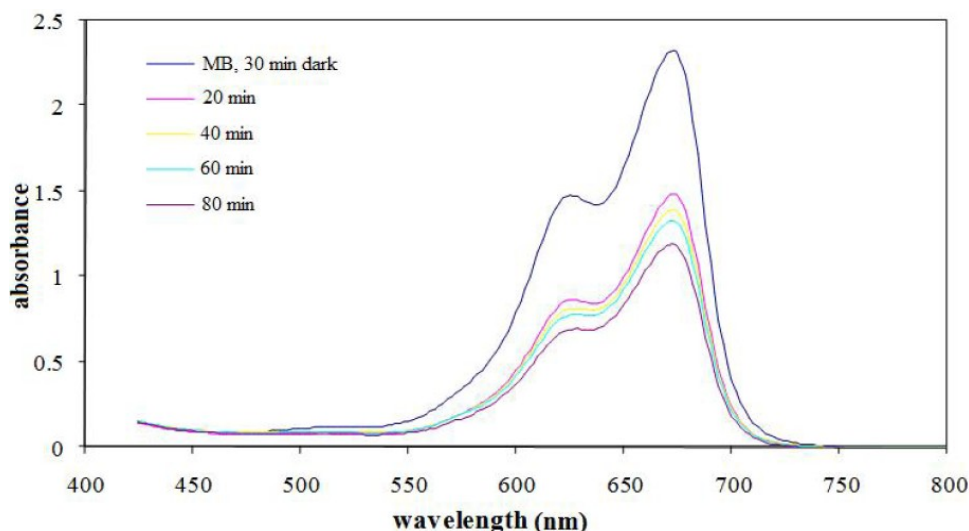**Figure 4 : Photocatalytic decolorization of 100 mL MB solution (1×10^{-5} mol L^{-1}) using 100 mg of CuO:MgO:Fe₃O₄ (30:50:20) catalysts**
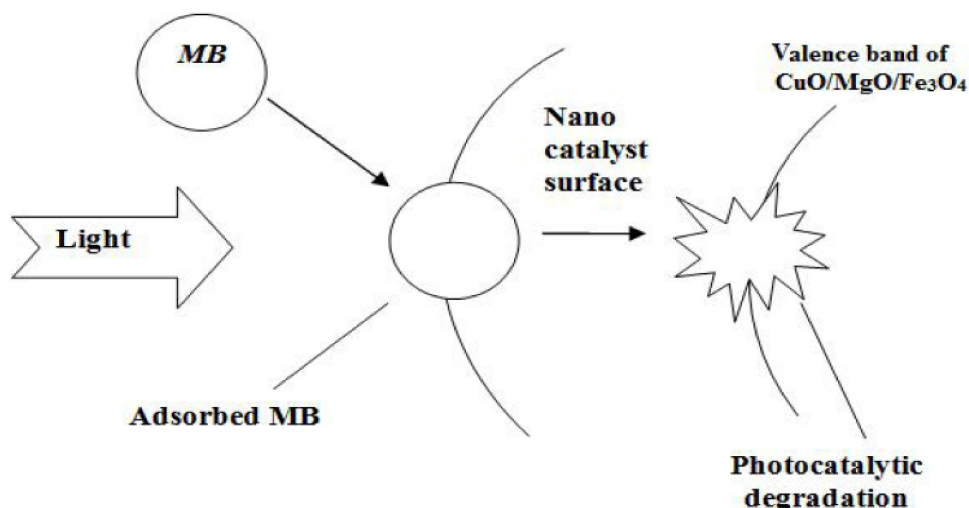

Figure 5 : The mechanistic scheme of the charge separation and photocatalytic reaction for CuO/MgO/Fe₃O₄ system

surface-to-volume ratios.

Figure 6 shows the -Ln C/C_0 of MB versus irradiation time t for the different catalysts. An approximate linear relationship of -Ln C/C_0 versus t indicate that the photodegradation processes of MB tended to follow pseudo-first-order kinetic model in the presence of the catalysts studied in this work. The apparent rate constant for CuO:MgO:Fe₃O₄ (30:50:20) was estimated from the slope of -Ln C/C_0 versus t to be 6.4×10^{-3} min^{-1}.

Influence of the catalyst amount

The effect of the catalyst concentration on the MB photodecolorization (Figure 7) was investigated for the CuO:MgO:Fe₃O₄ (30:50:20) nanocomposite since it was the material with the best photoactivity for MB decolorization. Figure 7 shows that the rate of MB de-

colorization is dependent on the Fe₃O₄/CuO/MgO concentration. The complete MB photodecolorization was achieved within 20 min using 100 mg of CuO:MgO:Fe₃O₄ (30:50:20). Longer times of 30 and 45 min were required when 50 and 150 mg were used, respectively. These results can be explained by two main reasons: first, and taking into account the 50 and 150 mg experiments, it must be considered that increasing the catalyst concentration the number of dye molecules adsorbed will increase and the number of photons absorbed will increase too. As a result of the high density of molecules in the area of illumination, the decolorization rate will be increased. However for a very high particles concentration (in this case 150 mg) the suspensions turbidity increases. In this situation the light penetration decreases, as a result of an enhanced light
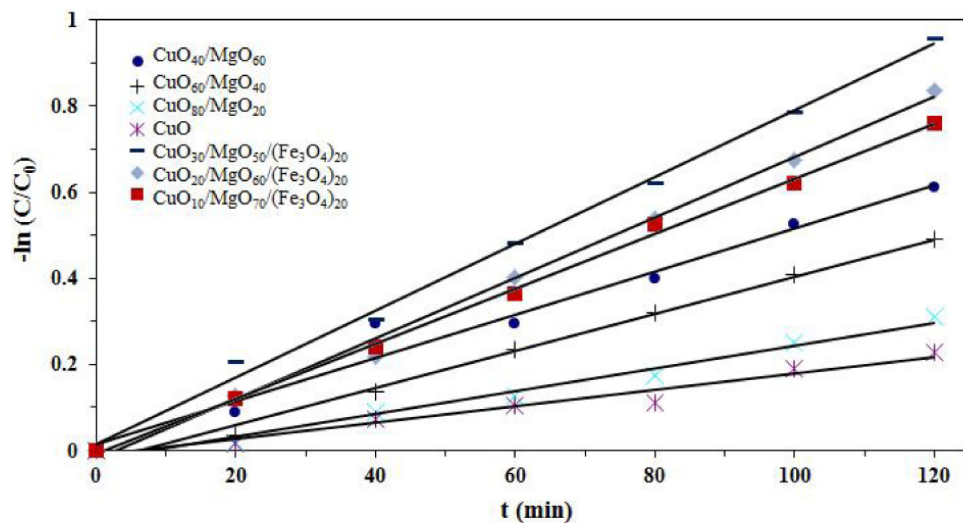
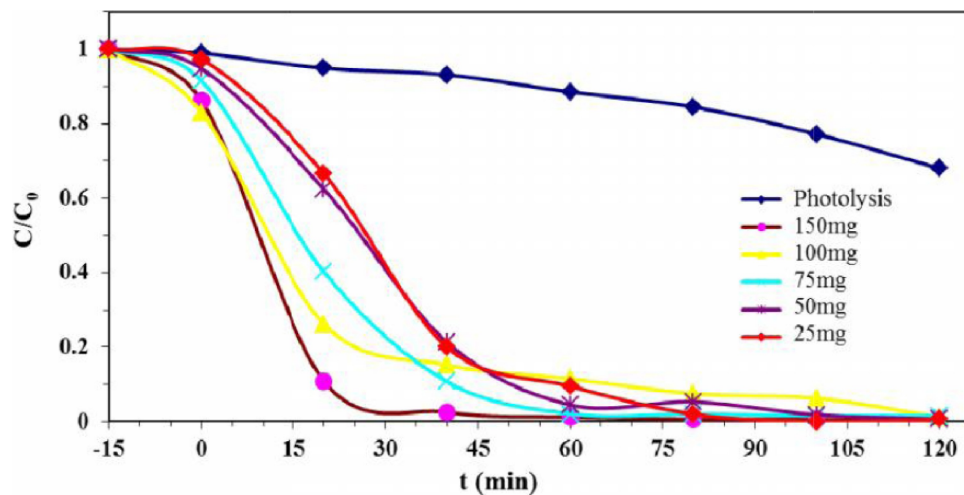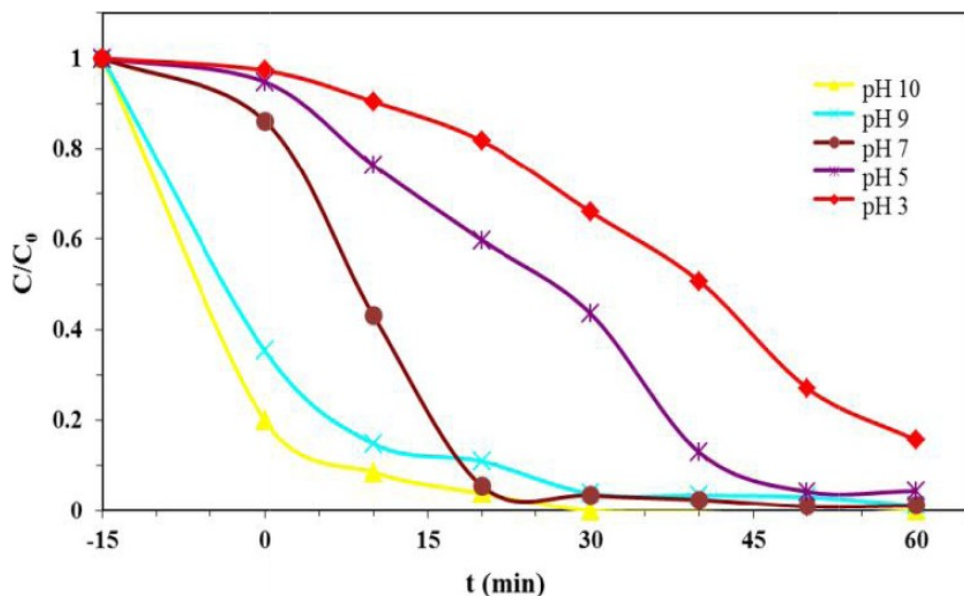**Figure 6 : Relationship between Ln C/C0 and irradiation time**

Figure 7 : The effect of the catalyst concentration on the MB photodecolorization

Figure 8 : Photocatalytic decolorization of a 1×10^{-5} mol L^{-1} MB solution using different initial pH values (100 mg CuO:MgO:Fe$_3$O$_4$ (30:50:20), 100 mL of MB aqueous solution)
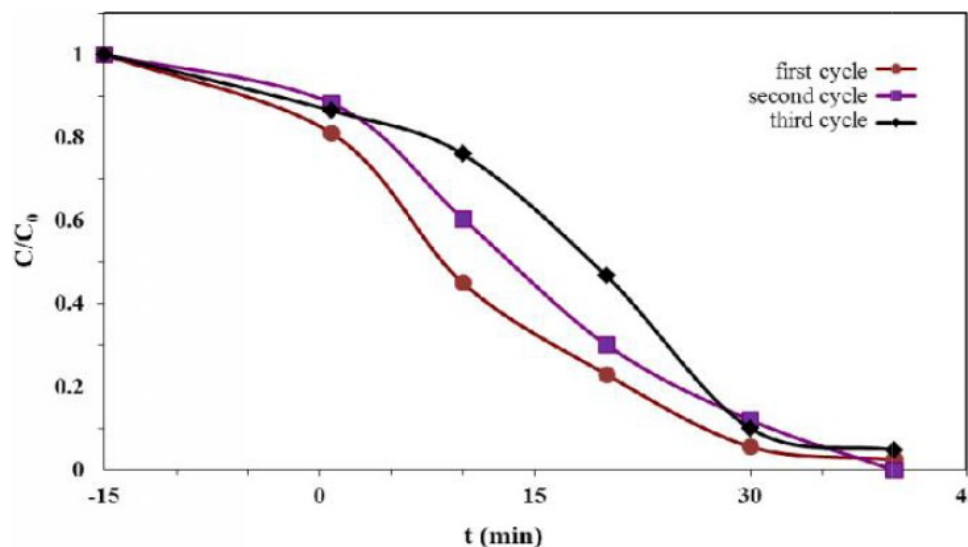
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Figure 9 : Reproducibility of CuO:MgO:Fe₃O₄ (30:50:20) as nanocatalyst for MB during a three cycles experiment

scattering effect, and consequently the photodecolorization will be less effective[30,31].

Influence of the pH

pH is an important parameter in the wastewaters characteristics of industrial and plays an important role in photocatalytic processes. The effect of the pH, on the Degradation rate, can be explained mainly by the modification of the electrical double layer of the solid electrolyte interface, which affects the adsorption–desorption processes and the separation of the photogenerated electron-hole pairs in the surface of the catalyst particles[35] Normally, in aqueous solution, the surface of the CuO/MgO is negatively in alkaline media and positively charged in acidic media, Therefore, the MB photodecolorization efficiency, is expected to increases with pH because of the electrostatic interactions between the MB cations and the negative catalyst surface. According to these actualities the investigation of the pH effect on the MB decolorization process was studied. In acidic media the adsorption of MB onto the CuO/MgO surface was very low. This can be refered to the positive charge of both, CuO/MgO and MB in this pH. In an opposite manner, for alkalis pH's a great amount of MB was adsorbed and observed a violet solid coloration that apparently correlated with the dye protonation/ deprotonationprocess[32]. At the neutral pH an intermediate adsorption was observed. Concerning the adsorption results, the photodecolorization was carried out at pH 3-10, during 80 min (Figure 8) in the presence of CuO:MgO:Fe₃O₄ (30:50:20). At pHs 3-5 the time requested for the complete decolorization pro-

cess was larger than or equal to 70 min. Compared with the 20 min this value is higher if needed at pH 7 and lower if compared with the 10 min necessary for pH 10. However at pH 10 it must be, remembered that at the starting irradiation time the percentage of the MB adsorbed was still very high, up to 80 %. After 10 min of irradiation the solution was completely decolorized but the catalyst remained violet. Increasing the irradiation time the color of the, catalyst did not change anymore. This fact can be associated with a strong adsorption/interaction between the violet dye form and the catalyst surface, at alkaline pH values[33]. The strong adsorption leads to a major decrease of the active sites and consequently a decrease of the absorbed light on the catalyst's surface. This could be the reason why the initial rate of decolorization is lower in alkaline solutions than in neutral pH. As a result the optimum pH, among those studied and under the experimental conditions tested, appears to be the neutral pH.

Reproducibility of the photocatalysts

Figure 9 shows the reproducibility of CuO/MgO/Fe₃O₄ as catalyst for MB during a three cycles experiment. Each experiment was carried out under identical conditions of 1×10^{-5} mol L^{-1} of MB, 100 mg of nanocatalyst, pH of 10, irradiation time of 30 min and at room temperature. After each degradation experiment, the concentration of MB was adjusted back to its initial value. It shows that the phase structure of photocatalyst remained consistent, but the efficiency decreased after each reuse. The drop in the photoactivity of reused photocatalyst may be due to the adsorption of the original

compound and/or by-products (adsorbed species) on the active sites of the catalyst surface, the reduction of the number of available photoactive sites resulted in the drop in the photoactivity[34]. As seen from Figure 9, a small and gradual decrease in the activity of nanocatalysts was observed at the first two cycles. But, decreasing of the activity was seen intense after the first and second cycles.

CONCLUSION

Different densities of copper acetate had been solute and its effects on these densities for MB color material degraded, hydroxide sodium solute in different densities as a titrant and its effect on MB degradation efficiency, too. Light degradation in spectra was examined in many times and the results were written under the figures. In different times the spectra showed the degradation percentage by irridation time increase. The $MgO/CuO/Fe_3O_4$ nanocomposite rate optimization was done in many samples. Photocatalytic degradation for optimization of catalystic value was examined for its effect. The optimization of MB color degradation by $CuO:MgO:Fe_3O_4$ (30:50:20) nanocomposite were examined in different moles and irradiation times for having the best results. The effect of indicator PH variety of matylen blue color at the presence of $CuO/MgO/Fe_3O_4$ was examined on the samples for absorption spectra. This change caused the disorder of irradiation time increase or decrease. The degradation percentage of MB color by nanoparticles of CuO, CuO/MgO, CuO/Fe_3O_4, $CuO/MgO/Fe_3O_4$ was also examined.

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