



Evaluation the Efficiency of CuFe_2O_4 Prepared Photolysis by OSD and Photo degradation

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ABSTRACT

The magnetic structure, optical properties of copper ferrite in photodegradation and Oxidative desulfurization were investigated in this paper. The product was characterized by XRD, SEM, TEM, EDXS, XPS, VSM, PL and FTIR. The results from XRD obviously revealed the tetragonal spinel structure of CuFe_2O_4 , while the FTIR analysis appeared as a fundamental vibration assigned to oxygen metal at octahedral and tetrahedral sites. The spherical morphology with the size in the nano range was obtained from SEM and TEM analysis, and these results were in agreement with the results from XRD. The magnetic properties were investigated using VSM, and the results showed the highest value of the saturation magnetization (M_s) (80 emu/g) with the low coercive force (72 Oe). The ratio percentage and its purity were explored from EDXM and XPS analysis, and the results obtained showed some carbon on the surface of ferrite, while the analysis of PL luminescent showed many emission peaks back to copper ferrite which was appeared in the visible region. The synthesized material showed very high efficiency to recover, and the degradation of sulfur compound and Azo dyes reached to 93% and 95%; respectively.

Keywords: Photolysis, OSD, CuFe_2O_4 , XPS

HOW TO CITE THIS ARTICLE: Rawnaq B. Jimaa, Zaid H. Mahmoud, Farah K. Ali, Evaluation the efficiency of CuFe_2O_4 prepared photolysis by OSD and photo degradation, Entomol Appl Sci Lett, 2018, 5 (2): 91-100.

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Received: 18/01/2018

Accepted: 27/04/2018

INTRODUCTION

The removal of sulfur compounds and Azo dyes from fuel oil and river water; respectively has been a global issue resulting from increasing the environmental regulations to reduce the level of sulfur compounds which emitted from petroleum fuel [1]. A vast variety of sulfur compounds have existed in light gas oil (LGO) as organic sulfur compounds represented by hydrogen sulfide, mercaptans, organic sulfides, disulfides, benzothiophenes and their alkylated derivatives. The reduction of the sulfur levels in gas oil and other fuels have been specifically interesting because their combustion has the ability to produce precursors to acid rain and airborne particulate materials [2, 3]. Oxidative desulfurization (ODS) process has been considered a highly effective deep desulfurization technique because it can be done at low temperature, pressure, and low expense

of operation. ODS consists of two steps: the first one has been the oxidation of organic sulfur compounds using oxidizing agents such as nitric acid, hydrogen peroxide, organic hydroperoxides, or ozone in the presence of a catalyst to produce sulfones compounds. Then, the oxidized molecules were removed by the extraction with acetonitrile in the second step [4-7]. In this paper, the oxidation of sulfur compounds and photodegradation of methyl orange was studied using CuFe_2O_4 which was prepared using UV-irradiation [8-12] as a catalyst and hydrogen peroxide and acetic acid as oxidants.

EXPERIMENTAL PART

Characterization

The characterization of prepared CuFe_2O_4 was done with utilizing XRD, VSM, PL, UV-Vis, FTIR, TEM, SEM, EDX and XPS techniques. Photoluminescent properties of the sample were investigated. The spectral properties were recorded by UV-Vis spectrophotometer and Fourier-transform infrared spectroscopy model

(V-650) and (65-FT-IR, Perkin Elmer, USA); respectively. The morphology, size and structure of the synthesized material were taken using Trans electron microscope (JEOL-ISM 2000), scanning electron microscope (inspect S50 from FEI) and X-ray Diffraction Cu K α radiation ($\lambda=1.5406 \text{ \AA}$) models (Shimadzu-XRD-6000); respectively. The measurement of magnetic for the sample was carried out by vibrating sample magnetometer (VSM) model (Lake Shore - 7474, USA) in an applied magnetic field between the positive negative 10^{+4} Oe at room temperature. The energy binding of the electron for elements of the sample and its percentage ratio was examined by X-ray photoelectron microscope model (Kratos Analytical Axis Ultra DLD) and energy- dispersive X-ray spectroscopy model (JEOL JSM-7600, USA).

Synthesis of CuFe₂O₄ NPs

A Stiochiomeric ratio of 1:1 for copper chloride and ferric chloride, were dissolved separately with continuous magnetic stirring in 50ml distilled water. Under continuous stirring, the two solutions were mixed together until a homogenous solution was formed, and it was irradiated using the irradiation system 125W as shown in figure 1. [13] The irradiation process continued until the color of the solution was changed from blue to orange with thick precipitate. The precipitate was collected and calcined at 400C, until a black precipitate with magnetic properties appeared.

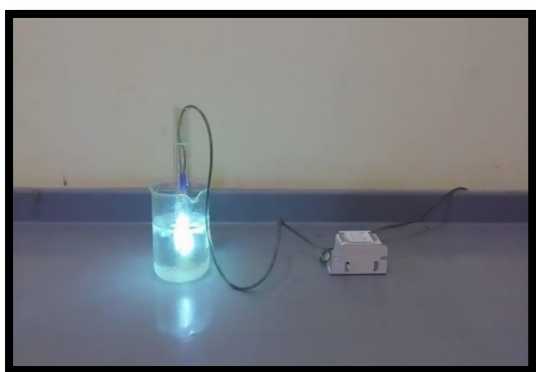


Fig. 1. Irradiation system

Procedure of oxidative desulfurization experiments:

The ODS experiment was performed in a water bath at 40C° with 5ml of glacial acetic acid, 10ml of H₂O₂ was mixed with 100ml of gas oil and 1gm of the catalyst Cu-Fe₃O₄ nanocomposite in a

round bottom flask with three necks. The mixture was stirred for 3h using a magnetic stirrer at 700rpm, during the stirring process, the solution of 2gm Na₂CO₃ was dissolved in 20ml of distilled water which was added drop by drop to the mixture. After the oxidation was finished, the mixture attained phase separation, and the oxidized sulfur was extracted with acetonitrile and 2M BaCl₂.2H₂O at room temperature. The ratio of acetonitrile and gas oil was 1:1 by volume, then the X-ray fluorescence spectrometer ARL 8410 (ASTM D4294 method) was used to separate and analyze the gas oil phase. The following equation was used to assess the removal efficiency of sulfur compounds:

$$\text{Efficiency of desulfurization} = (S_0 - S_1 / S_0) * 100$$

Where S₀ is the initial S-content and S₁ is the final S-content after (ODS). The results indicated that the catalyst was efficient to remove sulfur from gas oil.

Photocatalysis experimental

To investigate the activity of copper ferrite photocatalytic, orange G dye was used as a target pollutant, and the experiments were carried out under UV and sunlight. In a container, the solution of the pollutant with 100ppm was prepared, then 0.00015g of NPs was added and aerated until getting the adsorption equilibrium (30min). After that, the mixture moved inside the vessel of irradiation cell with the distance of 15cm from the UV source of 125Watts, and the experiments were carried out at room temperature. During the irradiation process, 5ml of mixture was taken at the fixed era time, then it was centrifuged for 5 min, and the absorption of it was measured using UV-Vis spectrophotometer. The degradation ratio of dye was calculated using the following equation:

$$\text{Degradation rate} = \frac{A_0 - A_t}{A_0} \times 100$$

Where A₀: the absorption at 0 min

A_t: the absorption at t time

RESULT AND DISCUSSION

Photoluminescent properties:

PL spectra and the data were valuable to test the luminescence properties with respect to the

recombination of photoexcited charge transporters. It has been a helpful strategy to comprehend the recombination idea of electron-hole pairs in the semiconductor particles. At 425nm emission line, the excitation spectra of NPs were depicted as shown in figure 2 as well they appeared at 313 and 323nm as shown in figure 2b. The results showed that the intensity of 313nm emission line was stronger than 323nm, and this indicated the efficient energy transfer, while appearing the peak at the

421nm emission line indicated to correspond to the blue emission because of the grain boundary and the radioactive disorder concerning the interface trips [14, 15]. The presence of deep level emission was stated, and the vacancy of the singly ionized oxygen caused the peak to appear at 532nm corresponding to the green emission as shown in figure 2c, as well, the intensity of PL for the sample increased because the vacancy of oxygen joined the electrons that resulted from induced to formed photo-excitons.

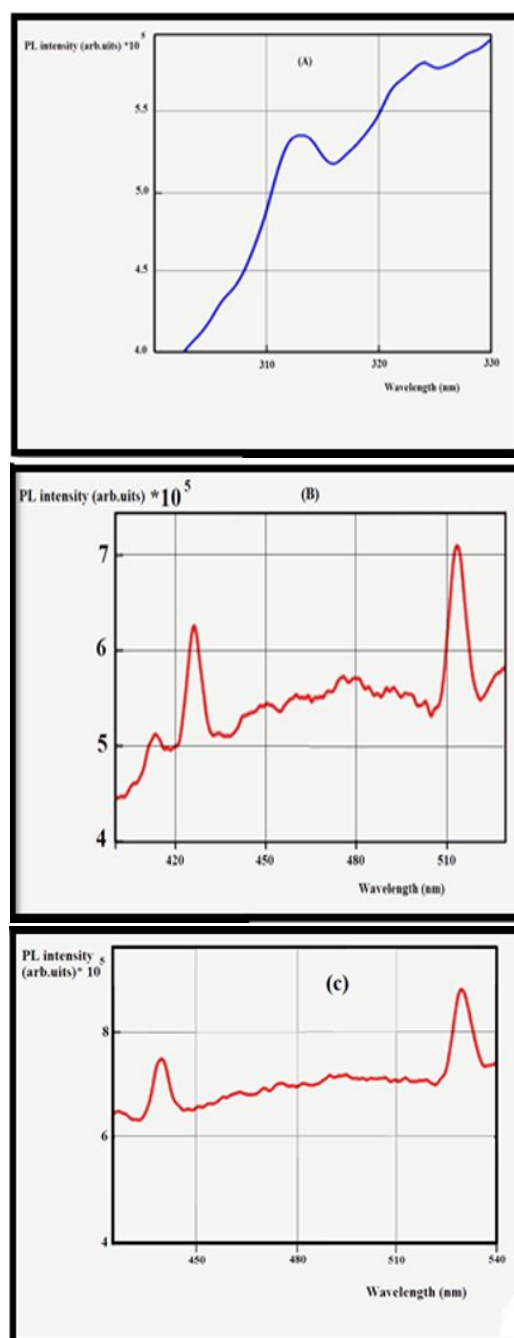
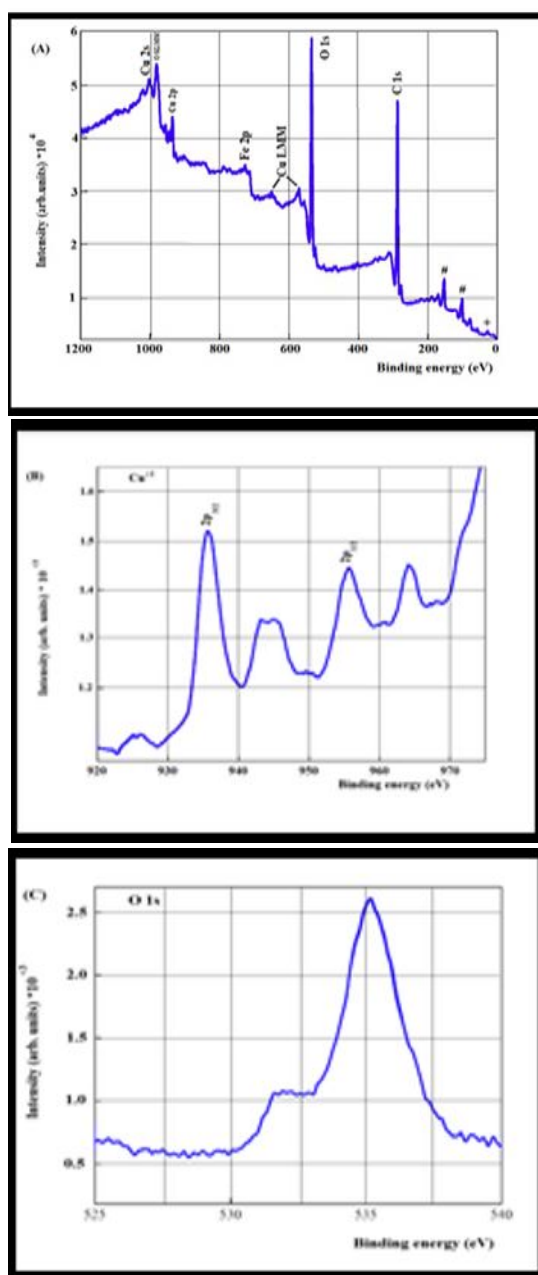


Fig. 2. PL spectrum of CuFe₂O₄

XPS analysis

The analysis of XPS for sample was carried out to examine if the ferric ions were found on the surface of the particles. In a vast energy range reaching to 1200eV, the analysis was carried out as shown in figure 3a, and the symbols (#) and (+) were used to indicate the level regions $\text{Cu}_{3s}/\text{Fe}_{3s}/\text{Cu}_{3p}/\text{Fe}_{3p}$ and O_{2s} [16]. Three pairs of the lines appeared in 935, 955 and 975 eV as shown in fig 3b assigned to Cu 2p line. Figure 3c shows the multi species of oxygen found on the surface resulting from O_{1s} asymmetric vacancies spectra. The crystal structure of

CuFe_2O_4 had two terminal groups of Fe-O vertical in the plane determined by four equatorial atoms of oxygen, and the bond of the terminal was shorter than the equatorial bonds about 0.1Å, and the two types of oxygen bond (terminal and equatorial) appeared in 531 and 535; respectively [17]. Four peaks were centered at 711, 718, 724 and 742 eV assigned to the spectra of Fe 2p as shown in figure 2d, while the figure 2e shows the additional lines appeared away from (Cu, Fe and O) back to carbon impurities.



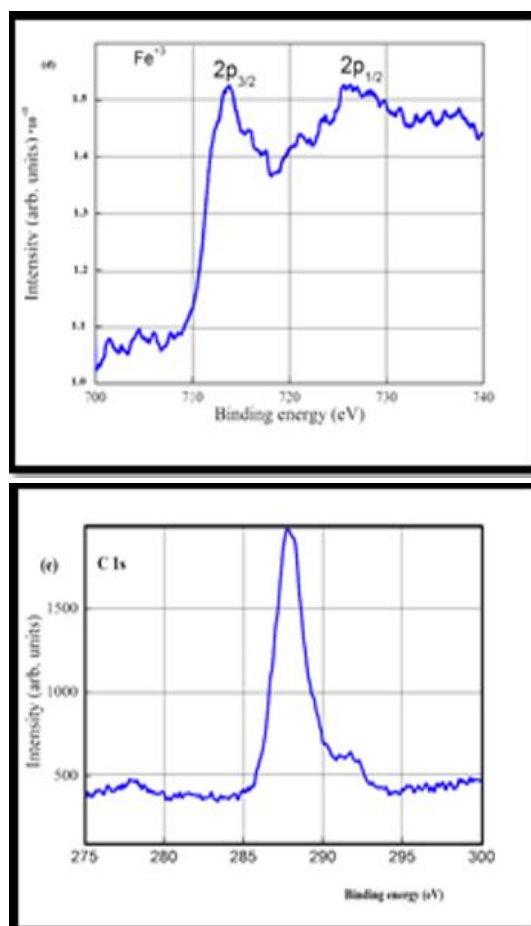


Fig. 3. XPS spectrum of CuFe₂O₄

XRD

The analysis of XRD was carried out with CuK α radiation having wavelength of 1.54Å and 2 θ between 20 to 80 to study the structure of CuFe₂O₄. The results from the patterns of XRD and comparing with XRD data files (JCPDS File No. 35-0425) confirmed the preparation of tetragonal phase of CuFe₂O₄ with a peak

position at 18.345 (111), 30.170 (220), 36.354 (311), 43.402 (400), 53.60 (422), 57.165 (511) and 62.75 (440) with the secondary phase of α -Fe₂O₃ and CuO as shown in figure 4. Debye-Scherrer equation was used to determine the average size of the particles and the measurement showed a particle in a size of 26nm.

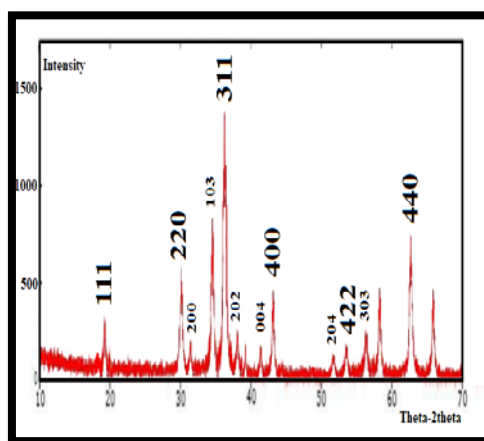


Fig. 4. XRD of CuFe₂O₄

VSM spectrum

To reform the magnetic properties of prepared CuFe_2O_4 nanostucture, the vibrating sample magnetometer (VSM) study has been examined under the field of 15kOe at room temperature, and got hysteresis loops from ferrite powder. All the results, shown in figure 5, were obtained by

plotting Magnetization (M) inverse applied field (H), and the figure illustrated getting high saturation magnetization (80 emu/g) with low the coercive force (72 Oe), and this high value was related to the composition of the excellent crystalline of ferrite, and no impurities of iron oxide were found inside the structure of ferrite.

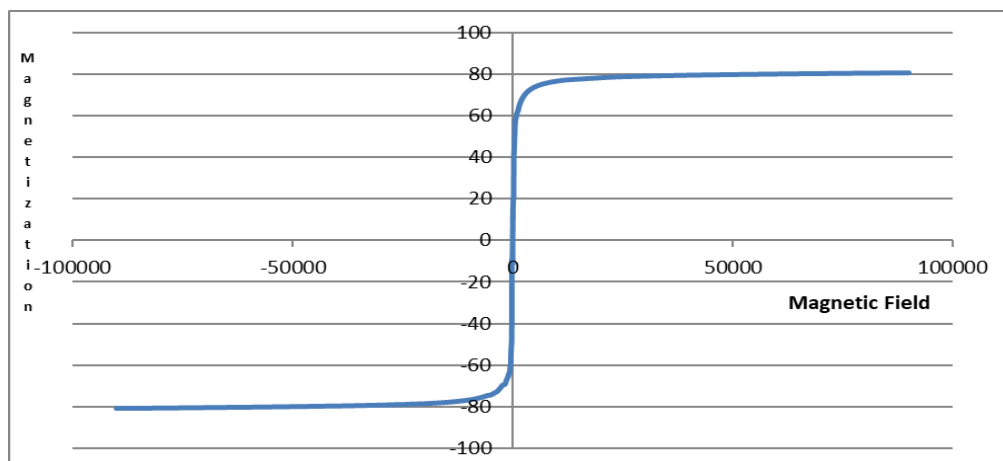


Fig. 5. VSM Curve of CuFe_2O_4

EDXS

The analysis of EDXS was carried out based the emission of energies of the elements which were the composite of the ferrite, and investigation of the identity of the elements and the spectrum confirmed the presence of the elements Cu, Fe and O in the percentages shown in Fig 6 inside the structure of the compound. No impurities were found inside the structure of copper ferrite which was confirmed via EDX spectrum, and this indicated the high purity of the product prepared using this novel method (photolysis).

SEM analysis

The morphology and the size of particles were examined using Scanning electron microscope. The obtained results indicated the particles in the size of 53nm with many spherical agglomeration and non-uniform cluster formation. The reason of the particle agglomeration was the interaction between the magnetic particles, and the time of the irradiation of the solution and the formation of the particles (see figure 7).

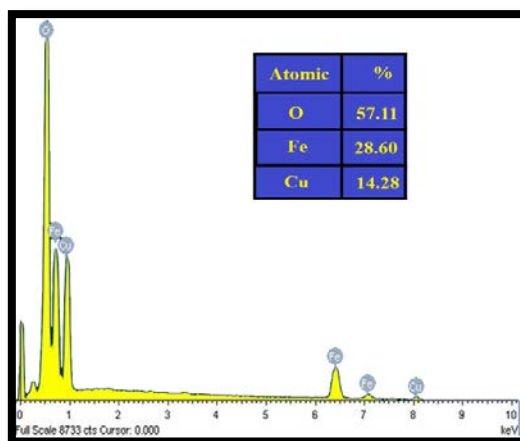


Fig. 6. EDXS of CuFe_2O_4

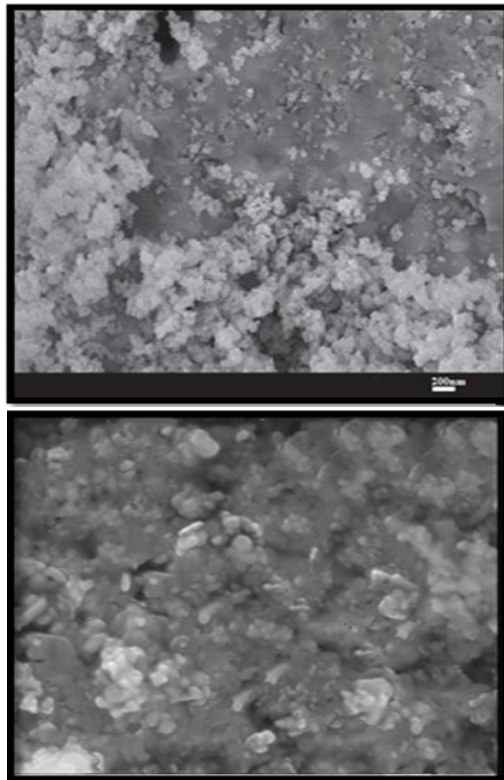


Fig. 7. SEM of CuFe_2O_4

TEM analysis

Figure 8 shows the TEM analysis of copper ferrite NPs prepared by photolysis method, and

the image showed a large number of the particle agglomeration in nano size. The analysis' results were in agreement with results that were obtained from SEM and XRD.

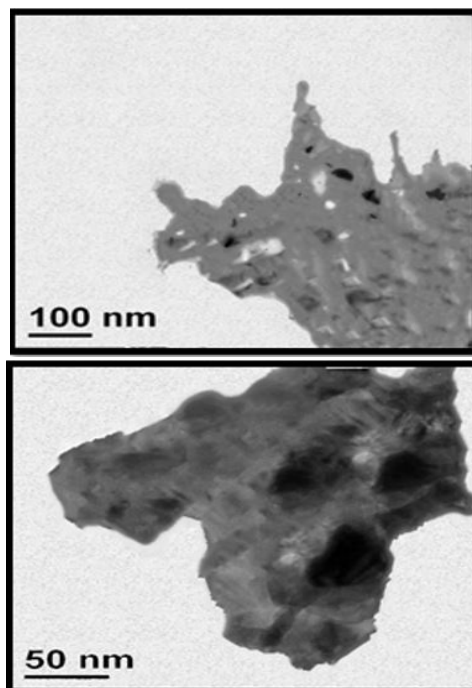


Fig. 8. TEM analysis of copper ferrite NPs prepared by photolysis method

FTIR discusses

The spectrum of Fourier Transform Infrared spectra (FTIR) for CuFe_2O_4 synthesized using UV irradiation was shown in figure 9. The spectrum showed two adsorption bands at 438cm^{-1} and 542cm^{-1} because of the vibration of (Fe-O and CuO) ions bond inside the lattices of ferrite spinel, and it corresponded to the site of octahedral and tetrahedral. These bands

differed in frequency due to the length of the oxygen-metal bond in octahedral and tetrahedral sites, and for this reason, a high frequency of stretching vibration was appeared at tetrahedral site, while the low frequency was related to the vibration of the octahedral [17, 18].

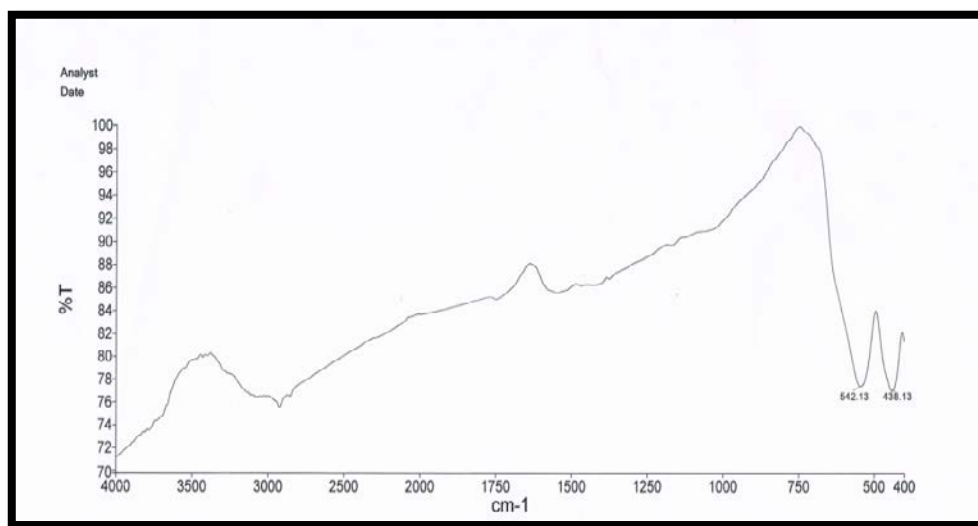
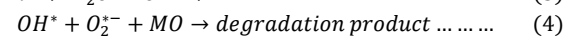
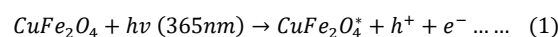


Fig. 9. FTIR spectrum of CuFe_2O_4

Degradation of Methylene Orange (MO) in aqueous CuFe_2O_4 suspension and remove of sulfur compound

The degradation of the MO in the presence of the H_2O_2 and CuFe_2O_4 by UV irradiation was illustrated in figure 10. The figure shows a strong absorbance band at 510nm assigned to $n\text{-p}^*$ transition, and its strength was due to the intense effect of the electron-donating dimethylamino groups on the Azo bonds to form a conjugated structure. 5 min after the beginning of the reaction, the strength of the band at 510nm was reduced, and the spectra showed the formation of another product 30min after the reaction as shown in scheme 1. According the proposed mechanism, the light of the source (UV lamp), hydrogen peroxide and catalyst were very necessary for the photo-oxidation reaction. Many control experimental were used to get the optimum condition for the degradation of MO as shown in figure 10 by plotting the ratio of the degradation as a function of time. The results showed no cognizable photobleaching when H_2O_2 was used

without UV irradiation (20%), but a slight change took place (39%), when the irradiation with H_2O_2 was used, because the irradiation generated OH radicals from H_2O_2 which were working on the degradation of dye. The optimum result was obtained by using the catalyst with H_2O_2 under UV irradiation, and the degradation of dye reached to 95% at 60min due to the irradiation in the presence of catalyst which increased the rate of OH radical formation and this increased the ability of the degradation [19, 20]. These meant that the synthesized material was suitable and had high potential properties to be applied as photodegradation catalyst under UV irradiation



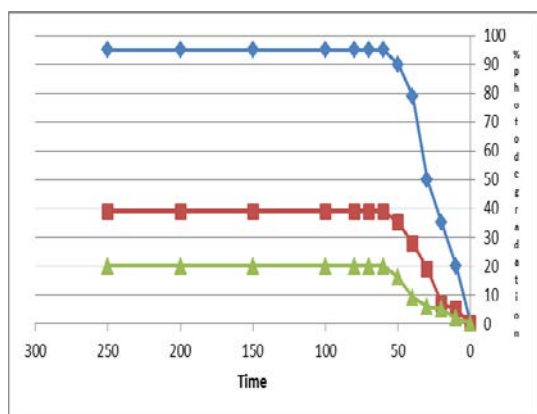


Fig. 10. Relationship of % degradation with time for Methyl orange

The sulfur content in LGO before and after the treatment was analyzed using X-ray fluorescence to evaluate the efficiency of the prepared catalyst. The concentration of sulfur compounds before the oxidation process was equal to 1.49ppm, then the concentration was reduced to 0.09ppm after the treatment process. Almost 94% of sulfur compounds was removed from the LGO, and this proved the efficiency of the prepared nanocomposite in the oxidative desulfurization technique.

CONCLUSION

The present work showed the efficiency of copper ferrite prepared photolysis for removing sulfur compound from gas oil and its ability in photodegradation of the Azo dye. The structure and spectral analysis proved that the photolysis method was very good to prepare copper ferrite. The inverse spinel with a tetragonal structure of CuFe_2O_4 was clearly appeared from XRD analysis, while PL spectrum caused many peaks which were appeared at the visible region. The image of TEM and SEM showed the particles in the nano range with a spherical shape. The study of EDX spectrum indicated that the ratio of iron was twice more than of copper with higher purity product, while the analysis data of XPS indicated some carbon on the material surface. The analysis of the VSM showed that the product had good magnetic properties.

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