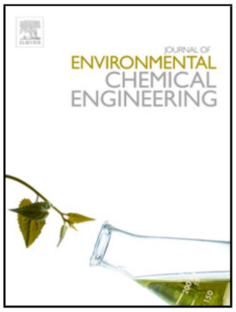

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Photocatalytic oxidative desulfurization of liquid petroleum fuels using magnetic CuO-Fe_3O_4 nanocomposites

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Abstract

In the present study, dual-functional CuO-Fe_3O_4 magnetic nanocomposites (MNCs) have been prepared through a simple impregnation method and used as catalyst for photocatalytic oxidative desulfurization of model-fuel (dibenzothiophene, DBT in n-hexane) and real naphtha at moderate conditions. The CuO-Fe_3O_4 MNCs were characterized by X-ray diffraction, BET surface area and pore volume using nitrogen adsorption–desorption and VSM methods. The effects of different reaction parameters such as initial DBT concentration in model-fuel, CuO-Fe_3O_4 MNCs dose, reaction time, H_2O_2/DBT molar ratio and CuO:Fe_3O_4 weight ratio of the MNCs were studied in detail. Results for model-fuel treatment showed that the prepared nanocomposite can eliminate 95.2% of DBT after 120 min under the following conditions: CuO:Fe_3O_4 weight ratio of 1:1, catalyst dose of 1o g/L, H_2O_2/DBT mole ratio of 7.5:1 and initial DBT concentration of 250 mg/L. Furthermore, 93% of sulfur conversion was obtained for naphtha fuel (initial sulfur concentration of 533 mg/L) after 240 min reaction time. The synthesized CuO-Fe_3O_4 magnetic nanocomposites combines the photocatalytic activity of CuO and the adsorption capacity of both Fe_3O_4 and CuO species, which make it have important applications in the deep desulfurization of liquid fuels.

Keywords: magnetic nanocomposites; oxidative desulfurization; photocatalyst; model fuel; naphtha.

1. Introduction

Existence of sulfur in liquid petroleum fuels may cause several significant problems such as catalyst poisoning in many oil refining processes. Furthermore, it's a main cause of corrosion in pumping, pipeline and burners. During combustion, liquid fuels, which contain high levels of sulfur, will generate SO_x emissions which are the main source of environment pollution and acid rains [1-3]. Consequently, removing of sulfur compounds (such as thiols, sulfides, and thiophenic compounds) from liquid fuels is highly significant in the petroleum refining industry.

Conventionally, hydrodesulfurization (HDS) process have been proposed for removing of sulfur from liquid fractions using catalyst under high temperature and pressure in the presence of hydrogen gas. HDS process is highly effective for the reduction of thiols, sulfides and disulfide, but aromatic sulfur compounds such as thiophene and its derivatives are recalcitrant and less reactive in HDS process [4, 5]. So as to meet the ultra-low sulfur level rules, the refractory thiophenic compounds should also be removed. HDS is very expensive and it is carried out under high conditions of temperature and pressure to be able to desulfurize these refractory sulfur compounds [6].

Numerous improving techniques such as reactive adsorption, extraction, biodesulfurization, and oxidative desulphurization are recommended to complement the conventional HDS process for clean fuels production [7]. Due to the availability of the required materials with no expensive operating conditions as in HDS, Oxidative desulfurization (ODS) is considered to be one of the favorable techniques for deep desulfurization of liquid petroleum fuels [8-12]. The photocatalytic oxidative desulfurization is attracting particular interest, due to its low operating cost and moderate conditions [13].

Several catalytic materials have been used for water treatment for kinds of pollutants. UV/TiO_2 system has appeared as a promising photocatalyst for the degradation of several organic pollutants in numerous applications [14]. Recently, many studies have been dedicated on applications of CuO in photocatalysis under visible light irradiation because of its excellent photoconductive and photochemical activity [15, 16]. Furthermore, Fe_3O_4 nanoparticles are also highly favored for removal of a wide range of pollutants, due to magnetic properties, high adsorption capacity, low cost, and ease of production [17]. Therefore, it can be expected that the CuO-Fe_3O_4 nanocomposites may possess a good capability of the organosulfur photocatalytic degradation from liquid fuels and can be easily recovered from the slurry reactor using an external magnetic field.

The details concerning photocatalytic oxidative desulfurization of liquid fuels using magnetic photocatalysts are still vague. There have been many reports in the literature on degradation of organic pollutants from wastewater using magnetic photocatalyst. However, there are limit studies on the using of magnetic nanocomposite as photocatalyst in the oxidative desulfurization of liquid fuels. Regarding the above remarks, the aim of this work is to synthesis magnetic CuO:Fe_3O_4 nanocomposites consists of magnetic Fe_3O_4 nanoparticles as a carrier coated with CuO with different CuO to Fe_3O_4 weight ratios and studied its performance for the first time for desulfurization model (DBT in n-hexane) fuel using photocatalytic oxidative desulfurization method. The effects of main factors on the sulfur conversion during photocatalytic reaction were studied. Finally, the applicability of the proposed photocatalytic oxidation system for real naphtha desulfurization is investigated.

2. Materials and Methods

2.1 Materials

All chemicals used were AR-grade. Ferric chloride $FeCl_3.6H_2O$ (98%), ferrous sulfate $FeSO_4.7H_2O$ (99%), sodium hydroxide (98%) and cupric chloride $CuCl_2.2H_2O$ were purchased from Merck and used directly to fabricate CuO-Fe_3O_4 MNCs. 30 wt% H_2O_2 (Merck) was used as oxidant. Dibenzothiophene, DBT (99.9 %) and n-hexane (99.8 %) supplied by Sigma-Aldrich were used to prepare the model-fuel. Naphtha fraction (30-182 ^oC) supplied by AL-Dura refinery, Middle Oil Company, Baghdad, Iraq was used as a real-fuel in this study. The characteristics of naphtha fraction are listed in Table 1.

2.2 CuO-Fe_3O_4 MNCs Synthesis and characterization

Fe_3O_4-CuO MNCs were prepared according to the method given by San C., et al. [18] in two steps. Firstly, Fe_3O_4 and CuO nanoparticles were prepared simply by chemical coprecipitation method. Then, CuO-Fe_3O_4 MNCs were prepared in different CuO: Fe_3O_4 weight ratios by simple impregnation of Fe_3O_4 MNPs in $CuCl_2.2H_2O$ solution.

Fe_3O_4 MNPs were prepared by dissolving the required amounts of $FeCl_3.6H_2O$ and $FeSO_4.7H_2O$ using magnetic stirrer at a mole ratio of 2:1 in 500 ml of distilled water at 70 ^oC for 60 min. Subsequently, 10 M NaOH solution was added dropwise into the solution to raise the pH about 10 to 11. The solution turned from brown to black evidence to precipitate the Fe_3O_4 MNPs. The resulting MNPs suspension was allowed to cool to room temperature and then magnetically separated using simple magnet, dried and stored in in a desiccator.

CuO NPs were synthesized according to [19] by precipitation in aqueous media using $CuCl_2$ as precursor. 0.1 M of copper chloride was prepared by dissolving the appropriate weight of $CuCl_2$ in 100 ml of deionized water. 0.1 M of NaOH solution was slowly added under stirring until pH reached to 14 where black precipitate was produced. The precipitate was then washed several times by deionized water and ethanol till pH reached 7. Then, the precipitate was dried at 90 °C for 16 h and lastly calcined at 500 °C for 3 h.

CuO-Fe_3O_4 MNCs were then fabricated by impregnation method with a known weight of as prepared Fe_3O_4 MNPs which previously dispersed in an ultrasonic stirrer (Sigma-Aldrich, Inc., Germany, at frequency of 50 kHz) for 1 h and a solution containing $CuCl_2.2H_2O$. The mixture was strongly stirred using magnetic stirrer for 10 h and added with 1 M NaOH to rise up pH to 13. After that, the CuO-Fe_3O_4 MNCs were magnetically separated and washed with water three times, then dried for 16 h at 60 ^oC under vacuum. Finally, the dry CuO-Fe_3O_4 MNCs were stored in a desiccator for supplementary use. CuO-Fe_3O_4 MNCs were prepared with weight ratio of 0.5:1, 1:1 and 2:1 of CuO to Fe_3O_4 and denoted as CF0.5, CF1 and CF2 respectively.

Structural phase analysis of the as-prepared Fe_3O_4 MNPs and CuO-Fe_3O_4 MNCs was performed by X-Ray Diffraction (XRD) by Rigaku, D/Max-2000 diffractometer using Cu Kα radiation using wavelength (λ) = 1.5406 A^0, tube-voltage = 40 kV, tube-current = 30 mA, and at 2θ range = 20^o to 70^o. For surface area and pore volume measurements, full N_2 adsorption-desorption isotherms at -196 °C were measured using Surface Area and Pore volume Analyzer (Quantachrome Autosorb-6iSA, USA). The N_2 uptake provided a linear fit to the Brunauer-Emmett-Teller (BET) equation. The magnetization properties of Fe_3O_4 MNPs and CF1 MNCs were examined using vibrating-sample-magnetometery VSM (model EZ7, Microsence, Japan).

The UV-visible absorption spectrum of as-prepared CuO, Fe_3O_4 and CuO-Fe_3O_4 (with different CuO:Fe_3O_4 weight ratio) were also studied using UV-visible photospectrometer model Perkin Elmer 5000, Italy. The CuO, Fe_3O_4 and CuO-Fe_3O_4 were dispersed in ethanol with concentration of each 0.01 g/ml before currying out the test.

2.3 Photocatalytic oxidative desulfurization experiments

A batch photocatalytic oxidative desulfurization technique was used to investigate DBT removal from model-fuel at ambient temperature. The adsorption property of CuO-Fe_3O_4 MNCs was also tested. The photocatalytic oxidative desulfurization experiments included studying the effect of different parameters such as CuO:Fe_3O_4 weight ratio of the catalyst (0.5:1, 1:1 and 2:1), initial DBT concentration (125-1000 mg/L), CuO-Fe_3O_4 catalyst loading (5-30 g/L) and H_2O_2/DBT mole ratio (5-10). The reaction system consisted of a 100 ml glass flask as photochemical reactor immersed in thermostatic water bath, magnetic stirrer (stirring speed of 350 rpm) and a 350 W HP Mercury lamp, 93136E (Philips Lighting Co., Ltd, Holland) as a visible light source with light intensity of 6.63 klux.

In a typical experiment, 0.5 g CuO-Fe_3O_4 (CF1) was dispersed in 50 mL model-fuel (giving a catalyst loading of 10 g/L) at an initial DBT concentration of 250 mg/L and added into the photocatalytic reactor with constant stirring, then, the mixed solution was placed in the dark for 30 min to reach adsorption-desorption equilibrium state [20]. Subsequently, a specific amount of H_2O_2 oxidant (H_2O_2/DBT mole ratio = 7.5:1) was added into the reactor and the reaction system exposed to irradiated with the HP Hg lamp. 2 ml of the suspension samples were collected every predetermined time period, centrifuged and the clear oil in the upper layer was analyzed.

Further photocatalytic reaction experiments were carried out for oxidative desulfurization of real naphtha fuel (Table 1). The operation conditions of these experiments include using CF1 as photocatalyst ($CuO:Fe_3O_4$ weight ratio = 1:1), naphtha-fuel volume = 50 ml, CF1 catalyst weight = 0.5 g (catalyst loading of 10 g/L), H_2O_2/S molar ratio = 7.5:1 (sulfur molecular weight was assumed to be the same of DBT), initial sulfur content = 533 mg/L and reaction temperature = 30°C. 3 ml samples were withdrawn from the reactor every a specific period of time, centrifuged and the upper (oil) layer of the sample was analyzed for sulfur concentration.

The sulfur concentration was determined by X-ray fluorescence sulfur in oil analyzer (model SLFA-2100, Horiba Ltd., Japan). In all desulfurization experiments, sulfur removal percent was determined in term DBT/sulfur conversion from the following relation:

$$X(\%) = \frac{C_o - C_t}{C_o} \times 100 \tag{1}$$

Where X(%) is the conversion, C_o is the initial DBT/sulfur concentrations (mg/L), C_t is the DBT/sulfur concentration (mg/L) at reaction time (t).

3. Results and Discussions

3.1 CuO-Fe₃O₄ MNCs characterization

The XRD pattern of the synthesized Fe_3O_4 MNPs, CuO NPs and $CuO\text{-}Fe_3O_4$ MNCs (CF1) at 2θ ranging from 20° to 70° is illustrated in Fig.1. A series of diffraction peaks (at 2θ = 30.336°, 35.73°, 43.393°, 54.79°, 58.8°, 62.99°) were present and matched very well with planes of (220), (311), (400), (422), (511), and (440) of standard Fe_3O_4 according to the JCPDs card (no. 88–0315). Besides Fe_3O_4 peaks, others new peaks for CuO-Fe3O4 sample at 2θ = 33.4°, 38.85°, 51.5° and 61.1° were recognized and they were indexed for the crystal planes of (110), (111), (020), (311) of CuO patterns according to the JCPDs card (no. JCPDs 48–1548) [21], which confirmed that the synthesized catalyst was CuO-Fe_3O_4. SEM image of the CuO-Fe_3O_4 nanocomposite (CF1) was presented in Fig.2.

BET analysis (S_{BET} and V_P), particle size (dp), and saturation magnetization (Ms) of Fe_3O_4 MNPs and CuO-Fe_3O_4 nanocomposites are summarized in Table 2.

According to the Brunauer Deming-Deming Teller (BDDT) classification [22], the shape of the N_2 absorption–desorption isotherm of the composite is analogous to IV type, and the hysteresis loops seem to be of H3 type. This specifies that CF1 nanocomposites have a mesoporous structure. As shown in the pore size distribution curve (insert Fig.3), the pore diameter within the range 2−50 nm, this result further confirmed that the nanocomposites are generally mesoporous. The BET surface area, pore size, and pore volume of the CF1 nanocomposite is 72.5 m^2/g, 8.6 nm, and 0.273 cm^3/g, respectively.

The magnetic hysteresis loops of as-synthesized Fe_3O_4 MNPs and the CF1 nanocomposite were determined at room temperature and the results are demonstrated in Fig.4. The magnetization/hysteresis curves show that both Fe_3O_4 MNPs and CF1 nanocomposite are magnetic and Fe3O4 have a magnetization saturation value (Ms) of 43.5 emu/g while that of CF1 nanocomposite is 31.4 emu/g. The two patterns look alike each other and the CuO-Fe_3O_4 nanoparticles have superparamagnetic properties. The magnetization decreased with the decreasing of the magnetic field, and reached zero at magnetic field of zero, therefore, no residual magnetization remained. The magnetic saturation moment per unit mass (Ms) was measured to be 31.4 emu/g. The Ms values of all CuO-Fe_3O_4 MNCs were lower than for pure Fe_3O_4 MNPs (Table 2), which is mainly attributed to the presence of nonmagnetic CuO shells on the Fe_3O_4 surface but it stills magnetic. This property of the nanocomposite remains magnetic when coated with CuO and specifies that it can be simply separated from the solution by using a magnet.

The optical properties of CuO, Fe3O4 and CuO-Fe_3O_4 samples were examined by UV–vis reflectance spectra. Fig.5 show the UV–Visible absorption spectrum of CuO, Fe3O4 and CuO-Fe_3O_4 (CF0.5, CF1 and CF2 nanocomposite samples) dispersed in ethanol

(0.01 g/ml). As shown in Fig.5, all samples presented broad absorption in the visible zone suggesting that CuO-Fe_3O_4 nanocomposites with different ratios have a strong absorption in UV zone and could appropriately absorb visible light and therefore, have good photocatalytic properties when irradiated under visible light. The imputation of visible light absorption may be owing to the surface plasmon resonance (SPR) effect [23] of CuO part in the synthesized composites.

3.2Photocatalytic oxidative desulfurization studies

3.2.1 Model-fuel desulfurization

3.2.1.1 Effect of CuO:Fe_3O_4 weight ratio

The catalytic activity of CuO-Fe_3O_4 MNCs with different CuO:Fe_3O_4 weight ratio (from 0.5:1 to 2:1) was investigated. The results were presented in Fig.6 (experimental conditions: mode-fuel = 50 ml, MNC catalysts =0.5 g, H_2O_2/DBT mole ratio = 7.5:1, initial DBT concentration = 250 mg/L and reaction temperature = 30°C). With the CuO:Fe_3O_4 weight ratio increasing from 0.5:1 to 2:1, the DBT conversion increased from 86% to 97% after 2 h. Though CF2 nanocomposites revealed better activity, but CF1 could also reach deep desulfurization (95.1% conversion) after reaction for 2 h with less CuO content. Therefore, from an economic and environmental point of view, CF1 nanocomposite was selected as a better weight ratio for further study.

Furthermore, the DBT removal efficiency was studied using only CF1 nanocomposite in dark and without H_2O_2 oxidant to investigate its adsorption properties. The results of DBT adsorption were inserted in Fig.5. It can be seen that only 19% of DBT was adsorbed onto the surface of CuO-Fe_3O_4 without light irritation and H_2O_2 oxidant after 2 h.

3.2.1.2 Effect of H_2O_2/DBT mole ratio

Different H_2O_2/DBT molar ratios (5:1, 7.5:1, 10:1 and 15:1) were investigated in the desulfurization system using 1:1-CuO-Fe_3O_4 MNC catalyst. Experimental conditions include CuO:Fe_3O_4 weight ratio = 1:1 (CF1), mode-fuel = 50 ml, MNC catalyst = 0.5 g (giving a catalyst loading of 10 g/L), initial DBT concentration = 250 mg/L and reaction temperature = 30°C. As can be seen from Fig.7, when the H_2O_2/DBT molar ratio was increased from 5:1 to 10:1, the DBT conversion efficiently increased from 83% to 95.9% after reaction for 2 h. this is because providing more oxygen radicals to oxidize the DBT, therefore the promoted reaction. The DBT conversion had only increased from 95.1% to 95.9% after increasing H_2O_2/DBT molar ratio from 7.5:1 to 10:1. Therefore, with the respect of cost, the H_2O_2/DBT molar ratio of 7.5:1 was appropriate and selected for further study. Increasing in H_2O_2/DBT molar ratio to 15:1 reduced the reaction conversion. This may attributed to the formation a liquid film on catalyst surface, which decreases the DBT adsorption to its active sites when increasing H_2O_2 amount to a certain level. Therefore, the reaction is limited under high H_2O_2 concentrations [24-26].

3.2.1.3 Effect of initial DBT concentration

The effect of initial DBT concentration in model-fuel on DBT conversion is shown in Fig.8 using CF1 catalyst (experimental conditions: mode-fuel = 50 ml, MNC catalyst = 0.5 g, H_2O_2/DBT molar ratio = 7.5:1, reaction time = 2 h and reaction temperature = 30°C). The DBT conversion decreased as the initial DBT initial concentration increased in the model-fuel. DBT conversion was maximum when the initial DBT concentration was 125 mg/L. On the other hand, the lowest DBT conversion rate was achieved at an initial concentration of 1000 mg/L. According to these results, CuO-Fe_3O_4 catalyst is suitable for deep oxidative-desulfurization.

3.2.1.4 Effect of CuO-Fe_3O_4 MNC catalyst loading

The effect of CuO-Fe_3O_4 catalyst loading on DBT conversion was investigated, and the results are displayed in Fig.9 at different reaction time. DBT conversion was enhanced as the catalyst loading increased from 5 to 30 g/L (0.25 to 1.5 g per 50 ml model-fuel). Experimental conditions include CuO:Fe_3O_4 weight ratio = 1:1, mode-fuel = 50 ml, initial DBT concentration = 250 mg/L, H_2O_2/DBT molar ratio = 7.5:1 and reaction temperature = 30°C. The reaction conversion could not clearly be enhanced when the catalyst loading was increased from 15 g to 30 g/L, probable because excess CuO-Fe_3O_4

catalyst causes agglomeration in the reaction mixture, thus reducing the availableness of active sites of catalyst surface.

3.2.1.5 Photocatalyst recycling study

The recyclability of the 1:1-CuO-Fe_3O_4 nanocatalyst was examined in the oxidation of DBT in model-fuel and the results are presented in Fig.10. The experimental conditions include using mode-fuel of 50 ml, catalyst = 0.5 g (catalyst loading of 10 g/L), initial DBT concentration of 250 mg/L, H_2O_2/DBT molar ratio of 7.5:1, reaction time of 2 h and reaction temperature of 30°C. At the end of each reaction experiment, 1:1-CuO-Fe_3O_4 catalyst were separated magnetically from the reaction mixture, dried in oven and then used in subsequent cycle. Experimental results indicate that this desulfurization system could be recycled five times with a little decrease in the DBT conversion, and therefore, catalyst activity. DBT conversion was 95.1%, 94 %, 91 %, 90.3%, and 88.7% respectively

3.2.2 Real-fuel desulfurization

Fig.11 shows the naphtha photocatalytic desulfurization experiments using CF1 nanocomposite. The experimental conditions include CuO:Fe_3O_4 weight ratio = 1:1 (CF1 sample), naphtha-fuel = 50 ml, catalyst = 0.5 g, initial sulfur content = 533 mg/L, H_2O_2/S molar ratio = 7.5:1 and reaction temperature = 30°C. The sulfur conversion increased with time and revealed that the sulfur contents can be decreased to below 38 mg/L and 93% conversion was achieved after reaction time of 6 h. These results have showed that a CuO-Fe3O4 magnetic nanocomposite is efficient for the deep oxidation of sulfur compounds in real naphtha fuel, and the deep oxidation is essential for a photocatalytic oxidative desulfurization.

3.3 Comparison of result obtains in this and other studies

According to the experimental results, CuO-Fe_3O_4 nanocomposites show excellent catalytic activity in deep oxidative desulfurization of liquid petroleum fuels. Table 3 shows a comparison between the results found in this study and other studies. Most of these studies established good results. By contrast, the CuO-Fe_3O_4 nanocomposites in this study can remove 100% DBT at initial DBT concentration of 125 mg/L within 2 h under simple conditions.

4. Conclusions

Magnetic CuO-Fe_3O_4 nanocomposites with different CuO:Fe_3O_4 weight ratios have been synthesized and used as oxidative desulfurization photocatalysts for removal both DBT from model-fuel and sulfur from naphtha fraction. Different reaction parameters such as H_2O_2/DBT molar ratio, initial DBT concentration, and catalyst amount have been studied on the reaction rate. The results indicate that 1:1 CuO:Fe_3O_4 weight ratio (CF1) of the nanocomposite as catalyst gave a proper reaction conversion (95%) after 2 h reaction time, initial DBT concentration of 250 mg/L, H_2O_2/DBT mole ratio of 7.5:1 and catalyst loading of 10 g/L. The recycling of the photocatalyst was also tested, and the photocatalytic activity of magnetic CuO-Fe_3O_4 nanocomposite on DBT did not decrease significantly after reusing five times. This photocatalytic oxidation desulfurization system was found to be suitable for the oxidative desulfurization of naphtha fuel.

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Figure captions

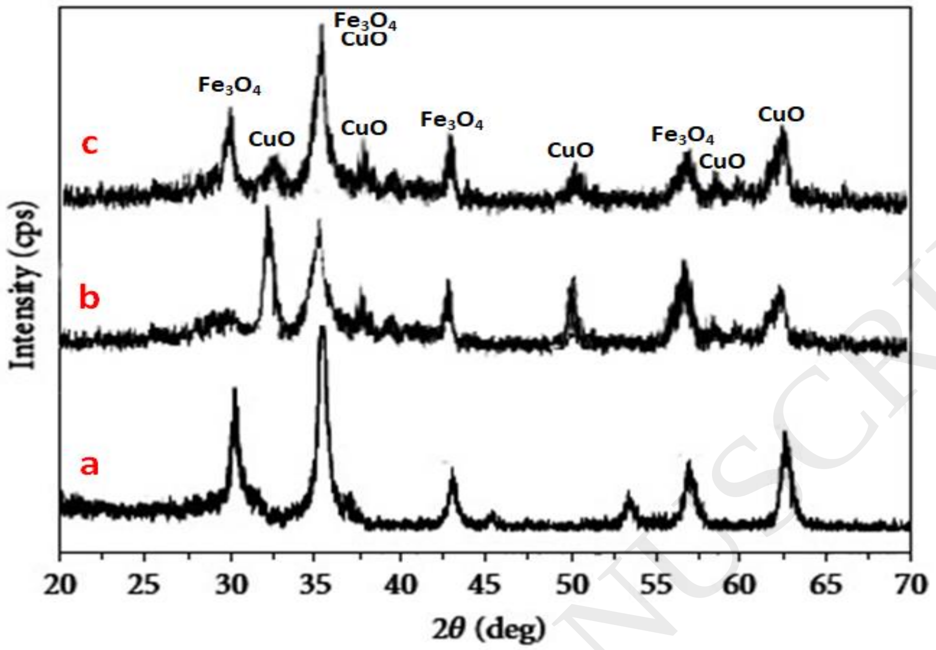

Fig.1 XRD spectrum of Fe_3O_4 MNPs (a), CuO NPs (b) and CuO-Fe_3O_4 nanocomposite (c).

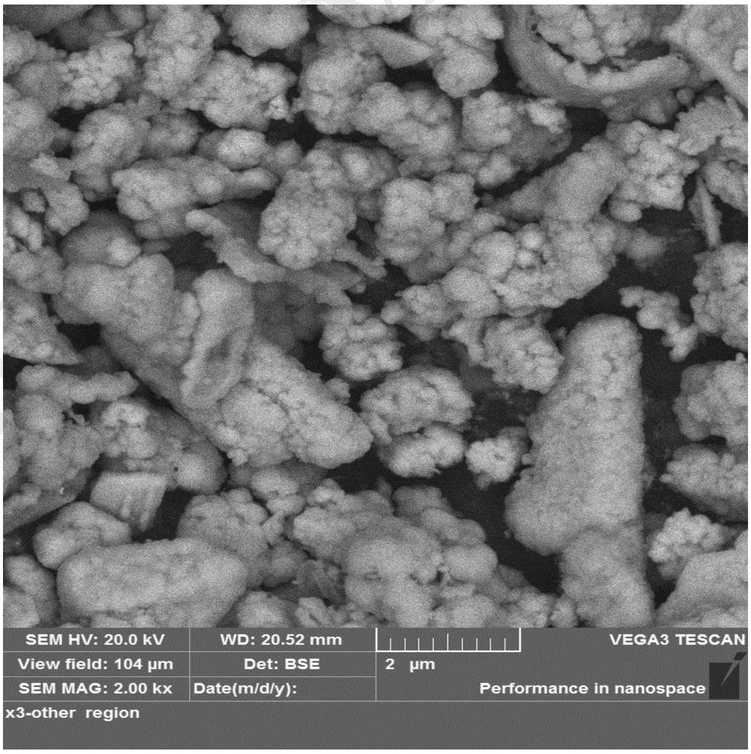

Fig.2 SEM image of the CuO-Fe_3O_4 nanocomposite (CF1).

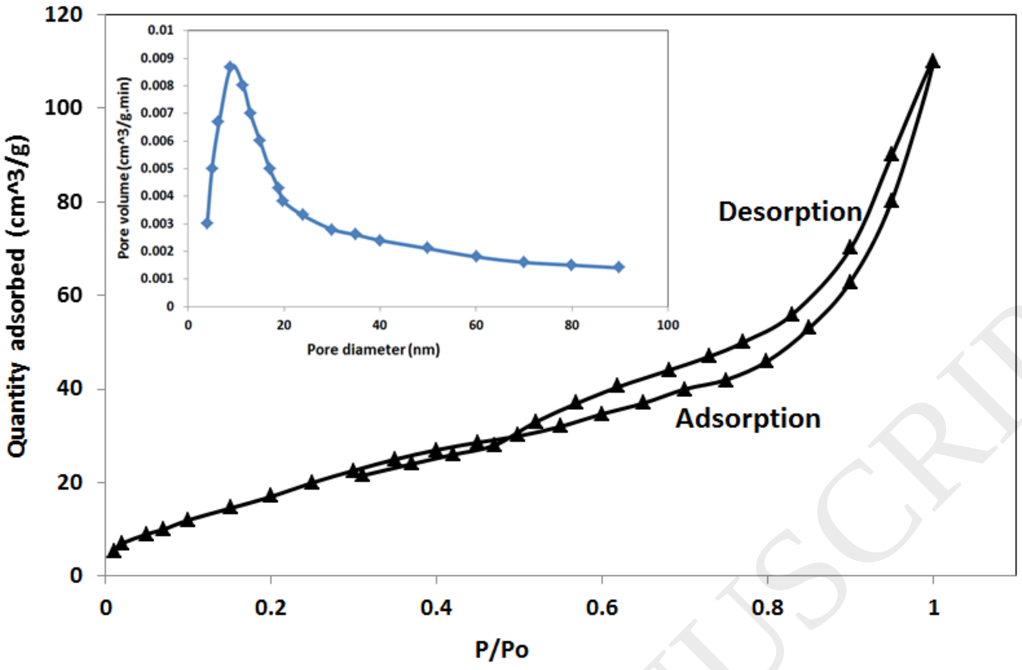

Fig3. N_2 adsorption-desorption isotherms and pore size distribution (insert) for CuO-Fe_3O_4 nanocomposite (CF1).

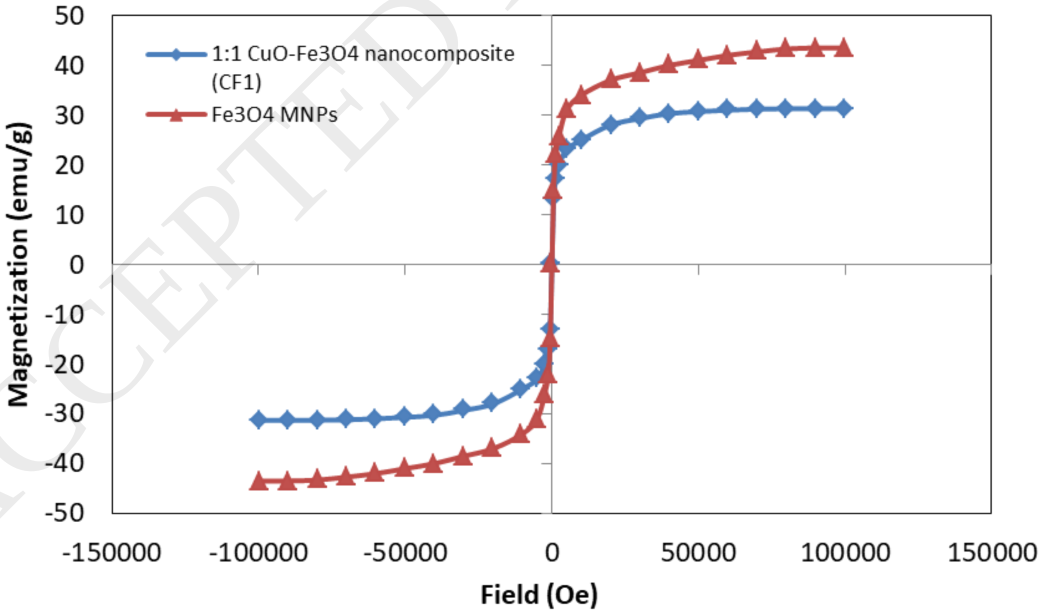

Fig.4 Magnetic hysteresis loop of Fe3O4 MNPs and CuO-Fe_3O_4 nanocomposite (CF1) carried out at room temperature.

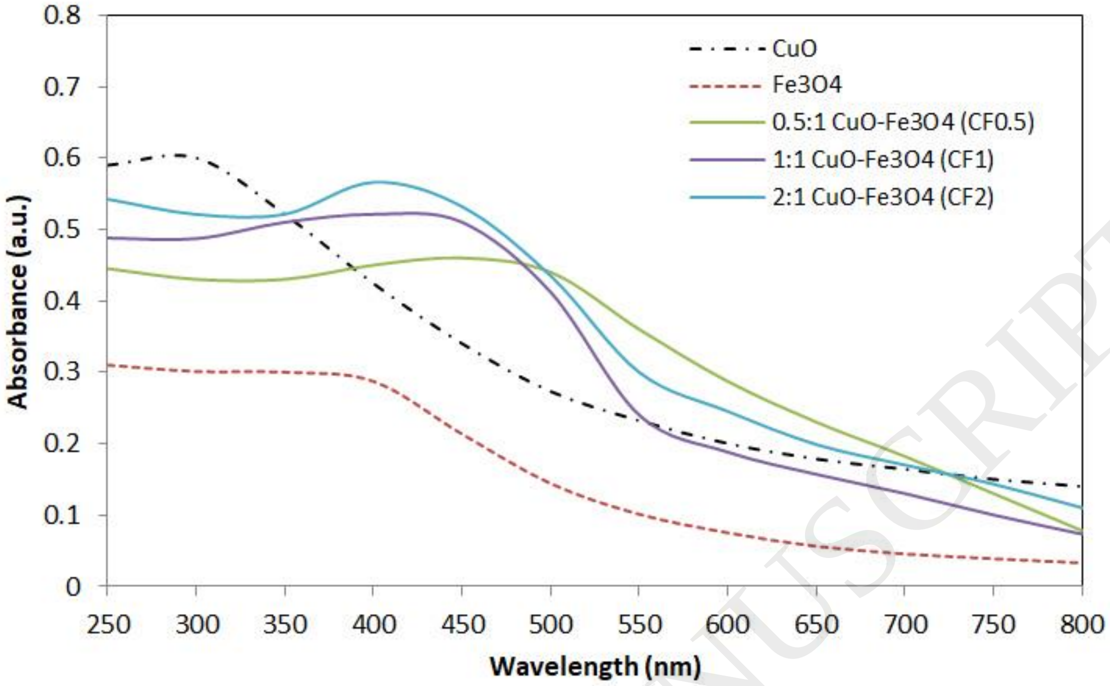

Fig.5 The UV–Visible absorption spectrum of CuO, Fe3O4 and CuO-Fe_3O_4 (with different ratio) dispersed in ethanol solution.

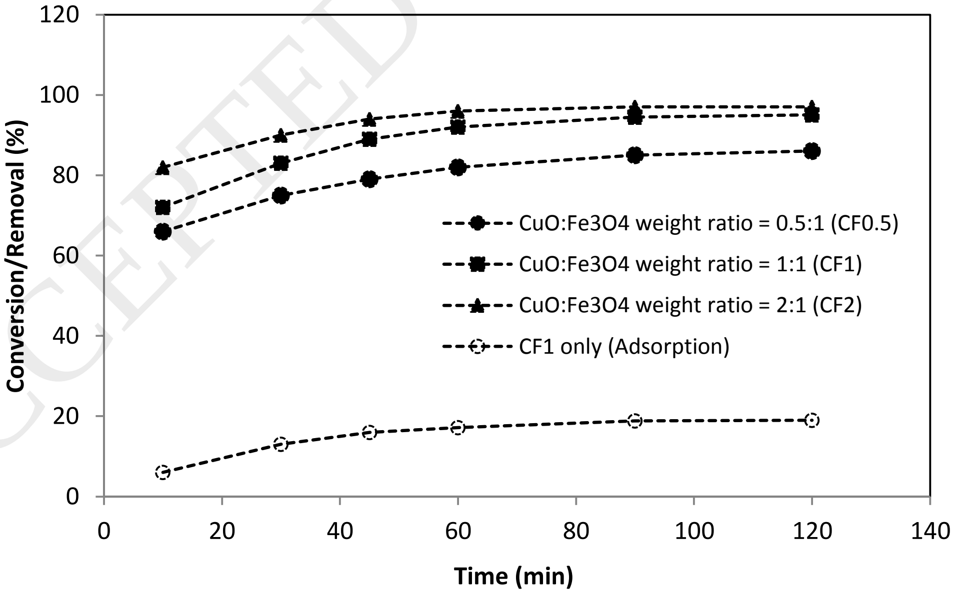

Fig.6 Effect of CuO:Fe_3O_4 weight ratio (experimental conditions: mode-fuel = 50 ml, MNC catalysts = 0.5 g, H_2O_2/DBT mole ratio = 7.5:1, initial DBT concentration = 250 mg/L, reaction temperature = 30°C).

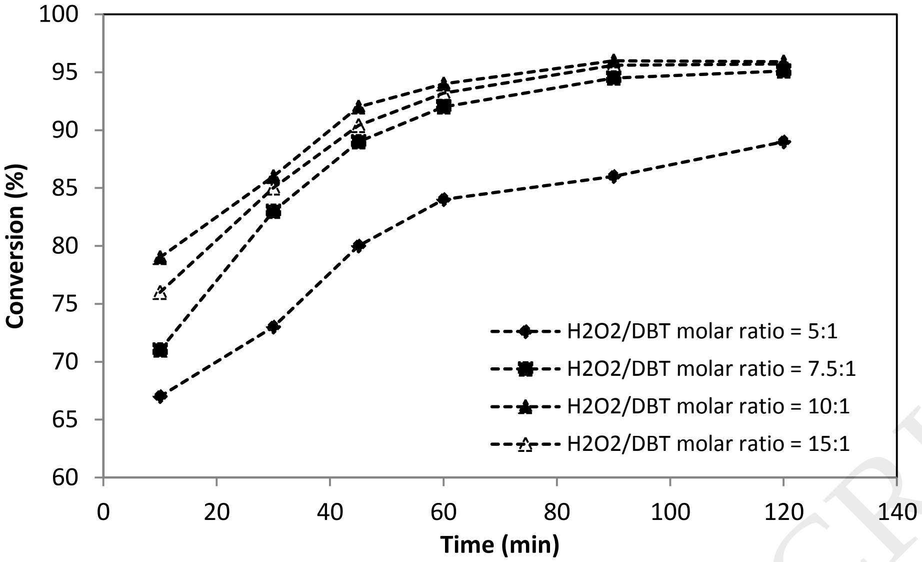

Fig.7 Effect of H_2O_2/DBT molar ratio (experimental conditions: CuO:Fe_3O_4 weight ratio = 1:1, mode-fuel = 50 ml, MNC catalyst = 0.5 g, initial DBT concentration = 250 mg/L, reaction temperature = 30°C).

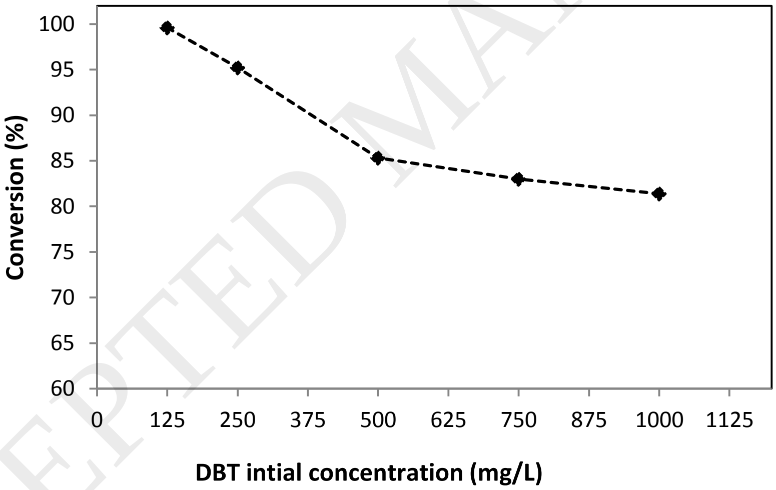

Fig.8 Effect of *initial DBT concentration* (experimental conditions: CuO:Fe_3O_4 weight ratio = 1:1, mode-fuel = 50 ml, MNC catalyst = 0.5 g, H_2O_2/DBT molar ratio = 7.5:1, reaction time = 2 h, reaction temperature = 30°C).

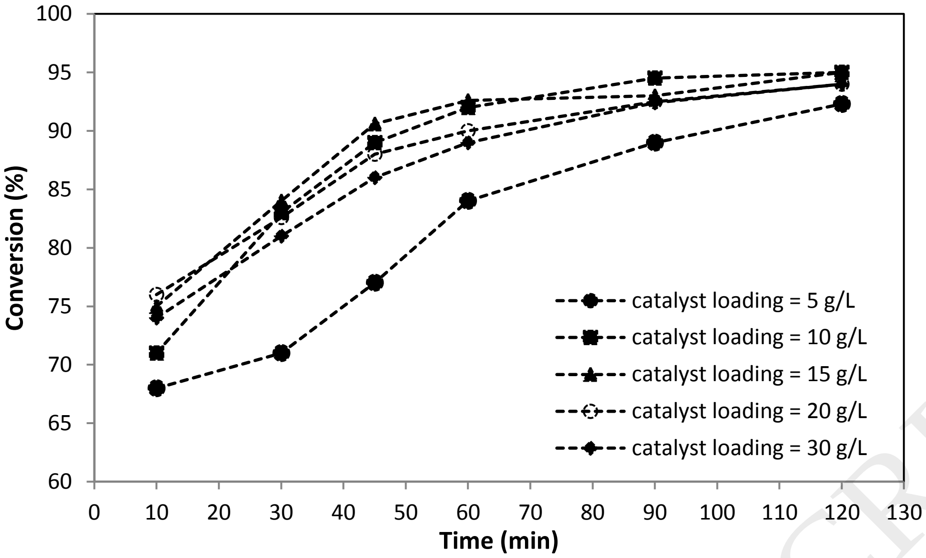

Fig.9 Effect of *catalyst loading* (experimental conditions: CuO:Fe_3O_4 weight ratio = 1:1, mode-fuel = 50 ml, initial DBT concentration = 250 mg/L, H_2O_2/DBT molar ratio = 7.5:1, reaction temperature = 30°C).

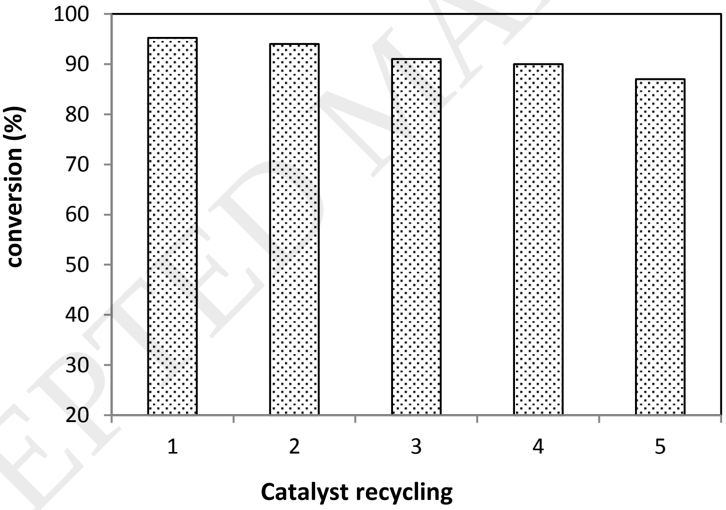

Fig.10 Catalyst recycling study (experimental conditions: CuO:Fe_3O_4 weight ratio = 1:1 (CF1), mode-fuel = 50 ml, catalyst = 0.5 g (catalyst loading of 10 g/L), initial DBT concentration = 250 mg/L, H_2O_2/DBT molar ratio = 7.5:1, reaction time = 2 h, reaction temperature = 30°C).

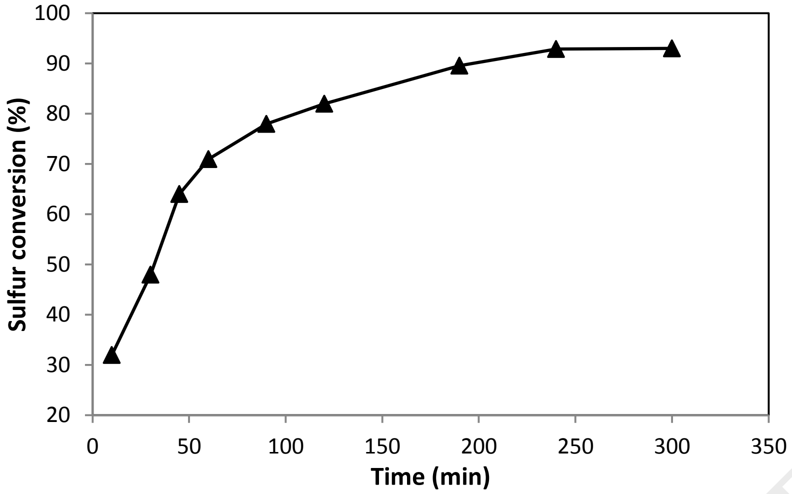

Fig.11 Real naphtha desulfurization study (experimental conditions: CuO:Fe_3O_4 weight ratio = 1:1 (CF1), naphtha-fuel = 50 ml, catalyst = 0.5 g, initial sulfur content = 533 mg/L, H_2O_2/S molar ratio = 7.5:1, reaction temperature = 30°C).

Table

Table 1 Naphtha fraction characteristics.

Property	**Value**
SG/60 ºF	0.681
Sulfur content, mg/L	533
Reid vapor pressure/37.8 ºC, kg/cm^3	14.2
Color (Saybolt)	25+
First boiling point, ºC	30
10% Vol. distillate, ºC	83
50% Vol. distillate, ºC	135
Final boiling point, ºC	182
RON	58

Table 2 Summary of Physicochemical properties of Fe_3O_4, and CuO-Fe3O4 nanocomposites.

Adsorbent	dp (nm)	Pore size (nm)	S_{BET} (m^2/g)	V_P (cm^3/g)	Ms (emu/g)
Fe_3O_4 MNPs	10-30	3.92	60.8	0.0897	43.5
CuO-Fe_3O_4 MNCs (CF0.5)	10-80	6.4	70.3	0.144	32.6
CuO-Fe_3O_4 MNCs (CF1)	4-70	8.6	72.5	0.273	31.4
CuO-Fe_3O_4 MNCs (CF2)	4-60	9.7	84.6	0.291	29.2

Table 3 Comparison of result obtains in this and other studies.

Photocatalyst system	DBT concentration (mg/L)	Reaction time	Conversion	Reference
TiO2/BC	1000	2.5 h	80	[27]
Fe–TiO2/UV	300	1 h	94	[28]
C/TiO2@MCM-41/UV	500	2.5 h	95.6	[29]
MWNTs/TiO2/UV	700	2 h	98	[25]
1:1 CuO-Fe_3O_4/UV	250	2 h	95.1	Present study