

# Adsorption and sonocatalytic performance of magnetite ZnO/CuO with NGP variation

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**Abstract.** A series of Fe<sub>3</sub>O<sub>4</sub>/ZnO/CuO/nanographene platelets (Fe<sub>3</sub>O<sub>4</sub>/ZnO/CuO/NGP) nanocomposites with various NGP weight percents were studied as catalysts for methylene blue removal under adsorption followed by sonocatalytic process. Weight percents (wt.%) of NGP in the nanocomposites were varied (5, 10, and 15 wt.%). The physicochemical properties of the samples were characterized using X-Ray diffraction (XRD), ultraviolet-visible (UV-VIS) spectroscopy, *Brunauer–Emmett–Teller* (BET) surface area analysis, and a vibrating sample magnetometer (VSM). The heterogeneous structure of all samples consisted of the cubic spinel structure of Fe<sub>3</sub>O<sub>4</sub>, hexagonal wurtzite structure of ZnO, monoclinic structure of CuO, and graphite-like structure of NGP. With increasing NGP weight percent, sample surface area increased from 14 m<sup>2</sup>/g to 23 m<sup>2</sup>/g. Adsorption and sonocatalytic activity were examined on degradation of methylene blue in alkaline conditions. The results show that the adsorption ability of samples increased with increasing NGP weight percent. However, in the sonocatalytic process, Fe<sub>3</sub>O<sub>4</sub>/ZnO/CuO/NGP with 10 wt.% NGP exhibited the maximum degradation. The effect of addition different radical scavenger was also examined to understand the sonocatalytic mechanism.

## 1. Introduction

Organic dyes used in industrial processes contaminate the environment and its surroundings [1-2]. For that reason, an effective method is needed to manage dye waste water before it is disposed of in the environment. Because it is cheap and easy, adsorption is the most commonly used method of organic dye removal [3-4].

The magnetic material is one of the potential adsorbent in adsorption process for organic dye removal. It has not only the good adsorption capacity but could make the separation process of material from organic dye solution became easier [5]. Among other magnetic material, Fe<sub>3</sub>O<sub>4</sub> is the promising material because it has high adsorption capacity and unique magnetic properties. [6].

Aside from the adsorption process, advanced oxidation processes (AOPs) have been used for the removal of organic dye, as their observed degradation ability is better than adsorption process and could mineralize hazardous substances into simple molecules [7]. The AOPs method recently used is photocatalytic. However photocatalytic process has limitation when applied to degrade the high concentrate organic dye due to limited light penetration [8]. It is thought that ultrasonic waves may resolve that issue because of their high penetration of any liquid medium [8-9]. Applying ultrasonic waves in water causes acoustic cavitation, consisting of processes of nucleation, rapid growth, and Applying ultrasonic waves in water causes acoustic cavitation, consisting of processes of nucleation,



rapid growth, and implosion, involving bubble collapse. This collapse produces high-temperature (5000 K) and high-pressure (1000 atm) “hot spots,” followed by light emission [10-11], commonly known as sonoluminescence that could interact with the catalyst to form electron-hole pairs that degrade the organic dye [12].

The semiconductor zinc oxide (ZnO) is commonly used in sonocatalytic process because it is chemically stable, cheap, and eco-friendly [13]. However, sonocatalytic activity of single ZnO is limited by the high rate of recombination of electrons and holes [14]. Combining ZnO with CuO and Fe<sub>3</sub>O<sub>4</sub> is believed to hamper electron-hole combination, therefore increasing the efficiency of organic dye removal [15-16]. Because of its large surface area and good electron transport, the addition of graphene is also believed to increase adsorption capacity and sonocatalytic activity [17]. In our previous works, we have investigated the sonocatalytic activity using NGP materials on Fe<sub>3</sub>O<sub>4</sub>/ZnO/CuO nanocomposites [18]. However, the influence of NGP loading as well as adsorption performance of Fe<sub>3</sub>O<sub>4</sub>/ZnO/CuO/NGP are also need to be investigate. Therefore, in this research we try to investigate the influence of NGP loading in the adsorption ability and sonocatalytic performance of Fe<sub>3</sub>O<sub>4</sub>/ZnO/CuO/NGP nanocomposites.

## 2. Materials and methods

Nanoparticles of CuO and Fe<sub>3</sub>O<sub>4</sub> and nanocomposite of Fe<sub>3</sub>O<sub>4</sub>/ZnO/CuO with molar ratio of Fe<sub>3</sub>O<sub>4</sub>:ZnO:CuO is 1:1:5 were synthesized as described in our previous study [19]. In synthesizing Fe<sub>3</sub>O<sub>4</sub>/ZnO/CuO/NGP, nanographene platelets (NGP) were purchased from Angstrom Materials. In the typical process NGP were dispersed into a mixture of water and ethanol, using an ultrasonic bath for 2 hours. The synthesized 2 g of Fe<sub>3</sub>O<sub>4</sub>/ZnO/CuO was then added to the solution and stirred with a magnetic stirrer for an hour to produce the homogeneous suspension. That suspension was then heated at 120°C for 3 hours, and the precipitate obtained by centrifugation was then dried at 70°C for 12 hours. For present purposes, the amount of NGP was varied at 5 wt.%, 10 wt.%, and 15 wt.%, respectively denoted as FZC, FZC-5 wt.% NGP, FZC-10 wt.% NGP, and FZC-15 wt.% NGP.

All the samples were characterized using X-ray diffraction (Rigaku Miniflex 600), Fourier transform infra-red spectroscopy, *Brunauer–Emmett–Teller* (BET) surface area analysis, UV-Vis Diffuse Reflectance Spectroscopy (DRS) Shimadzu, and a vibrating sample magnetometer Oxford Type 1.2 T.

Adsorption and sonocatalytic process were analyzed using methylene blue as a model of the organic pollutant. For present purposes, concentration of methylene blue was 20 mg/L, and catalyst dosage was 0.3 g/L. Typically, the methylene blue solution was poured into a 100 mL beaker; Fe<sub>3</sub>O<sub>4</sub>/ZnO/CuO/NGP nanocomposite was then added to the solution and stirred using a magnetic stirrer. Adsorption of methylene blue was performed in dark conditions for 4 hours. Meanwhile, the sonocatalytic process was analyzed using an ultrasonic bath operating at a frequency of 40 kHz and 150 W. At specified intervals, the methylene blue solution was taken and analyzed for color degradation by UV-Vis spectroscopy, using the following equation:

$$\text{Decolorization} = \frac{C_t}{C_0}$$

where  $C_t$  and  $C_0$  are the concentrations of methylene blue at time  $t$  and in the initial condition (mg/L). The adsorption capacity of the samples was analyzed using the equation

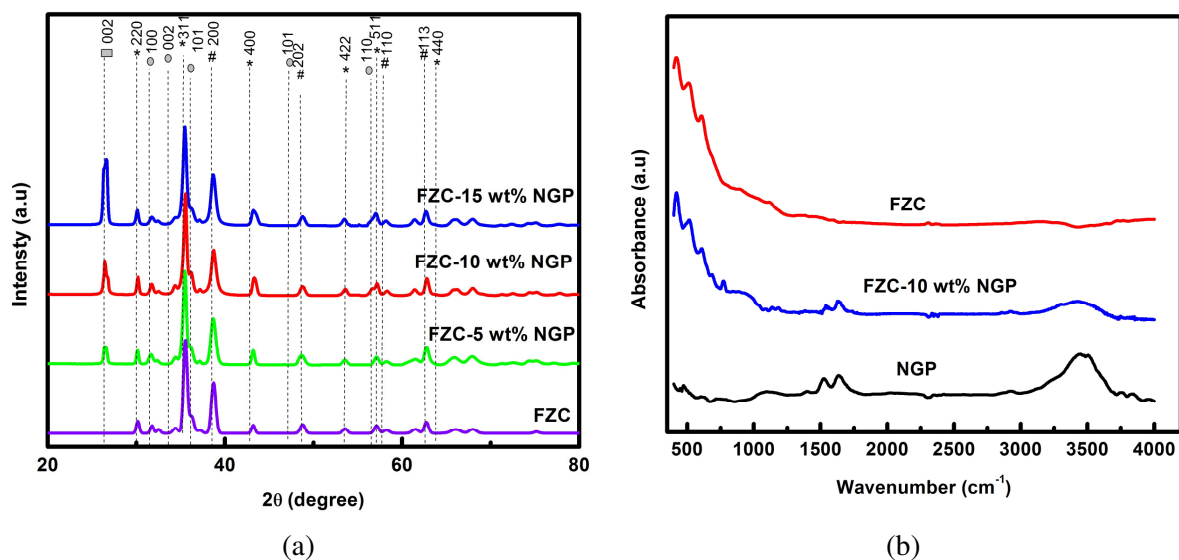
$$q_e = \frac{(C_0 - C_t)V}{m}$$

where  $q_e$  is the equilibrium adsorption capacity (mg/g),  $V$  is the volume of solution (mL), and  $m$  is the amount of catalyst used (g).

### 3. Results and discussion

Figure 1a shows the results of XRD measurement for  $\text{Fe}_3\text{O}_4/\text{ZnO}/\text{CuO}/\text{NGP}$  nanocomposite variations of 5, 10 and 15 wt.% (respectively denoted as FZC-5 wt.% NGP, FZC-10 wt.% NGP, and FZC-15 wt.% NGP). For comparison, the XRD spectra of  $\text{Fe}_3\text{O}_4/\text{ZnO}/\text{CuO}$  nanocomposite (FZC) were also plotted. These spectra show the cubic spinel crystal structure of  $\text{Fe}_3\text{O}_4$ , hexagonal wurtzite structure of ZnO, and monoclinic structure of CuO. The presence of NGP was confirmed at a value of  $2\theta = 26^\circ$ , indicating the existence of a graphitic-like crystal structure. Lattice parameter values of  $\text{Fe}_3\text{O}_4$ , ZnO, CuO, and NGP were analyzed using the Rietveld refinement method. As seen in table 1, the lattice parameter values of  $\text{Fe}_3\text{O}_4$ , ZnO, CuO, and NGP did not change significantly, indicating that the formation of  $\text{Fe}_3\text{O}_4/\text{ZnO}/\text{CuO}/\text{NGP}$  nanocomposite does not alter the crystal structure of each material.

FT-IR measurement of FZC-10 wt.% NGP nanocomposite is shown in figure 1b and the results for FT-IR of NGP and FZC nanocomposite are also shown. NGP's vibration mode at wavenumbers 1050 and  $1621\text{ cm}^{-1}$  indicates vibration mode C-C and C=O, while vibration mode of OH was detected at wavenumber  $3400\text{ cm}^{-1}$  [20]. The FZC nanocomposite material's vibration mode at wavenumbers 400 to  $800\text{ cm}^{-1}$  indicates Cu-O, Fe-O and Zn-O vibration [21-23]. For the FZC-10 wt.% NGP nanocomposite, all vibration modes for FZC as well as NGP could be detected, indicating the presence of  $\text{Fe}_3\text{O}_4/\text{ZnO}/\text{CuO}$  nanocomposite and NGP in the sample.



**Figure 1.** (a) XRD and (b) FT-IR spectra of  $\text{Fe}_3\text{O}_4/\text{ZnO}/\text{CuO}/\text{NGP}$ .

**Table 1.** Lattice parameter and grain size of  $\text{Fe}_3\text{O}_4/\text{ZnO}/\text{CuO}/\text{NGP}$  with different NGP weight percent.

Sample	Lattice parameter ( $\text{\AA}$ )						
	$\text{Fe}_3\text{O}_4$	ZnO	CuO			NGP	
	a	a=b	c	a	b	c	a=b=c
FZC	8.373	3.249	5.217	4.689	3.436	5.138	
FZC-5 wt.% NGP	8.373	3.260	5.204	4.687	3.445	5.129	3.645
FZC-10 wt.% NGP	8.366	3.252	5.215	4.683	3.427	5.144	3.638
FZC-15 wt.% NGP	8.381	3.248	5.212	4.687	3.428	5.147	3.643

The surface areas of all samples are tabulated in table 2. The results confirm that addition of NGP increases sample surface area. The surface area of  $\text{Fe}_3\text{O}_4/\text{ZnO}/\text{CuO}$  nanocomposite modified with NGP increased from  $14.42 \text{ m}^2/\text{g}$  to  $23.15 \text{ m}^2/\text{g}$ . Surface area can influence the sample's adsorption capacity and sonocatalytic activity.

UV-Vis diffuse reflectance measurements for the samples (FZC, FZC-5 wt.% NGP, FZC-10 wt.% NGP and FZC-15 wt.% NGP) are shown in figure 2a, representing samples' reflectance ability. The results show that sample reflectance ability gradually decreased in the visible light range with incorporation of 5, 10, and 15 wt.% NGP. The value of the energy gap was analyzed using the Kubelka-Munk equation [24], extrapolating the  $F(R)^2$  curve to the energy value in  $F(R)^2 = 0$ . The results confirm that addition of NGP reduced the energy gap value from 2.53 eV to 2.32 eV.

VSM measurements for FZC and FZC-10 wt.% NGP nanocomposites are shown in figure 2b, which also shows the VSM measurement of  $\text{Fe}_3\text{O}_4$  nanoparticles for comparison. The results show that magnetization of FZC-10 wt.% NGP nanocomposites is lower than that of  $\text{Fe}_3\text{O}_4$  nanoparticles but higher than the magnetic saturation value of FZC-10 nanocomposites. The high magnetization value is very potential for reusability of catalyst by using magnetic separation technique. The inset in figure 2b shows the separation of FZC-10 wt.% NGP nanocomposites material from degraded methylene blue solution using an external magnet, showing that the FZC-10 wt.% NGP nanocomposite can be easily attracted by an external magnetic.

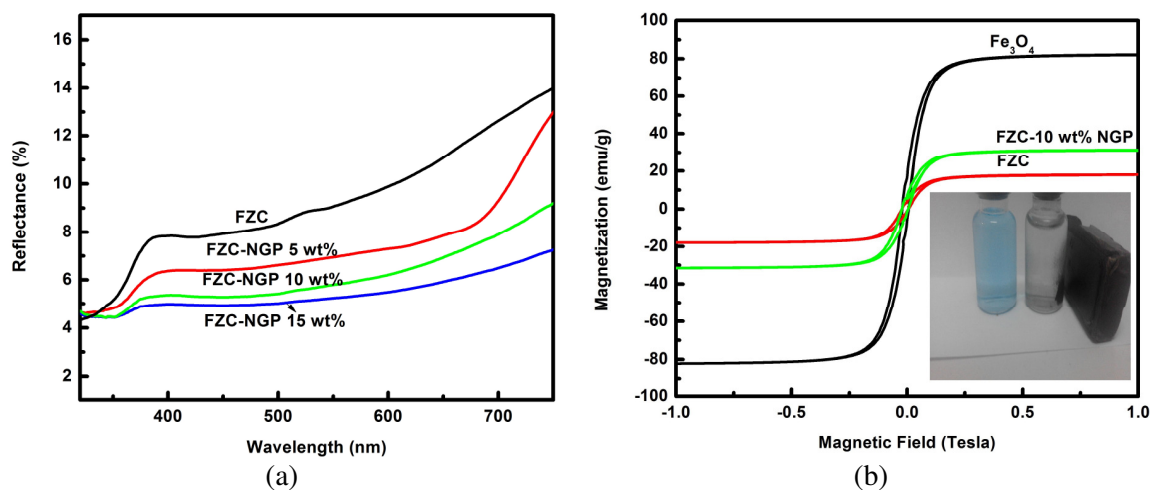
The adsorption ability of FZC, FZC-5 wt.% NGP, FZC-10 wt.% NGP and FZC-15 wt.% NGP nanocomposite samples is shown in figure 3a. The results show that FZC-5 wt.% NGP, FZC-10 wt.% NGP and FZC-15 wt.% NGP nanocomposites have better adsorption ability than FZC nanocomposites; addition of 15 wt.% NGP shows the best decolorization results. Adsorption capacity values are presented in table 2, showing that FZC-15 wt.% NGP has the highest adsorption capacity ( $26.68 \text{ mg/g}$ ).

The sonocatalytic activity of all samples is shown in figure 3b. The results indicate that the addition of NGP to  $\text{Fe}_3\text{O}_4/\text{ZnO}/\text{CuO}$  nanocomposite can increase the degradation efficiency of methylene blue through sonocatalytic process, but only up to 10 wt.% NGP. Addition of 15 wt.% of NGP reduced the efficiency of methylene blue degradation through sonocatalytic process. It is probably due to the higher NGP loading reduce the active sites on the sonocatalytic process. The catalyst stability result detailed in figure 4a shows that repeated (four times) usage of  $\text{Fe}_3\text{O}_4/\text{ZnO}/\text{CuO}/\text{NGP}$  nanocomposite reduced degradation efficiency only until 92%, indicating the good stability of the  $\text{Fe}_3\text{O}_4/\text{ZnO}/\text{CuO}/\text{NGP}$  sample. On the other hand, separation using an external magnet (inset figure 2b) minimized the occurrence of catalyst weight loss.

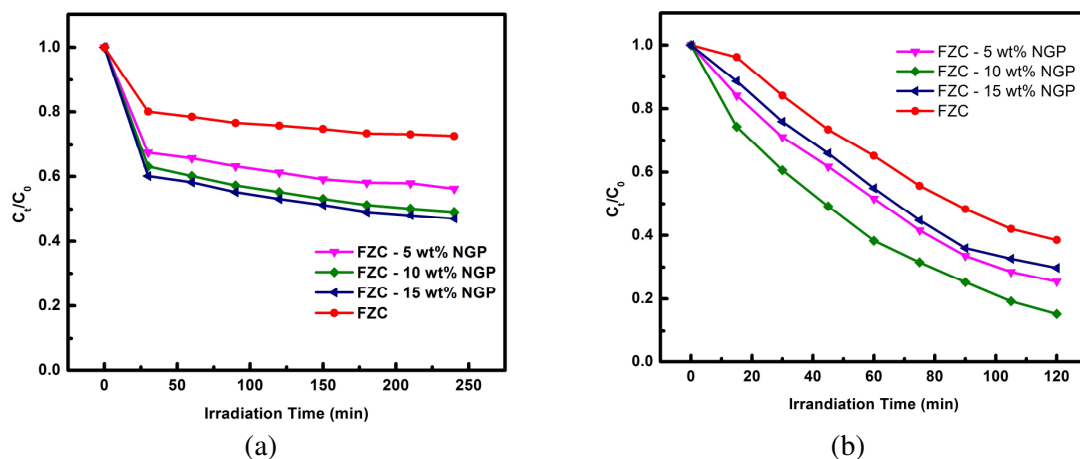
To understand the sonocatalytic mechanism, various scavengers were added. There are three type of scavenger: (1) sodium sulfate as electron scavenger, (2) ammonium oxalate as hole scavenger, and (3) tert-butyl alcohol as hydroxyl radical scavenger. The results (figure 4b) indicate that the addition of electron, hole, and hydroxyl radical scavengers reduce sonocatalytic performance. The addition of a scavenger could trap active species involved in the sonocatalytic process and it cannot react in methylene blue degradation therefore the sonocatalytic performance decrease. The addition of hole and OH radical

**Table 2.** BET surface area, band gap and adsorption capacity of  $\text{Fe}_3\text{O}_4/\text{ZnO}/\text{CuO}/\text{NGP}$  with different NGP weight percent.

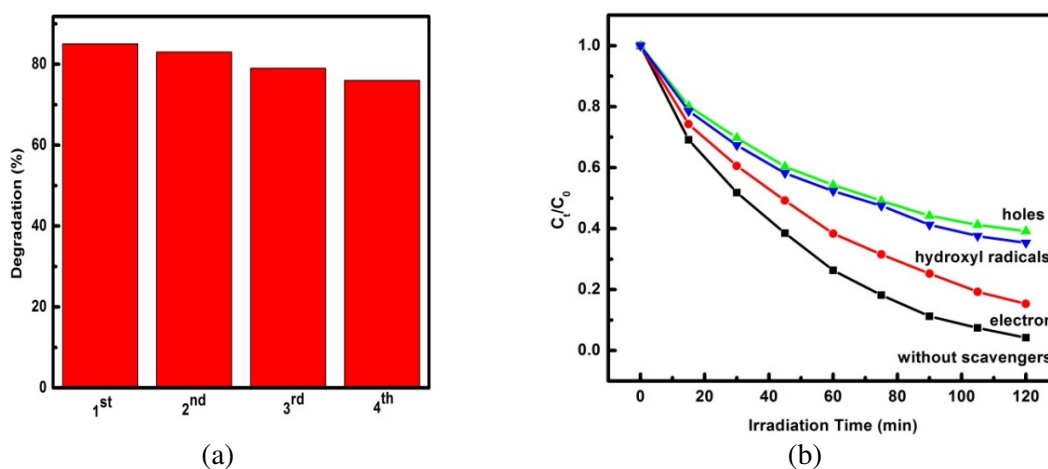
Sample	Surface Area ( $\text{m}^2/\text{g}$ )	Band gap (eV)	Adsorption Capacity ( $\text{mg/g}$ )
FZC	14.42	2.53	16.54
FZC-5 wt.% NGP	20.85	2.47	21.92
FZC-10 wt.% NGP	21.80	2.35	24.97
FZC-15 wt.% NGP	23.15	2.32	26.68



**Figure 2.** (a) UV Vis DRS spectra and (b) magnetization of Fe<sub>3</sub>O<sub>4</sub>/ZnO/CuO/NGP



**Figure 3.** (a) Adsorption and (b) sonocatalytic performance of Fe<sub>3</sub>O<sub>4</sub>/ZnO/CuO/NGP nanocomposites with different NGP weight percent.



**Figure 4.** (a) Reusability of catalyst and (b) the effect of scavenger addition on sonocatalytic performance of the samples.



scavengers exhibit the lowest sonocatalytic performance, indicating that holes and OH radicals are the main active species in the degradation process.

Under ultrasound irradiation, the Fe<sub>3</sub>O<sub>4</sub>/ZnO/CuO/NGP take energy from the sonoluminescence process that has wide range spectrum including visible and UV light. When Fe<sub>3</sub>O<sub>4</sub>/ZnO/CuO/NGP is irradiated by sonoluminescence, electron-hole pairs are created for both ZnO and CuO. The presence of Fe<sub>3</sub>O<sub>4</sub> can improve both separation and degradation by acting as an electron acceptor that prevents recombination of electrons and holes. When electron was captured by Fe<sup>3+</sup> holes are still has enough time to react with water molecules to produce hydroxyl radicals and attack directly the methylene blue solution therefore OH radicals and holes are the main active species on the degradation process. The addition of NGP materials could improve the charge separation process due to its could act as electron acceptor that could prevent recombination electron and holes [25].

#### 4. Conclusions

The addition of NGP material can increase the adsorption capacity and sonocatalytic activity of Fe<sub>3</sub>O<sub>4</sub>/ZnO/CuO samples. Addition of NGP up to 15 wt.% shows the highest adsorption capacity; for the sonocatalytic process, addition of 10 wt.% NGP shows the best degradation capacity. After four repetitions of the sonocatalytic process the catalytic performance only reduced about 92% indicated the Fe<sub>3</sub>O<sub>4</sub>/ZnO/CuO/NGP nanocomposite have good stability and degradation efficiency.

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