

Effect of Fe₂O₃ loading on CuO/CNT photocatalyst for degradation of *p*-Chloroaniline

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Abstract. Chloroaniline and its derivatives are generated from industrial chemical manufacturing processes including agricultural chemical, azo dyes and pigments, pesticides and herbicides. These compounds are found to be toxic and dangerous to aquatic and human life. Hence, their discharge into the environment must be regulated. Photocatalytic degradation is one of a promising method to remove such compounds due to its safety, low energy consumption and high efficiency. In this study, the research focused on the effect of iron oxides (Fe₂O₃) loading (5-50 wt%) on copper-carbon nanotubes (CuO/CNT) photocatalyst for degradation of *p*-chloroaniline (PCA) under visible light irradiation. The synthesized catalysts were characterized using Fourier Transform Infrared Spectroscopy to analyze its functional groups. Besides Fe₂O₃ loading, various parameters such as effect of PCA pH solution (3-11), catalyst dosage (0.125- 0.625 g L⁻¹) as well as PCA initial concentration (10-100 mg L⁻¹) were investigated. It was found that the highest degradation (75 %) of 10 mg L⁻¹ PCA was achieved using 0.325 g L⁻¹ 10 wt% Fe₂O₃/50 wt% CuO/CNT at pH 7. Kinetics study showed that the PCA photodegradation followed pseudo first-order Langmuir-Hinshelwood model. It is believed that the Fe₂O₃/CuO/CNT can be a potential photocatalyst for degrading organics pollutant efficiently.

1. Introduction

Chlorinated *p*-chloroaniline (PCA), is widely used as an intermediate during variety of chemical manufacture, including agricultural chemicals, plastic, azo dyes and pigments, production of synthetic organic chemicals and polymers like polyurethanes, rubber additives, pharmaceuticals, cosmetic products, pesticides and herbicides, and drugs [1,2]. The widespread use of these compounds has resulted in their ubiquity in industrial effluents, sludge and agriculture soils. As one of persistent organic pollutants and was widely distributed in the environment, PCA is a priority toxic pollutant listed in US EPA and EU legislation and has imposed a serious risk on public health and on the environment [3,4]. Several technologies such as photocatalysis [5], biodegradation [6,7] and radiochemical methods [8] were used to remove this compound. All the methods have their restrictions such are high cost, unfriendly environment, low efficiency and limited resources.

As of late, photocatalytic technology has turned into an imperative strategy to control ecological contamination. It includes concurrent utilization of more than one oxidation procedure to fasten the generation of reactive hydroxyl free radicals. There are incorporated homogeneous and heterogeneous photocatalyst under ultraviolet (UV) or visible light (VL) irradiation. In the past few decades, the explorations of various suitable photocatalysts for the removal of organic pollutants from wastewater have been done using various type of photocatalysts [9-11]. However, their relatively low activity and low efficiency under VL irradiation limited their practical use in water treatment.



Nowadays, CNTs have been used in many research area such as adsorption [12], photocatalytic [8] and sonocatalytic [13] reactions. Interestingly, CNTs are good candidates to enhance the photocatalytic activity under VL irradiation due to their unique chemical, physical, electronic and high thermal properties. In recent approaches, CNT has been used to mitigate the support effect [13]. Due to the one-dimensional nanostructure and high specific surface area of CNTs, various inorganic nanoparticles such as metals, metal oxides and semiconducting nanoparticles were attached on the CNTs surface to obtain nanotube/nanoparticle hybrid materials with useful properties [3]. The unique properties of these structures guaranteed inconceivable relevance and hence pulled in a lot of intrigue that proceeds right up till today particularly in photocatalytic reaction.

CuO is one of the significant narrow band gap semiconductor, which act as visible light driven. However, CuO can only absorb a small amount of solar spectrum in the UV region which result in low photocatalytic efficiency [10]. In order to improve its efficiency, several studies have been performed: synthesizing nanosized CuO particles to increase its surface area, hybridizing it with other metals or semiconductors as well as supporting it onto materials such as silica, alumina, zeolite, CNTs etc. Although the expansive endeavors have been attempted to locate the appropriate catalyst for photodegradation organic pollutants in wastewater, a great deal of major issues are not clearly yet. Nonetheless, the recovery of the used photocatalyst is also rarely studied. As known, Fe_2O_3 have its magnetite properties which is expected can overcome this issue. With respect to the component, the objective of this study is to study the effect of second metal loading which is Fe_2O_3 onto CuO/CNT catalyst for photodegradation of PCA.

2. Experimental Procedure

2.1 Synthesis of catalyst

The $\text{Fe}_2\text{O}_3/\text{CuO}/\text{CNT}$ composite samples were prepared using an electrolysis preparation technique. Firstly, to synthesize CuO/CNT, 15 mL of DMF solution was added to a normal one-compartment cell fitted with a Pt plate (2 cm x 2 cm) cathode and a Cu plate (2 cm x 2 cm) anode which containing of 0.1M tetraethylammonium perchlorate (TEAP), naphthalene (1.66 mmol) and CNT (1 g). Then, the electrolysis was conducted at a constant current density of $120 \text{ mA}/\text{cm}^2$ and continuously stirred under nitrogen atmosphere. After the required amount of CuO was reduced, the Fe plate (2 cm x 2 cm) anode was used instead of Cu plate and the electrolysis was continuously carried out under the same procedure to form $\text{Fe}_2\text{O}_3/\text{CuO}/\text{CNT}$. Figure 1 illustrate the electrolysis set up for the synthesis process.

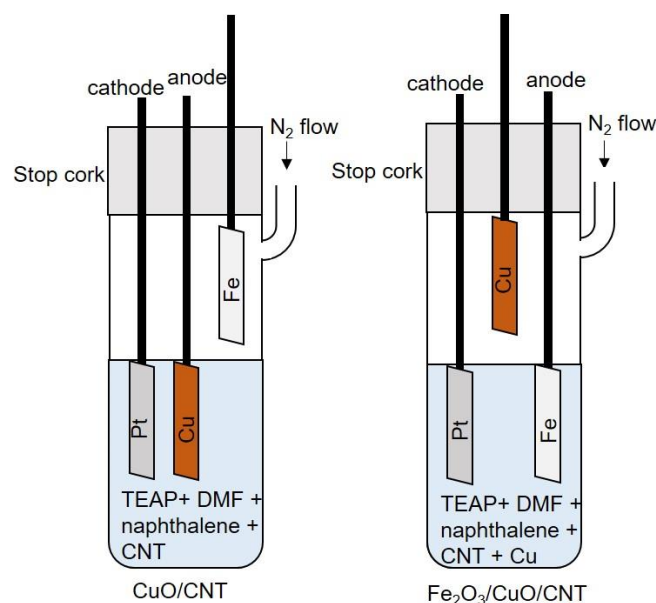


Figure 1. Electrolysis set up

After electrolysis, the sample was impregnated, oven dried overnight at 105°C, and calcined at 300°C for 3 h. The required copper and iron loading onto CNT support was calculated based on the Faraday's law of electrolysis as follows,

$$n = \left(\frac{It}{F} \right) \left(\frac{1}{z} \right) \quad (1)$$

where n is the number of moles of metal, I is constant current of electrolysis (A), t is the total time the constant current was applied (s), F is the Faraday constant (96,487 C mol⁻¹), and z is the valence number of ions of the substance (electron transferred per ion). In fact, the copper used in this study was 50 wt% for all catalysts. The as-prepared catalyst was obtained and ready for characterization and reaction testing.

2.2 Characterization

The chemical functional groups present in the catalyst were identified by FTIR (Perkin Elmer GX FTIR spectrometer) using KBr method with a scan range of 400-4000 cm⁻¹. A 0.04 g catalyst was mixed with KBr powder and 0.07 of the mixture was pelletized using hydraulic press (8 tons), Then, the sample was placed in sample holder before the spectra was recorded.

2.3 Photodegradation

The photoactivity of catalysts was tested on the photodegradation of PCA. The photocatalytic reaction was carried out in a batch reactor fixed with VL lamp (4 × 400 W; 400 nm emission). A 0.375 g L⁻¹ of catalyst was added to 10 mg L⁻¹ PCA solution and stirred for 1 h in dark to achieve adsorption-desorption equilibrium. The initial pH of PCA solution was 7 and it was carried out at 27°C. Then, the reaction was carried out for another 3 h under VL light irradiation. The concentration of PCA prior to irradiation was used as the initial value for the PCA degradation measurements. The samples were then collected at regular interval of 1 h and centrifuged in a Beckman Coulter Microfuge 16 Centrifuge at 14,000 rpm for 10 min before it being analyzed by UV-Vis Spectrophotometer (Agilent Technology Cary 60 UV-Vis) for the residual concentration of PCA. The PCA degradation was measured at maximum adsorption peak at 238 nm. The degradation percentage was calculated using following equation,

$$\text{Degradation (\%)} = \left(\frac{C_0 - C_t}{C_0} \right) \times 100 \quad (2)$$

where C_0 and C_t are the PCA initial concentration and concentration at time t , respectively.

3. Result and Discussion

3.1 Characterization of Catalyst

Figure 2 shows the FTIR spectra of Fe₂O₃/CuO/CNT catalysts with different weight loading of Fe. The band at 2360 cm⁻¹ supposed to be C-H stretching vibration originated from the surfaces of the CNT, and the bands observed at 1384 cm⁻¹ and 1087 cm⁻¹ specified the existence of C-O [14]. While, the band at 551 and 510 cm⁻¹ indicated the presence of Fe-O and CuO stretching vibrations, respectively [15,10]. The presence of the above mentioned bands in the synthesized catalysts verified the successfully loading of both Cu and Fe elements on the CNT catalyst. Meanwhile, the different intensity of all bands observed after varying the Fe contents might indicate the change in the interaction of dopants-CNT support [16,17].

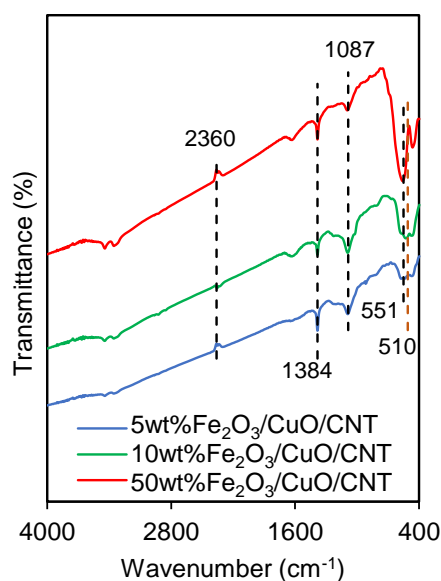


Figure 2. FTIR spectra of the synthesized catalysts.

3.2 Photocatalytic testing

In this study, the photocatalytic activity of the $\text{Fe}_2\text{O}_3/\text{CuO}/\text{CNT}$ catalysts were studied towards degradation of PCA under VL irradiation. In order to obtain the optimum conditions of the photodegradation, the experiment was carried out under various operation conditions such as pH, catalyst dosage, Fe loading and initial concentration. Then, the kinetics study was investigated using pseudo first order Langmuir-Hinshelwood model. The results were discussed below.

3.2.1 Effect of Fe Loading

The photocatalytic degradation of 10 mg L^{-1} PCA under various Fe loading (5-50 wt%) is shown in Figure 3. It was observed that the photoactivity of the catalysts was in the following order: 10 wt% $\text{Fe}_2\text{O}_3/\text{CuO}/\text{CNT}$ (75%) > 5 wt% $\text{Fe}_2\text{O}_3/\text{CuO}/\text{CNT}$ (61.8%) > 50 wt% $\text{Fe}_2\text{O}_3/\text{CuO}/\text{CNT}$ (45.9%).

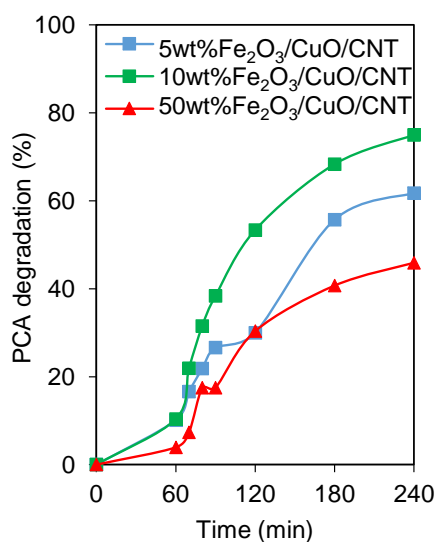


Figure 3. Effect of Fe loading on degradation of PCA [$C_{\text{PCA}} = 10 \text{ mg L}^{-1}$, $\text{pH} = 7$, $t = 1 \text{ h}$ (dark) 3h (VL), $W = 0.375 \text{ g L}^{-1}$].

The increase amount of Fe loading onto Cu/CNT was hypothetically increased the production of generated electron-hole and hydroxyl radical which led to higher activity of the catalyst [18]. However, excess Fe loading resulted in its agglomeration on the surface of CuO/CNT that reduce the surface area of the catalyst and also light penetration, therefore low photocatalytic performance was observed [19].

3.2.2 Effect of pH

In general, the photocatalytic reaction would greatly influenced by the pH solution of reactant [20]. Herein, the activity of 10 wt% Fe₂O₃/CuO/CNT catalyst was explored under various pH of PCA solution in the range of 3 to 11. As shown in Figure 4A, the photodegradation increased from 47.9% to 75.0% when increasing pH from 3 to 7. The point of zero charge (*pzc*) of 10 wt% Fe₂O₃/CuO/CNT was found to be at pH 6, implying the catalyst carries a positive charge below that value (in an acidic medium) and vice versa above pH 6 (in alkaline). Thus, at higher pH (pH > 6), the positively charged PCA is attracted to the negatively charged surface of the catalyst [21]. However, further increase of pH seems to reduce the photodegradation, which most probably due to the saturation of PCA surround the catalyst surface that reduce the penetration of VL irradiation.

3.2.3 Effect of catalyst dosage

Figure 4B shows the degradation of 10 mg L⁻¹ PCA over 10 wt% Fe₂O₃/CuO/CNT under different catalyst dosage (0.125 - 0.625 g L⁻¹) at pH 7. It is seen that the increasing of catalyst dosage from 0.125 to 0.375 g L⁻¹ increased the degradation percentage and the highest percentage (75 %) was achieved using 0.375 g L⁻¹ of catalyst. It is postulated that the increase of catalyst dosage has also increased the active surface area for more adsorption of photon and PCA molecules, thus enhanced performance. However, excess catalyst used has led to a greater turbidity of the suspension, which reduced the light penetration and thus, inhibited photodegradation [19].

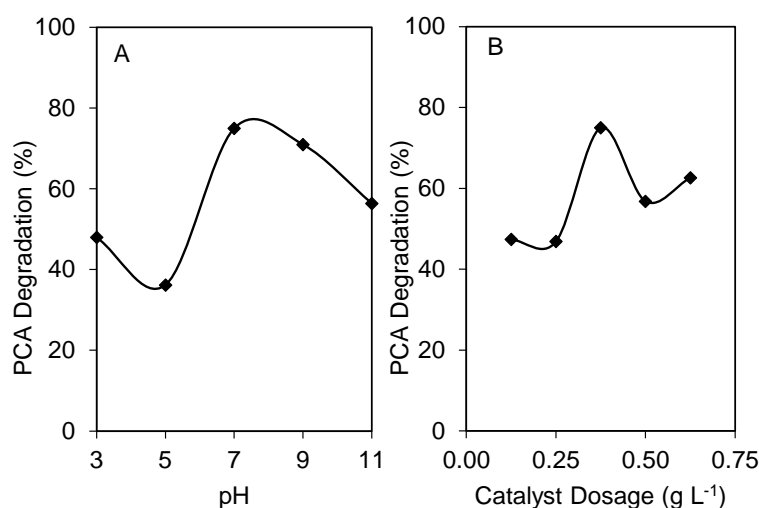


Figure 4. (A) Effect of pH and (B) Effect of catalyst dosage on photodegradation of PCA over 10 wt% Fe₂O₃/CuO/CNT [$C_{PCA}=10 \text{ mg L}^{-1}$, $W=0.375 \text{ g L}^{-1}$, $t=1 \text{ h}$ (dark) 3 h (VL)].

3.2.4 Effect on initial concentration

Figure 5 shows the degradation of PCA at pH 7 using 0.375 g L⁻¹ of 10 wt% Fe₂O₃/CuO/CNT catalyst under different initial concentration (10-100 mg L⁻¹). The initial concentration of 10 mg L⁻¹ gave the highest percentage of PCA degradation (75%) as compared to 30, 50, 70 and 100 mg L⁻¹, which were 52.5, 49.1, 37.5 and 27.9 %, respectively. A more efficient photocatalytic degradation was observed at lower initial concentration, demonstrating that the system was favorable at low concentration [16]. This is because the higher concentration of PCA has saturated the surface of catalyst and then decreased the efficiency of photodegradation [22].

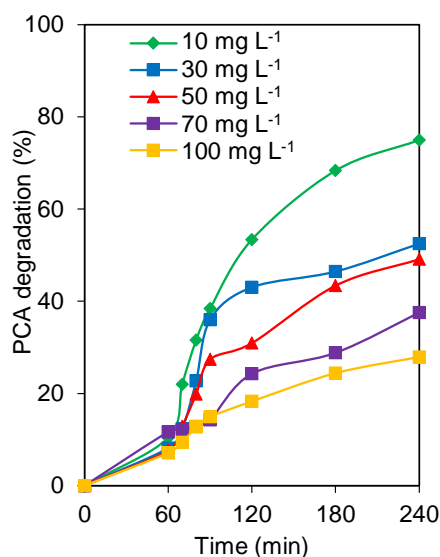


Figure 5. Effect of initial concentration on degradation of PCA over 10 wt% $\text{Fe}_2\text{O}_3/\text{CuO}/\text{CNT}$ [$W=0.375 \text{ g L}^{-1}$, $\text{pH}=7$, $t=1 \text{ h}$ (dark) 3 h (VL)].

3.3 Kinetic of photocatalytic degradation of PCA

Next, the data from Figure 4 was used to study the kinetics of the PCA photodegradation. Figure 6A shows the value of $\ln(C_0/C_t)$ versus time for 10 wt% $\text{Fe}_2\text{O}_3/\text{CuO}/\text{CNT}$ under different concentration.

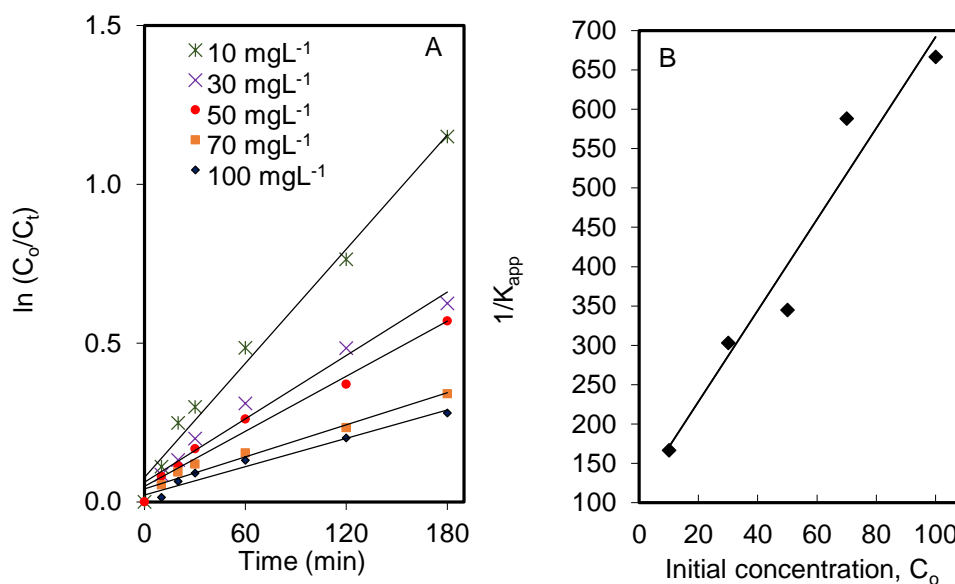


Figure 6. (A) Kinetic study of 10 wt% $\text{Fe}_2\text{O}_3/\text{CuO}/\text{CNT}$ on degradation of PCA (B) The relationship of $1/K_{app}$ and C_0 .

The apparent first order rate constant, K_{app} was defined from calculation of the slope of linear straight regression. The equation (3) can be used to calculate r_0 .

$$r_0 = K_{app} * C_0 \quad (3)$$

Figure 6B was plotted based on tabulated data in Table 1. The photodegradation of PCA fitted well with the Langmuir-Hinshelwood (LH) kinetic model. Based on the L-H formula Eq. (4) and the straight line, the value of K_r and K_{LH} were calculated to be $0.173 \text{ mg L}^{-1} \text{ min}^{-1}$ and 0.0512 L mg^{-1} , respectively. It was observed that the value of $K_r > K_{LH}$, thus suggested that the reaction would occur on the surface of the catalyst [14].

$$\frac{1}{r_0} = \left(\frac{1}{k_r K_{LH}} \right) \left(\frac{1}{C_0} \right) + \frac{1}{k_r} \quad (4)$$

Table 1. Pseudo first order apparent constant values for PCA degradation.

Initial PCA Concentration (mg L^{-1})	Rate constant, K_{app}	R^2	Initial reaction rate, $r_0 = K_{app} \times C_0$
10	0.0060	0.985	0.060
30	0.0033	0.969	0.099
50	0.0029	0.976	0.145
70	0.0017	0.961	0.119
100	0.0015	0.964	0.150

3.3 Catalyst Recovery

The combination of double metal oxides and CNT not only improved the photocatalytic degradation of PCA but it is also advantageous when coupling with magnetically recoverable metal oxide such as Fe_2O_3 . It clearly shown from Figure 7 that the used catalyst could be easily recovered by using external magnet. Thus, the development of a simple recyclable photocatalyst prevents the excessive use of photocatalysts, and also eases the recovery of deactivated photocatalysts, thereby reducing the total cost.

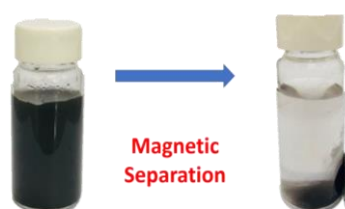


Figure 7. Catalyst Recovery

4. Conclusion

In conclusion, 10 wt% $\text{Fe}_2\text{O}_3/\text{CuO}/\text{CNT}$ catalysts that prepared via electrochemical method gave the highest photodegradation of PCA (75%) under optimum conditions of 0.375 g L^{-1} catalysts dosage at pH 7 with 10 mg L^{-1} PCA concentrations after 3 h of contact time under visible light irradiation. The kinetics studies showed the degradation followed pseudo first-order Langmuir-Hinshelwood model, and the rate constants were determined to be $K_r=0.173 \text{ mg L}^{-1} \text{ min}^{-1}$ and $K_{LH}=0.0512 \text{ L mg}^{-1}$, indicating the reaction occurred on the surface of catalyst. This system exhibits a great potential for improving the quality of the wastewater discharged from textile or other industries.

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