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Enhanced Photodegradation of Paracetamol Using Magnetite Loaded on Waste Tyre Carbon Catalyst

Nurfatehah Wahyuny Che Jusoh[1,2]*, Nur Adilla Abd Kadir[1], Ahmad Masudi[1]

[1] *Department of Chemical and Environmental Engineering, Malaysia-Japan International Institute of Technology (MJIIT), Universiti Teknologi Malaysia Kuala Lumpur, Jalan Sultan Yahya Petra, 54100 Kuala Lumpur, Malaysia*
[2] *Center of Hydrogen Energy, Universiti Teknologi Malaysia Kuala Lumpur, Jalan Sultan Yahya Petra, 54100, Kuala Lumpur, Malaysia.*

**Corresponding Author: nurfatehah@utm.my*

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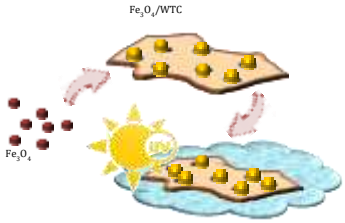
GRAPHICAL ABSTRACT



ABSTRACT

In the recent years, traces of pharmaceutical waste particularly paracetamol (PCT) in water body had increases due to the increasing of its usage and production. Since the discharge of wastewater containing PCT into water body cause harm to environment and human health, it is crucial to find a suitable treatment method to overcome this problem. In this study, a series of magnetite, Fe_3O_4 loaded on waste tyre carbon (WTC) catalyst was synthesized *via* electrochemical method. The different weight loading of Fe_3O_4 loaded on WTC was evaluated for degradation of PCT under UV light irradiation. The catalyst was subjected to X-ray diffraction (XRD), Fourier Transform Infrared (FTIR) and N_2 adsorption-desorption to study their physicochemical properties. The highest degradation percentage of PCT (76%) with initial degradation rate of 0.024 mg/L.min was achieved with 5% Fe_3O_4 loaded on WTC. This optimum degradation was notice at PCT concentration of 5 mg/L (pH 5) using 0.4 g/L of 5% Fe_3O_4/WTC for 2 h reaction. Finally, the result could contribute to electrosynthesis advancement of Fe_3O_4 loaded on abundant waste tyre carbon for the removal of pharmaceutical waste in wastewater.

Keywords: Paracetamol; magnetite; waste tyre carbon; degradation

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1. INTRODUCTION

Water pollution is one of the major problems faced by human in the world today. Among the long list of pollutants, pharmaceutical waste is one of the most hazardous waste that could give adverse effects not only to the environment, but also to human beings and animals when it contaminates water body. Until this day, many researchers and environmental agencies around the world had reported the presence of pharmaceutical compounds at alarming concentrations in water body. Due to the fact that pharmaceuticals generally dissolve easily in aqueous media and do not usually evaporate at normal temperatures or pressure, they make their way into the soil and aquatic environments via sewage, treated sewage sludge, and irrigation with reclaimed waters [1].

Paracetamol, for example, is one of the top 200 prescriptions worldwide [2]. Besides widely used as pain relief and fever reducer, especially for humans and animals, it is also used as an important material for the manufacturing of azo dyes and photographic chemicals. The large production and usage quantity of paracetamol had caused it to be found frequently in the environment, especially in the aquatic environment with 0.01 mg/L to 0.3 mg/L concentration. Apart from industrial sector, users are also among the main contributor to this problem. 58% - 68% of paracetamol and its metabolites are excreted from the body during therapeutic use [3].

Nowadays, there are a few techniques or method that had been used for the removal of contaminant from pharmaceutical wastewater. Among the established treatment technologies includes biological process and physical-chemical process. However, both processes are not that effective in treating the contaminant. Biological processes such as aerobic and anaerobic digestion is limited to biodegradable substance with low toxicity towards the biological culture [4]. On the other hand, physical-chemical processes such as adsorption and reverse osmosis does not destroy the pollutants. Instead, these processes only transfer the pollutants from one phase to another [5].

Heterogeneous photocatalysis is an advanced oxidation process that receives significant attention among

researchers for water treatment from organic pollutants. This method has high degradation efficiency, high mineralization efficiency, low toxicity, low cost, and ability to function under ambient conditions [6]. Photocatalysis degrades or oxidize organic substrates into a reduced form which are less harmful. Among the interesting photocatalyst that could be used is magnetite (Fe_3O_4) due to its good magnetic properties. Compared to other photocatalyst, Fe_3O_4 could be effectively separated and recycled by applying an external magnetic field. Besides that, it also has simple preparation method, low toxicity, biocompatibility and low cost [7-9].

One of the possible ways to increase removal of paracetamol is by incorporating adsorption method with carbon as the adsorbate in the photocatalytic process. Carbon has high efficiency for removal of pollutant, and it can reach almost 100% removal efficiency in some application due to its high adsorption capacity as well as removal efficiency for certain organic substances [10]. Therefore, this study proposed to use easily separated magnetite loaded on waste tyre carbon, (WTC) as photocatalyst for degradation of paracetamol in wastewater.

2. EXPERIMENTS

2.1 Preparation of Waste Tyre Carbon (WTC)

A waste tyre w collected in a local car workshop area and cut into small pieces. The cut tyres were then treated with 30 wt. % of Hydrogen Peroxide (H_2O_2) solution using immersion and sonication method to remove impurities. After 2 hours, the treated sample was washed with distilled water and centrifuged for 5 minutes. This step was repeated three times to ensure H_2O_2 was removed from the sample. Then, the sample was dried in an oven (2 hours) at temperature of 110 ^{0}C and calcined at 900 °C (2 hours), before grinded and sieved to obtained WTC.

2.2 Catalyst Preparation

An electrochemical cell was set up in an open system electrolysis cell which was fitted with a magnetic stirrer and a platinum plate cathode (2 × 2 cm^2) facing an iron plate anode (2 × 2 cm^2). Next, the solution media was prepared by dissolving 1.0 M of TEAP with 10 mL of distilled water in the electrolysis cell. The cell was placed in an ice bath to reduce the heating effect of the electrolysis process. 1 g of the prepared WTC was then added in the cell. Then the electrolysis process was started to produce 5, 10, and 15 wt. % of Fe_3O_4 loaded on WTC. The percentage of Fe_3O_4 loaded was estimated using the time taken for the electrolysis process, estimated using Faraday's law of electrolysis as shown in Equation 1 below.

$$w/M = It/zF \quad (1)$$

Where w is mass of the iron plate, M is the molar mass of the iron plate, I is current supplied, t is time it take for the electrolysis process, z is number of electrons, and F is Faraday constant (96485 C/mol). The electrolysis process was supplied with constant current at 480 mA. After the process, the catalyst obtained was filtered, washed and dried at 110 ^{0}C overnight.

2.3 Characterization

The crystalline structures of the catalysts were determined by X-ray diffraction (XRD) method was used with Cu-kα radiation, λ = 1.54 Å as X-ray source at 25°C using the Empyrean Multi-Purpose Research X-Ray Diffractometer. The accelerating voltage was 40 kV and the applying current was 40 mA. Then, Fourier Transform Infrared Spectrophotometer (Model IRTracer-100, Shimadzu) was used to observe the chemical properties of the synthesized catalyst in wave range of 1000–400 cm^{-1}.

2.4 Photodegradation of Paracetamol (PCT)

A 200 ml of Paracetamol solution (pH5) was poured in a 250 ml conical flask and placed in the photocatalytic reactor. Then, 0.08 g of catalyst was added in the solution and stirred for 15 mins in dark condition to ensure it mixed well. 3 ml of the solution was withdrawn, centrifuged and the tested for absorbance using UV-vis spectrophotometer. The mixture was then exposed to UV irradiation for photodegradation process. The samples were withdrawn periodically, centrifuged and analyzed at 15 minutes interval for 2 hours contact time. The photodegradation percentage at each time was calculated using Equation 2 as shown below:

$$\text{Photodegradation percentage } (\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

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

3. RESULTS AND DISCUSSION

The XRD analysis was conducted on WTC, 5% Fe_3O_4/WTC, 10% Fe_3O_4/WTC and 15% Fe_3O_4/WTC catalysts. Fig. 1 shows the XRD pattern obtained for the all the samples. All four patterns show broad and intense peaks at 2θ = 24° - 25° and 42° - 43°, which is corresponding to (002) and (100) reflections of amorphous carbon. The diffraction peaks at 2θ = 30.2°, 35.71°, 43.53°, 54.4°, 57.4° and 63° corresponded to (220), (311), (400), (422), (511) and (440) planes, which by comparison with JCPDS NO. 89-3854 were well match with Fe_3O_4 revealing the loaded iron species on the carbon is in form of magnetite [11]. The diffraction peaks of Fe_3O_4 have wide peaks which indicates good dispersion of Fe_3O_4 on the surface of the WTC. The peak of Fe_3O_4 also increased as the percentage of loading

increases. Furthermore, it was also found that peaks at 26.93°, 28.52°, 30.53°, 39.65°, 47.55°, 51.79°, 56.4°, and 57.8° were corresponds to Zinc Sulphide, ZnS. The presence of ZnS was resulted from the decomposition of Zinc Oxide (ZnO) with Sulphur (S) during the calcination process of WTC [12]. These peaks tend to decrease with increasing of Fe_3O_4 loading might be due different ratio of ZnS and Fe_3O_4 in WTC.

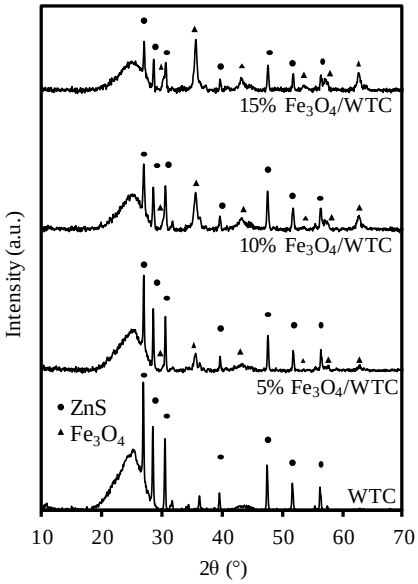

Fig. 1 XRD pattern of WTC and Fe_3O_4/WTC catalysts

In order to characterize the qualitative organic part of the synthesized catalyst, FTIR analysis was carried out on all the catalysts. The FTIR spectra of the catalysts in a range of 400 to 1000 cm^{-1} was shown in Fig. 2. As can be seen, a weak band around 600-700 cm^{-1} in WTC are likely to be associated with the out-of-plane bending mode of C-H or O-H groups [13]. On the other hand, the vibration band of Fe-O in Fe_3O_4/WTC catalyst can be detected around the same range (500-700 cm^{-1}). This band was observed at 580 and 668 cm^{-1} [14]. The band at 580 cm^{-1} increases as the loading of Fe_3O_4 increased which proved the higher amount of Fe_3O_4 was loaded onto the WTC. Similarly, the Fe-O vibration band at 668 cm^{-1} also increase in all the catalysts. Interestingly, this band intensity is higher for 5% Fe_3O_4/WTC than the other loading percentage catalysts indicating the interaction of Fe_3O_4 with WTC for possible formation of Fe-O-C bond [15].

The surface characteristics of WTC and Fe_3O_4/WTC catalysts are summarized in Table 1. Accordingly, it clearly shows that WTC has the largest surface area of 240.077 m^2/g. After loading with Fe_3O_4, the surface area and pore volume was decreased might be due to Fe_3O_4 particle which might block some of the external surface area [11]. Interestingly, at amount of 5% Fe_3O_4, the

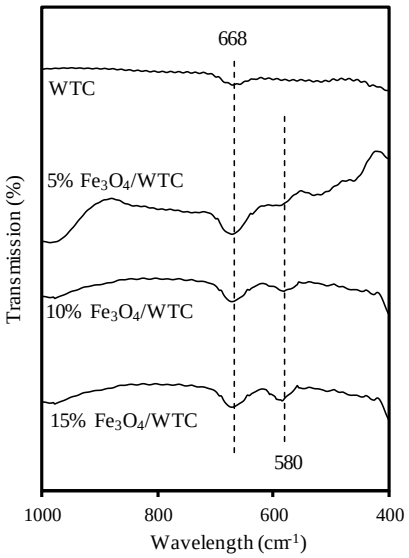

Fig. 2 FTIR analysis of WTC and Fe_3O_4/WTC catalysts

pore volume shows an increment compare to WTC. This could be due to the external pore volume and well dispersion of Fe_3O_4 particles [16]. This external pore volume presence in this catalyst also reduce its average pore radius since the pore size of Fe_3O_4 is smaller than WTC. However, the increased of Fe_3O_4 up to 10 and 15 % significantly decreased the pore volume due to the blockage of WTC pore in higher Fe_3O_4 loading. Additionally, the average pore radius also increases. This indicates that an extra mesoporous structure is being formed when high amount of Fe_3O_4 particles were loaded. These mesopores were mainly originated from the inter-aggregation of Fe_3O_4 particles and the pertinent continuous magnetite layers, imparting accessible active surface for the adsorption of nitrogen physisorption [17].

Table 1 Surface characteristics of WTC and Fe_3O_4/WTC catalysts

Sample	Surface area, (m^2/g)	Total pore volume, (cm^3/g)	Average pore radius, (nm)
WTC	240.077	1.7213	3.8978
5% Fe_3O_4/WTC	203.890	1.7403	3.6405
10% Fe_3O_4/WTC	188.687	1.6656	4.9347
15% Fe_3O_4/WTC	182.766	1.3938	5.0385

Fig. 3 shows the photocatalytic performance of all catalysts. As can be seen, WTC also show an amount of PCT degradation. This is attributed to the presence of ZnS in the sample, which also act as photocatalyst [18]. The efficiency of the degradation could be influenced by the metal dispersion on the support surface, the structure of the catalyst, or a synergetic effect between the metal and

support. The 5% Fe_3O_4/WTC shows highest degradation percentage (76%) compared to 10% Fe_3O_4/WTC and 15% Fe_3O_4/WTC, suggesting a good dispersion of Fe_3O_4 on the WTC surface which resulted from higher surface area and pore volume. In contrast, Fe_3O_4 might be agglomerated on the surface of 10% Fe_3O_4/WTC and 15% Fe_3O_4/WTC which then reduced the surface area available for PCT attraction and light penetration for an efficient photocatalytic degradation.

Table 2 shows the kinetics parameter for different concentrations of PCT degradation. Based on this table, it shows that the rate of reaction increases up to maximum of 0.08 *mg/L.min* as the initial concentration increase. This is due to the increase in the amount of PCT molecules in the solution that decreases the relative distance between the pollutant and the catalyst. However, the rate of reaction decreases to 0.053 *mg/L.min* for initial concentration of 20 mg/L. This could be due to the too high turbidity of the solution that hinders the light from penetrating the solution for photocatalytic reaction [19].

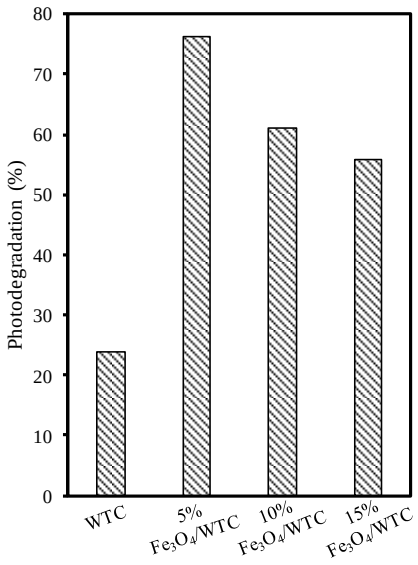

Fig. 3 Photocatalytic performance of WTC and Fe_3O_4/WTC catalysts for degradation of PCT [PCT = 5 mg/L, pH=5, W= 0.4 g/L, t=2 h, pH=5, T= 30°C].

Table 2 Percentage degradation at different initial concentration of PCT and pseudo-first-order apparent constant values for PCT degradation using 5% Fe_3O_4/WTC [W= 0.4 g/L, t=2 h, pH=5, T= 30°C].

Initial PCT concentration, C_o (mg/L)	Degradation, (%)	Reaction rate, k_{app} ($x10^{-2}$ min^{-1})	Initial reaction rate, r_o *(mg/L.min)*
5	76	3.56	0.024
10	55	2.14	0.069
15	40	1.43	0.080
20	20	0.56	0.053

4. CONCLUSION

In this study, Fe_3O_4/WTC catalyst were prepared *via* electrochemical method. The physicochemical properties of the synthesized catalyst were studied by XRD, FTIR and N_2 adsorption-desorption. The XRD reveals the presence of amorphous carbon, Fe_3O4, and ZnS in the synthesized catalyst. Furthermore, the FTIR spectroscopy analysis shows the presence of Fe-O stretch which increases as the loading percentage increases. The BET analysis results show that the surface area reduces as the amount of Fe_3O_4 loaded increase. The higher surface area of 5% Fe_3O_4/WTC catalyst as well as the good distribution of metal on the carbon surface lead to its highest degradation performance of this catalyst compare to 10% Fe_3O_4/WTC and of 15% Fe_3O_4/WTC catalysts. These findings suggested that WTC as support material was remarkably important for an efficient degradation of PCT. For future prospect, the combination of Fe_3O_4 with other metal oxides will be a great contribution to enhance the photocatalytic activity and stability of the catalyst.

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