Fenton Reaction of 4-Chlorophenol Degradation Using Fe-TiO_2 /Diatomite

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ABSTRACT

The degradation of 4-chlorophenol using Fenton reaction via Fe-TiO_2/Diatomite was studied. The Fe-TiO_2/Diatomite catalysts prepared via sol-gel method were characterized by XRD, BET surface area and FT-IR. The XRD results showed that the synthesized Fe-TiO_2/Diatomite catalysts was crystalline quartz and anatase TiO_2. Furthermore, BET showed that the surface area of Fe-TiO_2/Diatomite catalyst was 20.06 m^2/g the average pore size was 13.53 nm. which indicated that it was a mesoporous material. FT-IR showed peaks between Si-O-Si bond, Ti-O stretching vibration and Fe-O-Ti bond stretching. The Fenton-like reactions were carried out in a batch reactor at pH (1-9), initial concentration of 4-chlorophenol (10 - 30 mg/L) and initial concentration of hydrogen peroxide (10 - 30 mmol/L). From the results obtained, the optimal condition for 4-chlorophenol degradation was found to be pH of 2, initial concentration of 4-chlorophenol 10 mg/L, initial concentration of H_2O_2 30 mmol/L. The 4-chlorophenol degradation at optimal condition was 84.46% for 240 minutes.

Keywords: *4-chlorophenol, Fenton, Diatomite*

1 INTRODUCTION

One of the pollutants from petrochemical industry effluent is chlorophenol and its derivatives. These compounds consist of phenol ring and bonded chlorine atoms and are colorless, poorly acidic, toxic and have low biodegradation and long half-life [1].

Numerous conventional methods were used for the degradation of chlorophenol. These include biodegradation, absorption, electro-coagulation, coagulation-flocculation processes, electrochemical reaction and oxidation. However, these processes are commonly slow and incomplete [2]. Therefore, the utilization of advanced oxidation process (AOPs) to generate hydroxyl radicals ($OH^{\cdot}$) to degrade chlorophenol to CO_2 and H_2O is explored.

Fenton reaction is an extensively used AOP for 4-chlorophenol degradation. Fenton mechanism involves H_2O_2 degradation catalyzed by iron ion to produce reactive species such as $OH^{\cdot}$ and $OOH^{\cdot}$ shown in equations 1 - 2 [3]:

$$Fe^{2+}(aq) + H_2O_2(aq) \longrightarrow Fe^{3+}(aq) + OH^{-}(aq) + OH^{\bullet}(aq) \qquad (1)$$

$$Fe^{3+}(aq) + H_2O_2(aq) \longrightarrow Fe^{2+}(aq) + H^{+}(aq) + OOH^{\bullet}(aq) \qquad (2)$$

Homogeneous catalysts are used for Fenton reactions. However, the difficulty in separating them from water and the possibility of discharging them to the environment impose a significant challenge for their extensive application [4]. To overcome the limitation of homogenous catalysts, heterogenous catalysts such as 7.2%Fe/TiO_2 [5], Nano-Fe_3O_4 [6] and Fe/OMC [7] were studied. At optimal condition, total organic carbon (TOC) removals of 7.2%Fe/TiO_2, Nano-Fe_3O_4 and Fe/OMC were 70%, 60% and 47.4%, respectively. Additionally, diatomite was applied as iron support because of its strong adsorptive capacity, low density, low thermal conductivity, high porosity, inertia and low cost [8], [9], [10]. Furthermore, previous studies showed that iron doped TiO_2 can efficiently degrade organic pollutants. However, the study of materials combining doped TiO_2 and diatomite for degradation of organic pollutants by Fenton reaction is relatively scarce. Hence it is necessary to investigate the potential application of the integration of doped TiO_2 with diatomite.

In this study, the Fenton degradation of 4-CP using immobilized diatomite doped with TiO_2 was investigated. Furthermore, characterization of the synthesized heterogeneous catalysts was performed to study the effects of the integration method on the properties and degradation efficiency of the heterogeneous catalysts.

2 MATERIALS AND METHODS

2.1 Chemicals and materials

Diatomite was obtained from TK diatomite. Diatomite was sieved through 200-mesh sieve. 4-CP, $C_{16}H_{36}O_4Ti$, $Fe(NO_3)_3.9H_2O$, H_2O_2, NaOH and HCl were of analytical grade and were purchased from Merck KGaA, China. CH_3COOH and C_2H_5OH were of analytical grade and were purchased from RCI Labscan Limited, Thailand.

2.2 Preparation of catalyst

The heterogeneous catalyst was prepared by sol-gel method. Liquid A was prepared by homogenizing 10 mL of tetrabutly titanate, the precursor of TiO_2, and 20 mL of pure ethanol. Liquid B was prepared by homogenizing 3 mL of deionized water, 10 mL of pure ethanol, 3 mL of pure acetic acid and 2.788 g (5wt.%) of iron(III)nitrate. The green sol was obtained by adding Liquid B to Liquid A dropwise with constant stirring at room temperature. After that, the 5.0 g of diatomite was added into the mixed solution and was continuously stirred until it becomes homogenous. NaOH was dropped slowly into mixture and the pH was adjusted until a gel was formed. The gel was dried at 60° C for 12 h. The obtained product was calcined at 400 C for 4 h in a muffle furnace, cooled to room temperature and grinded.

2.3 Characterization

The morphology of catalyst was analyzed by X-ray diffraction (XRD) (6100Shimadzu x-ray diffractometer). The structure of catalyst was recorded by Fourier transform infrared (spectrometer (TruDefender^{TM} FTX Handheld). While the surface area, pore size distribution and total pore volume were measured by Brunauer-Emmett-Teller (BET). The iron leaching in solution was detected by Atomic absorption spectrophotometry (AAS) (Shimadzu AA-6200). 4-CP content was analyzed quantitatively by high performance liquid chromatography (HPLC, SP Thermoseparation product, P2000) consisting UV/vis detector at 254 nm and reversed-phase column of Luna hexyl-phenyl. The acetonitrile-ultrapure water mixture (30:70) was used at a flow rate of 1.0 mL/min under mobile phase and under room temperature. Samples of 20 μL were injected into the column by micro syringe.

2.4 Catalyst activity test

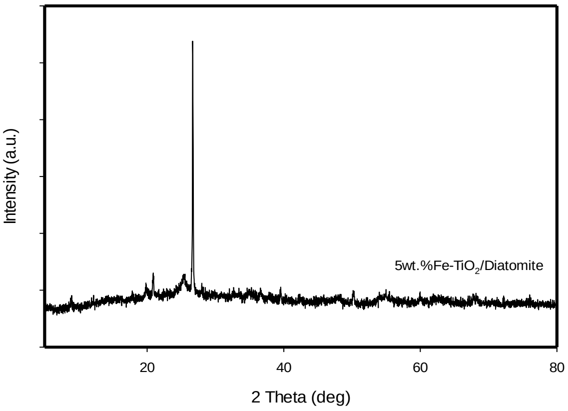
The experimental process was carried out in a batch reactor where 20 mg/L concentration of heterogeneous catalyst was suspended in a 250 mL aqueous solution of 4-CP. The solution was then stirred in the dark for 60 min to establish an adsorption-desorption equilibrium. Samples were taken at different time intervals during the course of the experimental process.

3 RESULTS AND DISCUSSION

3.1 The characterization of catalyst

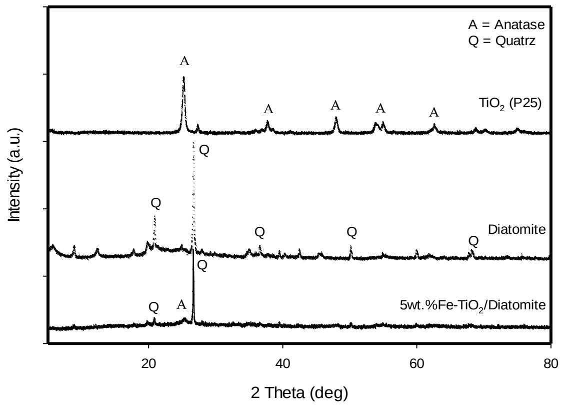
The XRD patterns of 5wt.%Fe-TiO_2/Diatomite samples illustrated in Fig.1a showed diffraction peaks has peaks at 20.9°, 25.3° and 26.6°. Using TiO_2 (P25) and Diatomite [11] XRD patterns (Fig.1b) as reference, Fig 1a indicates that the obtained sample is anatase TiO_2 and quartz SiO_2.

The FT-IR spectrum of 5wt.%Fe-TiO_2/Diatomite shown in Fig.2 illustrates peaks at 1010 cm^{-1} (Si-O-Si bond) and at 670 cm^{-1} (Ti-O stretching vibration) which confirmed the presence of diatomite [12] and TiO_2 structure [13], respectively. Moreover, the peak observed at 1465 cm^{-1} (Fe-O-Ti bond stretching vibration) indicated that iron was successfully immobilized onto TiO_2 [14].



a)

Fig. 1 XRD Patterns of Samples (a) 5wt.%Fe-TiO_2/Diatomite Prepared by Sol-Gel Method, (b) 5wt.%Fe- TiO_2/Diatomite Compared with TiO_2 (P25) and Diatomite (cont.)



b)

***Fig. 1** XRD Patterns of Samples (a) 5wt.%Fe-TiO$_2$/Diatomite Prepared by Sol-Gel Method, (b) 5wt.%Fe-TiO$_2$/Diatomite Compared with TiO$_2$ (P25) and Diatomite*

In addition, BET result indicated that BET surface area, pore volume and pore size of catalyst are 20.06 m^2/g,

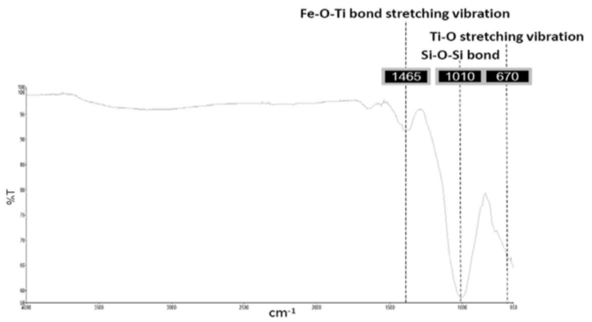


***Fig. 2** FT-IR spectrum of 5wt.%Fe-TiO$_2$/Diatomite in the region between 650 to 4000 cm^{-1}0.068 cm^3/g and 13.53 nm, respectively. The pore size of catalyst also shows that it is a mesoporous material.*

3.2 Effect of pH

The effect of initial pH on the degradation of 4-CP was studied by varying the pH from 1 to 9. Results in Fig. 3a shows that the optimum pH for 4-CP degradation was found at pH 2 with 37.40% 4-CP degradation for 120 min. At pH 2, OH radical production decreased due to the formation of complex species [Fe(H$_2$O)$_6$]$^{2+}$. This then decreased the amount of ferrous ion. In addition, the low efficiency at lower pH could form oxonium ion by proton solvating of H$_2$O$_2$ [4] following Equation (3).

$$H_2O_2(aq) + H^+(aq) \longrightarrow H_3O_2^+(aq) \qquad (3)$$

At pH 3, 6 and 9, ferric ion precipitates as Fe(OH)$_3$ and H$_2$O$_2$ is decomposed into O$_2$ and H$_2$O, causing a decrease in 4-CP degradation following Equations (4,5).[4]

$$2H_2O_2(l) \longrightarrow H_2O(l) + O_2(g) \qquad (4)$$

$$Fe^{3+}(aq) + 3OH^-(aq) \longrightarrow \mathrm{Fe(OH)_3(s)} \qquad (5)$$

Moreover, ferrous hydroxide that can be formed at pH values over 5 following Equation (6) together with ferric hydroxide consume the ferrous ion and ferric ion and inhibit the Fenton reaction, by reducing the transmission of radiation into the water through an increase in the turbidity of solution. [15]

$$Fe^{2+}(aq) + 2OH^-(aq) \longrightarrow \mathrm{Fe(OH)_2(s)} \qquad (6)$$

3.3 Effect of 4-chlorophenol concentration

The effect of 4-CP concentration on Fenton reaction using 5wt.%Fe-TiO$_2$/Diatomite is illustrated in Fig.3b. The highest degradation percentage was 42.41% at 10 mg/L of 4-CP concentration and 120 min. Lower degradation at higher 4-CP concentrations may be due to chloride ions formed from Fenton reaction that can react with hydroxyl radicals and generate anion radicals that are less reactive compared to hydroxyl radicals. The reactions follow —Eqs.(7), (8). Furthermore, the interaction of chloride with ferrous or ferric ions may produce complex chemical substances following Eqs.(9), (10) [15].

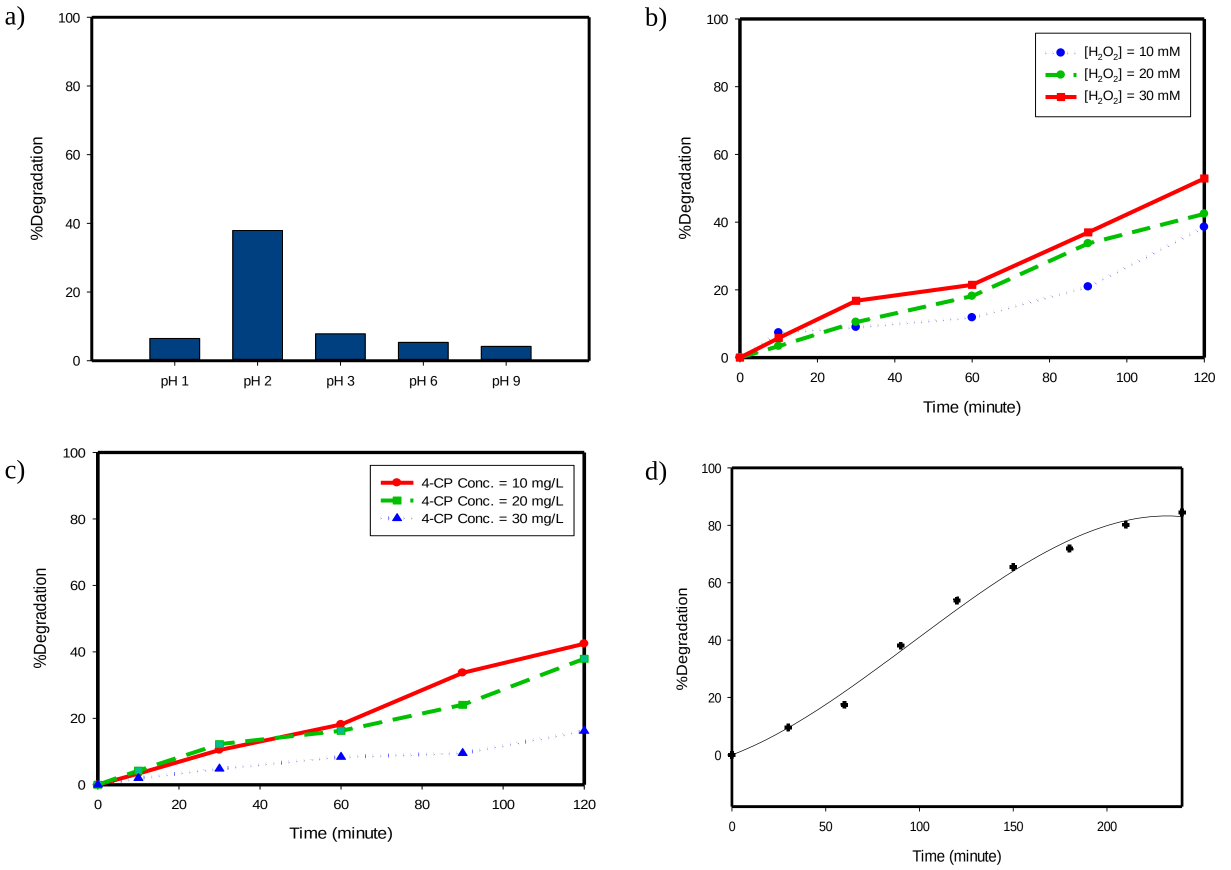


Fig. 3 *Degradation of 4-chlorophenol using 5wt.%Fe-TiO$_2$/Diatomite at 1 g/L of catalyst loading (a) effect of pH : [4-CP] = 20 mg/L, [H$_2$O$_2$] = 20 mmol/L and 120 min, (b) effect of 4-CP concentration : pH = 2 and [H$_2$O$_2$] = 20 mol/L, (c) effect of H$_2$O$_2$ content : pH = 2 and [4-CP] = 10 mg/L, (d) optimal condition : pH = 2, [4-CP] = 10 mg/L and [H$_2$O$_2$] = 30 mmol/L.*

$$Cl^{-}(aq) + OH^{\bullet}(aq) \longleftrightarrow ClOH^{\bullet -}(aq) \longleftrightarrow Cl^{\bullet}(aq) + OH^{-}(aq) \tag{7}$$

$$ClOH^{\bullet -}(aq) + H^{+}(aq) \longleftrightarrow ClOH^{\bullet}{}_{2}(aq) \longleftrightarrow Cl^{\bullet}(aq) + H_2O(aq) \tag{8}$$

$$Fe^{2+}(aq) + Cl^{-}(aq) \longrightarrow FeCl^{+}(aq) \tag{9}$$

$$Fe^{3+}(aq) + Cl^{-}(aq) \longrightarrow FeCl^{2+}(aq) \tag{10}$$

3.4 Effect of H_2O_2 content

The effect of H$_2$O$_2$ concentration was studied by varying it from 10, 20 and 30 mmol/L. Results illustrated in Fig.3c show that 30 mmol/L of H$_2$O$_2$ content the highest degradation (52.91%) for 120 min. High H$_2$O$_2$ concentration favor the hydroxyl radical generation. However, it has to be noted that very high H$_2$O$_2$ concentration may produce perhydroxyl radicals. (Eq.(11)), which have lower oxidation potential than hydroxyl radicals [15], [16].

$$H_2O_2(aq) + OH^{\bullet}(aq) \longrightarrow H_2O(aq) + OOH^{\bullet}(aq) \tag{11}$$

3.5 Optimal condition

The optimum condition for 4-chlorophenol degradation via Fenton using 1 g/L 5wt.%Fe-TiO$_2$/Diatomite catalyst loading was found to be pH 2, 10 mg/L of 4-CP concentration and 20 mmol/L of H$_2$O$_2$ for (Fig.3d). At these conditions, 84.46% degradation of 4-CP was achieved at 240 min. Additionally, low 4-CP degradation at 0 to 60 minutes was observed to be due to hydroxyl generation stage while rapid increase in degradation at 60 to 210 minutes was accounted to the reaction of readily generated hydroxyl radicals at this stage. The reaction was then limited by H_2O_2.

AAS results for iron leaching which is shown in Fig. 4. Although 5wt.%Fe-TiO_2/Diatomite catalyst was already stable at pH 3, small amount of iron leached from $Fe(OH)_2$ or $Fe(OH)_3$. Additionally, higher leaching was observed at pH 2 (11.46%) compared to pH 3 (1.43%) indicating that homogeneous process also took place in the system. Therefore, the combined heterogeneous-homogeneous mechanism can be considered.

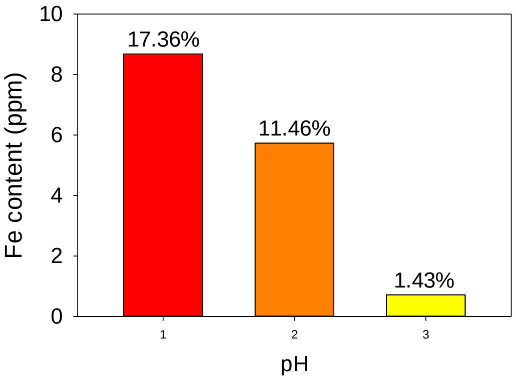


Fig.4 *Leaching of iron by varying pH at [4-CP] = 20 mg/L, [H_2O_2] = 20 mmol/L and 1 g/L of catalyst loading.*

4 CONCLUSIONS

The synthesized 5wt.%Fe-TiO_2/Diatomite catalyst was successfully used for 4-CP degradation. 84.46% 4-CP removal was obtained from the catalyst produced at the optimal condition of pH 2, 10 mg/L of 4-CP concentration, 30 mmol/L of H_2O_2 content and 1 g/L of catalyst loading. XRD patterns revealed that the catalyst has crystalline structure of quartz and anatase phase, and FT-IR spectrum showed Si-O-Si bond, Ti-O stretching vibration and Fe-O-Ti bond stretching vibration. Moreover, surface area (20.06 m^2/g), pore volume (0.068 cm^3/g) determined by BET indicated that the catalyst can be classified as a mesoporous material. Lastly, the combined heterogeneous-homogeneous mechanism was noted through 11.46% iron leaching observed at pH 2.

5. ACKNOWLEDGEMENTS

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