Degradation of Methyl Orange by Photo-Fenton over Fe-Diatomite Catalyst

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A Report Submitted in Partial Fulfillment of the Requirements
for the Degree of Bachelor of Engineering (Petrochemical Engineering)
Department of Chemical Engineering, Faculty of Engineering,
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โดยใช้เหล็กบนไดอะตอมไมต์เป็นตัวเร่งปฏิกิริยา

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Title	Degradation of methyl orange by photo-Fenton over Fe-diatomite catalyst
By	Wonsgsakorn Songmuangkean
Field of Study	Petrochemical Engineering
Advisor	Asst.Prof.Dr. Pornsawan Assawasaengrat

Accepted by the Faculty of Engineering, King Mongkut's Institute of Technology Ladkrabang in Partial Fulfillment of the Requirements for the Degree of Bachelor of Engineering (Petrochemical Engineering).

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Abstract

The degradation of methyl orange by photo-Fenton process using Fe-diatomite as catalyst was studied. Fe-diatomite was prepared by dry-impregnation method. The effects of hydrogen peroxide concentration (100 to 500 mg/l), catalyst dosage (0.4 to 0.6 g/l), and initial pH of dye solution (3 to 10) were investigated in UV reactor. Photo-Fenton tests were carried out using initial methyl orange concentration of 75 mg/l at room temperature. The results showed that the degradation of methyl orange by using hydrogen peroxide at 100, 300 and 500 mg/l were 96%, 98%, and 99% respectively at 30 minutes. The different catalyst dosage of 0.4 0.5 and 0.6 g/l given similar result of 96% methyl orange degradation but using different equilibrium time of 60, 30, and 20 minutes respectively. The effect of initial pH of dye solution carried out at 10, 7, 4, and 3 approximated 96% of methyl orange degradation using decreasing equilibrium time of 50, 40, 30, and 10 minutes respectively. The optimal condition for 95% of methyl orange degradation at 10 minutes with 75 mg/l initial concentration of methyl orange were 100 mg/l of hydrogen peroxide concentration and 0.5 g/l of catalyst dosage at pH 3. The reduction of total organic carbon (TOC) was 47%. After the reaction, the amount of iron leached into the solution was 5.28 mg or 33% approximately.

Keywords: photo-Fenton; methyl orange; Fe-diatomite

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เรื่อง การสลายสีย้อมเมทิลออเรนจ์ด้วยกระบวนการโฟโตเฟนตันโดยใช้ตัวเร่งปฏิกิริยาเหล็กไดอะตอมไมต์
โดย วงศกร สองเมืองแก่น
อาจารย์ที่ปรึกษา ผศ.ดร. พรสวรรค์ อัศวแสงรัตน์
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บทคัดย่อ

งานวิจัยนี้ศึกษาการสลายสีย้อมเมทิลออเรนจ์ด้วยกระบวนการโฟโตเฟนตันโดยใช้ตัวเร่งปฏิกิริยาเหล็กไดอะตอมไมต์ (Fe-diatomite) โดยเตรียมตัวเร่งปฏิกิริยาเหล็กไดอะตอมไมต์ด้วยวิธีการจุ่มชุบแบบแห้ง (dry-impregnation) ศึกษาปัจจัยที่มีผลต่อการสลายสีย้อมเมทิลออเรนจ์ ได้แก่ ความเข้มข้นของไฮโดนเจนเปอร์ออกไซด์ (H_2O_2) 100 300 และ 500 มิลลิกรัมต่อลิตร ปริมาณตัวเร่งปฏิกิริยา 0.4 0.5 และ 0.6 กรัมต่อลิตร และ pH เริ่มต้นของสารละลายสีย้อมในช่วง 3-10 ทำการทดลองภายในตู้แสงยูวี (UV reactor) ณ อุณหภูมิห้อง ที่ความเข้มข้นเริ่มต้นของสารละลายเมทิลออเรนจ์ 75 มิลลิกรัมต่อลิตร จากผลการทดลองพบว่าความเข้มข้นของไฮโดรเจนเปอร์ออกไซด์ 100 300 และ 500 มิลลิกรัมต่อลิตรที่เวลา 30 นาทีมีประสิทธิภาพในการสลายสีย้อมใกล้เคียงกันคือ 96% 98% และ 99% ตามลำดับ ผลของปริมาณตัวเร่งปฏิกิริยาเมื่อเพิ่มปริมาณตัวเร่งปฏิกิริยาจาก 0.4 0.5 และ 0.6 กรัมต่อลิตรเมื่อพิจารณาที่ประสิทธิภาพการสลายสีย้อมที่ใกล้เคียงกันคือ 96% ใช้เวลาในการทำปฏิกิริยาลดลงจาก 60 เป็น 30 และ 20 นาทีตามลำดับ ผลของ pH เริ่มต้นของสารละลายสีย้อมพบว่าเมื่อลด pH เริ่มต้นของสารละลายสีย้อมจาก 10 เป็น 7 4 และ 3 ตามลำดับ พบว่าเวลาในการทำปฏิกิริยาลดลงเท่ากับ 50 40 30 และ 10 นาทีตามลำดับ โดยมีประสิทธิภาพการสลายสีย้อมที่ใกล้เคียงกันคือ 96% ในงานวิจัยนี้ได้ภาวะที่เหมาะสมในการสลายสีย้อมเมทิลออเรนจ์ที่ความเข้มข้นเริ่มต้น 75 มิลลิกรัมต่อลิตร คือความเข้มข้นของไฮโดรเจนเปอร์ออกไซด์ 100 มิลลิกรัมต่อลิตร ปริมาณตัวเร่งปฏิกิริยา 0.5 กรัมต่อลิตร pH เริ่มต้นของสารละลายสีย้อม 3 ให้ประสิทธิภาพในการสลายสีย้อม 95% ที่เวลา 10 นาที สามารถลดค่าคาร์บอนอินทรีย์รวม (TOC) ได้ 47% หลังปฏิกิริยาวัดปริมาณเหล็กที่หลุดออกมาจากตัวเร่งปฏิกิริยาเหล็กไดอะตอมไมต์ในสารละลาย พบว่ามีปริมาณเหล็ก 5.28 มิลลิกรัม หรือคิดเป็น 33% ของเหล็กในไดอะตอมไมต์ที่ใช้ในปฏิกิริยา

คำสำคัญ: โฟโตเฟนตัน, เมทิลออเรนจ์, ไดอะตอมไมต์

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CHAPTER I

INTRODUCTION

1.1 Background

Synthetic dyes are widely used in textile industry, and over 10% of dyes from dyeing process are released into wastewater during the process. The effluents discharged from these industries are usually strongly colored, and the direct release of the wastewater into environment will cause damage to both aquatic life and human beings due to their toxic, carcinogenic and mutagenic effects. A variety of physical, chemical, and biological methods are presently available for treatment of wastewater discharged from various industries. Biological treatment is a proven technology with cost-effective, but it suffers from many of disadvantages. Physical methods such as liquid-liquid extraction, ion-exchange, adsorption, etc. are ineffective on pollutants, which are not readily absorbable or volatile, and have further disadvantage that they simply transfer the pollutant to another phase rather than eliminate them. In contrast, chemical oxidation methods can result in almost complete mineralization of organic pollutants and are effective for a wider range of organics.

Advanced oxidation processes (AOPs) have been considered as promising technologies to decontaminate wastewater effectively and environmentally friendly. Photo-Fenton is one of the AOPs, has attracted wide interests in wastewater. An important process in photo-Fenton processes to generate hydroxyl radical is using the $Fe^{2+}/H_2O_2/UV$ system, called homogeneous photo-Fenton process. However, it should be pointed out that homogeneous photo-Fenton process has low pH condition limits. In comparison, heterogeneous photo-Fenton process has shown good performance in a wide range of pH, and catalysts can be easily separated from solution. Catalysts can decompose hydrogen peroxide to hydrogen radical like homogeneous photo-Fenton process, and prevent precipitating of iron hydroxide. The key factors in heterogeneous photo-Fenton process are the suitable catalyst and reaction conditions.

Following the green chemistry principles, several recent studies have proposed the use of natural materials as catalysts. Diatomite is extremely cheap, ecofriendly materials, and highly available worldwide. They have porous structure, low density, and high surface area and iron content.

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According to the literature, there exists a complex network of interaction between the species involved in the photo-Fenton process, which depends on the concentration of hydrogen peroxide, catalyst and initial pH of solution. All of these parameters define the efficiency of the process. Therefore, this project studied the optimum condition of photo-Fenton by using Fe-diatomite catalyst.

1.2 Objective

To study the degradation efficiency of methyl orange by heterogeneous photo-Fenton process over Fe-diatomite catalyst.

1. 3 Scopes of work

1.3.1 Prepare Fe-diatomite for heterogeneous photo-Fenton process.

1.3.2 Characterize catalysts by following methods:

1.3.2.1 Composition of diatomite and Fe-diatomite were determined by X-ray fluorescence (XRF)

1.3.2.2 Structure and crystallinity of catalyst were determined by X-ray diffraction (XRD).

1.3.3 Study the activity of catalyst for degradation of methyl orange by following parameters:

1.3.3.1 The concentration of hydrogen peroxide in the range of 100 to 500 mg/l.

1.3.3.2 The amount of catalyst dosage in the range of 0.4 to 0.6 g/l.

1.3.3.3 The initial pH of methyl orange solution in the range of 3 to 10.

1.3.3.4 Amount of iron in solution was determined by Atomic Absorption Spectrophotometer (AAS).

1.3.3.5 Total organic carbon (TOC) was determined by TOC analyzer.

1.4 Expected outputs

1.4.1 Understand the Fenton reaction and heterogeneous photo-Fenton process.

1.4.2 Reduce the wastewater pollution from synthetic dyes.

1.4.3 Apply as a guide of the treatment of wastewater from industrial.

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CHAPTER II

LITERATURE REVIEW

2.1 Fenton reaction

Fenton reaction is one of advanced oxidation processes (AOPs), it has been considered as promising technology to decontaminate wastewater effectively and environmentally friendly. Among all AOPs, Fenton reaction can produce free radicals that degrade pollutants with strong non-selective oxidizing ability, but the condition limits its application. Catalyst can decompose hydrogen peroxide (H_2O_2) to hydroxyl radical (•OH) like in Fenton reaction, and prevent precipitating of iron hydroxide. Fenton reaction is used for wastewater treatment from industrial such as textile, plastic, pulp and paper, food, cosmetic, and pharmaceutical industries [1].

2.1.1 Mechanisms of Fenton reaction

The Fenton reaction was shown in equation (2.1). The oxidation reaction between hydrogen peroxide (H_2O_2) and ferrous ion (Fe^{2+}) were reacted to create hydroxyl radical (•OH).

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + \bullet OH \qquad (2.1)$$

Next reaction, hydroxyl radical and ferrous ion were reacted to form ferric ion (Fe^{3+}) as shown in equation (2.2).

$$\bullet OH + Fe^{2+} \longrightarrow Fe^{3+} + OH^- \qquad (2.2)$$

At the same time, organic compound was oxidized by hydroxyl radical as in equation (2.3).

$$\bullet OH + \text{Organic Compound} \longrightarrow \text{Oxidized Product} \qquad (2.3)$$

Equations (2.4) and (2.5) were the reaction to produced oxygen and perhydroxyl radical. Normally, the concentration of ferrous ion is not changed, while the concentration of hydrogen peroxide is decreased.

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + H^+ + HOO\bullet \qquad (2.4)$$

$$Fe^{3+} + HOO\bullet \longrightarrow Fe^{2+} + H^+ + O_2 \qquad (2.5)$$

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2.2 Photo-Fenton process

The UV radiation was used in photo-Fenton process, it was found that the irradiation of Fenton reaction systems with UV light accelerated the rate of degradation of a variety of pollutants, as shown in equation (2.6).

$$H_2O_2 + UV \longrightarrow 2{\bullet}OH \qquad (2.6)$$

The factor affecting on the photo-Fenton oxidation are as the following:

2.2.1 Concentration of iron

Fenton reagent defined as a mixture of hydrogen peroxide and ferrous ion is currently accepted as one of the most effective for the oxidation pollutants. In the absence of iron, there is no evidence of hydroxyl radical formation. For example, hydrogen peroxide is added to a phenolic wastewater without iron, but no reduction occurred in the system. As the concentration of iron is increased, phenol removal accelerates until a certain point that an addition of iron becomes inefficient. This feature is characteristic of Fenton reagent, although the appropriate of the range varies depends on type of wastewater.

2.2.2 Concentration of hydrogen peroxide

Because of the indiscriminate nature by which hydroxyl radicals oxidize organic materials, it is important to profile the reaction in the reaction in the laboratory for each waste to be treated. The concentration of hydrogen peroxide is affected to amount of hydroxyl radical and efficiency of treatment system. If the concentration of hydrogen peroxide was enough, the oxygen and water were produced.

2.2.3 Temperature

The rate of reaction with Fenton's reagent increase with increasing temperature, with the effect more pronounced at temperature less than 20 ^{o}C. However, as temperature increase above 40 to 50 ^{o}C, the efficiency of hydrogen peroxide decreases. This is due to the accelerated decomposition of hydrogen peroxide into oxygen and water. Most commercial applications of Fenton reaction occur at temperature between 20 and 40 ^{o}C.

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2.2.4 pH

The optimal pH occurs between 3 and 6. The drop in efficiency on the basic reaction is attributed to the transition of iron from a hydrated ferrous ion to a colloidal ferric species. Therefore, hydrogen peroxide was decomposed to oxygen and water.

2.3 Diatomite

Diatomite, also known as diatomaceous earth, is the naturally occurring fossilized remains of diatoms. Diatoms are single celled aquatic algae. Diatomite is a near pure sedimentary deposit consisting almost entirely of silica. It has particle size ranging from less than 3 micrometers to more than 1 millimeter. Depending on the granularity, this powder can have an abrasive feel, similar to powder, and has a low density as a result of its high porosity [2].

Diatomite has a wide variety of uses, such as a filtration aid, mechanical insecticide, absorbent for liquids, porous support for chemical catalyst, a stabilizing component of dynamite and a thermal insulator.

2.3.1 Compositions

Each deposit of diatomite is different, with varying blends of pure diatomite combined with other natural clays and minerals. The diatom is containing different amounts of silica. The species of diatom is depend on the age and environment of the deposit.

2.3.2 Applications

Diatomite is available commercially in several forms. First, granulated diatomaceous earth is a raw material simply crushed for convenient packaging. Second, milled or micronized diatomaceous earth is especially fine and used for insecticides. Finally, calcined diatomaceous earth is heat-treated and activated for filters.

2.3.2.1 Filter aids

The naturally occurring fossilized remains of diatoms have innate filtering characteristics due to their unique honeycomb structure. Their filtering qualities are used in beer and wine manufacturing, pharmaceutical manufacturing, motor oil processing and to filter swimming pool water.

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2.3.2.2 Functional additive

In paints, diatomite alters glass and sheen, extends primary pigments, adds bulk and strength, controls permeability and enhances coating. In plastic, diatomite serves as an antiblocking agent which helps in the separation of plastic parts in manufacturing, and in the separation of plastic bags by the consumer.

2.3.2.3 Absorbents

Due to such characteristics as porosity and high surface area, diatomite is highly absorbent and is very useful in the clean-up of spills in the automotive, industrial, janitorial and waste remediation industries.

2.3.2.4 Soil amendments

When diatomite is incorporated into soil, it serves to reduce compaction, and increase water and air permeation. It also increases plant available water, firms soggy soils, loosens hard to work soils, provides better drainage, aids in nutrient transfer, and improves root growth. In such applications as golf courses, and other landscaped areas it helps absorb and hold water, reducing the amount of water used.

2.3.2.5 Natural insecticide

When insects come in contact with diatomaceous earth, it absorbs their protective wax coating and their shells are damaged by the glassy diatoms. This combination causes them to die by dehydration. There is no survival and no built-up immunity as there is with chemical insecticides. Also, it does not break down as chemicals do.

2.4 Dyes

The dyes are colored organic or inorganic compounds that are used to coat color to various substrates, including paper, leather, fur, hair, drugs, cosmetics, waxes, greases, plastic and textile materials. Dyes are normally water soluble or water dispersible organic compound that are capable of being absorbed into the substrate destroying the crystal structure of the substance. Dye molecules are usually chemically bonded to the surface and become a part of the material on which it is applied. The color intensity of the dye molecule depends on how strong it absorbs radiation in the visible region, which extends from 400 to 700 nm [3].

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2.4.1 Classification of dyes according to application

2.4.1.1 Acid dyes

Acid dyes are water soluble anionic dyes, containing one or more sulfuric acid substituents or other acidic group. Acid dyes are largest class of dyes utilized in textile processing and finishing industries.

2.4.1.2 Cationic (Basic dyes)

Cationic dyes are water soluble dyes applied to paper, polyacrylonitrile (e.g. Dralon), modified nylons, and modified polyesters, binding to acidic groups, yielding colored cations in solution.

2.4.1.3 Disperse dyes

Disperse dyes are substantially water insoluble nonionic dyes for application to synthetic hydrophobic fibers from aqueous dispersions. Disperse dyes are applied as very finely divided materials which are adsorbed onto the fibers with which they then from a solid solution. These dyes are primarily used for polyester and acetate fibers.

2.4.1.4 Direct dyes

Direct dyes are water soluble anionic dyes, but are not classified as acid dyes because the acid groups are not the means of attachment to the fiber. They are used for the direct dyeing of cotton and regenerated cellulose, paper and leather. They are also used to dye union goods and to a lesser extent nylon fiber.

2.4.1.5 Reactive dyes

Reactive dyes have simpler, adsorption spectra show narrower absorption bands, and the dyeing are brighter and hence are preferred over direct dyes. They form a covalent bond with the fiber through OH^-, NH^-, or SH^- groups in the fibers. The reactive group is often a heterocyclic aromatic ring substituted with chloride or fluoride or vinyl sulphone.

2.4.1.6 Metal complex dyes

Metal complex dyes are strong complexes of one metal atom and or two dye molecules. The phthalocyanine metal complex dyes are commonly used in the textile dyeing industry.

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2.4.1.7 Solvent dyes

Solvent dyes are non-ionic water insoluble dyes solvent solution and are generally non-polar or slightly polar. They are not often used for textile processing but their application is widely applied in plastics, varnish, ink and waxes.

2.4.1.8 Sulfur dyes

Sulfur dyes are applied to cotton from an alkaline reducing bath with sodium sulfide as the reducing agent. Sulfur dyes are water insoluble but they are soluble in their reduced form and exhibit affinity for cellulose. The actual structure of sulfur dyes is largely unknown although it is considered that they processes sulfur-containing heterocyclic rings. Their low cost and good wash fastness properties make this class important from an economic point of view, constituting 15% of the global dye production. They are mainly used for dyeing cellulose fibers.

2.4.1.9 Vat dyes

Vat dyes are insoluble complex polycyclic molecules based in the quinone structure. They belong to a class of chemical dyes containing anthraquinone and indigoids moieties on the solubility in the reduced form. Alternate reduction and oxidation process was used for dyeing these dyes to fiber. Vat dyes are applied for dyeing cellulose fibers as well as rayon and wool.

2.5 Methyl orange: MO

Methyl orange have molecular formula of $C_{14}H_{14}N_3NaO_3S$, as shown in fig. 2.1, and molecular weight of 327.33 g/mol, it is an intensely colored compound used in dyeing and printing textile. Chemists use methyl orange as a pH indicator of weak bases with strong acids. It changes from red (at pH 3.1) to orange-yellow (at pH 4.4) Methyl orange is synthesized by reaction of sulfanilic acid, sodium nitrite and dimethylaniline [4]. The basic properties of methyl orange as shown in table 2.1 [5].

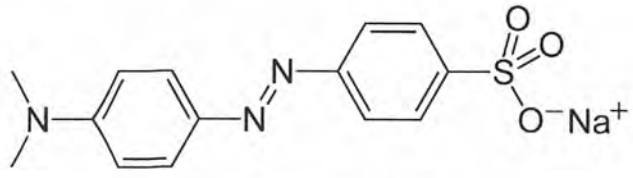

Fig. 2.1 Structure of methyl orange

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Table 2.1 Property of methyl orange

Properties	
Chemical formula	$C_{14}H_{14}N_3NaO_3S$
Molar mass (g/mol)	327.33
Density (g/cm^3, solid)	1.28
Solubility (g/100 mL) in water at 20 °C	0.5
Melting point (°C)	more than 300

2.6 Literature review

Fenton demonstrated that mixture of hydrogen peroxide and ferrous ion in acidic medium had very powerful oxidizing properties. Nowadays, the Fenton reaction is used to treat a large variety of water pollution such as phenols, formaldehyde, BTEX, pesticides, and rubber chemicals. This research will discuss on Fenton process in wastewater treatment from dyeing.

The research of degradation of dyes by Fenton process is study on the effect of different parameters such as amount of catalyst, hydrogen peroxide concentration, initial pH of the dye solution and, initial dye concentration. And find the optimum condition for maximum efficiency degradation of dyes.

Yucan Liu et al., studied a heterogeneous Fenton catalyst $NiFe(C_2O_4)_x$. The methyl orange removal efficiency was 98% in heterogeneous Fenton system using $NiFe(C_2O_4)_x$. The $NiFe(C_2O_4)_x$ had a synergistic effect of catalyst of 24.7 for methyl orange removal, and the dope of Ni significantly reduced the leaching of Fe by 77%. The reaction was investigated. Under the optimum conditions, 0.4 g/l of catalyst dose and 10 mmol/l of hydrogen peroxide concentration, 98% of methyl orange was removed within 20 minutes. The suitable pH range for heterogeneous Fenton system was wide from 3 to 10 [6].

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Zhihui Xu et al,. studied the photodegradation efficiency of ammonium and hydronium jarosite in a photo-Fenton process using methyl orange as target pollutant. The degradation of methyl orange over ammonium and hydronium jarosite under various conditions, such as catalysts loading, hydrogen peroxide concentration, and initial pH, has been investigated. The reactivity of jarosite toward the mineralization methyl orange was higher for hydronium jarosite, less ammonium jarosite. Synthetic parameters need to be optimized for higher photodegradation efficiency of jarosite minerals [7].

Nadia A. Youssef et al,. studied oxidation by Fenton process for destruction of variety of hazardous pollutants in wastewater. The effects of different parameters such as dosages of hydrogen peroxide and ferrous ion, initial concentration of dye and pH of solution were studied. The results indicated that the dye can be most effectively oxidized in aqueous solution at dye: ferrous ion: hydrogen peroxide molar ratio 1:3.5:4.2. It was found that more than 97% removal of the dye could be achieved in 15 min in the pH 2.79 [8].

Guang-Tao Wei et al,. studied photo-Fenton degradation of methyl orange by HPW-Fe-Bent as heterogeneous catalyst. The impacts of various operating on degradation were analyzed. The photo-Fenton degradation of methyl orange by HPW-Fe-Bent was impacted by hydrogen peroxide concentration, catalyst dosage, and initial pH. HPW-Fe-Bent had a wide applicable range of pH for wastewater treatment [9].

N. Inchaurrondo et al., studied about Fenton oxidation of the anionic azo-dye Orange II. The experiments were performed by varying the diatomite calcination, reaction temperature, catalyst load, hydrogen peroxide concentration, initial pH, and initial dye concentration. The best results were obtained with samples calcined at 700 ^{o}C, with initial pH 3, at 70 ^{o}C and using the stoichiometric amount of hydrogen peroxide, since complete degradation, TOC reduction close to 67%. The stability of the catalyst maintain after 10 hr. of usage, with a final Fe loss of 2.25% [10].

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Table 2.2 Optimum conditions for degradation of dyes by heterogeneous and homogeneous process.

Target dye	Catalyst	Dye conversion (%)	pH	Operating conditions	Ref.
Methyl orange (MO)	$NiFe(C_2O_4)_x$	98	3-10	MO 20 mg/l, H_2O_2 10 mmol/l, 0.4 g/l catalyst, 25 °C, 20 min.	[6]
Methyl orange (MO)	Ammonium jarosite	100	4.5	MO 90 mg/l, H_2O_2 600 mg/l, 200 mg/l catalyst, 25 °C, 60 min.	[7]
Methyl orange (MO)	Hydronium jarosite	100	4.5	MO 80 mg/l, H_2O_2 600 mg/l, 200 mg/l catalyst, 25 °C, 40 min.	[7]
Methyl orange (MO)	Ferrous sulfate	97	2.79	MO $5.4x10^{-5}$ mol/l, H_2O_2 $2.93x10^{-3}$ mol/l, $1.9x10^{-4}$ mg/l catalyst, 25 °C, 15 min.	[8]
Methyl orange (MO)	$H_3PW_{12}O_{40}$ supported Fe-bentonite	78	5	MO 10 mg/l, H_2O_2 0.5 mol/l, 0.75 g/l catalyst, 30 °C, 1 hr.	[9]
Orange II	Diatomite	100	3	OII 100 mg/l, H_2O_2 13.7 mmol/l, 100 mg/l catalyst, 70 °C, 1 hr.	[10]

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CHAPTER III

EXPERIMENTAL

3.1 Equipment

1. Visible Spectrophotometer
2. UV reactor
3. Magnetic stirrer
4. pH meter
5. Centrifuge

3.2 Chemicals

1. Methyl orange
2. Hydrogen peroxide (H_2O_2)
3. Ferric sulfate (Fe_2SO_4)
4. Diatomite
5. Sodium hydroxide (NaOH)
6. Hydrogen chloride (HCl)
7. Deionized water

3.3 Experiment

3.3.1 Prepare the Fe-diatomite

1.1 Weigh the diatomite and ferric sulfate at weight ratio of 1:0.199.

1.2 Dissolve the ferric sulfate in deionized water, and mix this solution with diatomite.

1.3 Finally, dry the solution at 100 °C for 24 hours.

3.3.2 Characterization of diatomite and Fe-diatomite by X-ray fluorescence (XRF)

The composition of diatomite and Fe-diatomite were performed by a X-ray fluorescence spectrometer (XRF) at research center of science, Faculty of Science at King Mongkut's Institute of Technology Ladkrabang.

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3.3.3 Characterization of diatomite by X-ray diffraction (XRD)

The crystallinity and X-ray diffraction (XRD) patterns of diatomite were performed by a X-ray diffractometer SHIMADZU XRD-6100. The operating conditions of measurement are shown below:

X-ray Tube	: Cu (1.54060 A)
Voltage	: 40.0 kV
Current	: 30.0 mA
Scan Range	: 50.00 – 80.00 degree
Step Size	: 0.02 degree
Count Time	: 0.6 sec

3.3.4 Plot calibration curve

3.1 Prepare the methyl orange solution at the concentration of 1, 4, 7, 11 and 15 mg/L.

3.2 Measure the absorbance of each concentration by using Visible Spectrophotometer at 464 nm which is the maximum absorbance wavelength of the methyl orange solution, and record the results.

3.3 Plot graph of relationship between the concentration of methyl orange solution and the absorbance.

3.3.5 Study on the effect of hydrogen peroxide concentration

4.1 Prepare 600 ml of methyl orange solution at concentration of 75 mg/L in 1,000 ml beaker, and take the beaker in UV reactor with turn of UV lamp.

4.2 Take sample of methyl orange solution before reaction for measure the absorbance.

4.3 Load 0.5 g/l of Fe-diatomite and 100 mg/l of hydrogen peroxide concentration in methyl orange solution. Turn on the UV lamp, and start the timer.

4.4 Take sample every 10 minutes and separate the Fe-diatomite by centrifuge for 5 minute. Measure the absorbance with wavelength at 464 nm and record the results. Do this step until the absorbance is equal to a constant.

4.5 Repeat step 4.1 – 4.4 and change the hydrogen peroxide concentration in step 4.3 to 300, and 500 mg/L.

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3.3.6 Study on the effect of catalyst dosage

5.1 Prepare 600 ml of methyl orange solution at concentration of 75 mg/L in 1,000 ml beaker, and take the beaker in UV reactor with turn of UV lamp.

5.2 Take sample of methyl orange solution before reaction for measure the absorbance.

5.3 Load 0.4 g/l of Fe-diatomite and 100 mg/l of hydrogen peroxide concentration in methyl orange solution. Turn on the UV lamp, and start the timer.

5.4 Take sample every 10 minutes and separate the Fe-diatomite by centrifuge for 5 minute. Measure the absorbance with wavelength at 464 nm and record the results. Do this step until the absorbance is equal to a constant.

5.5 Repeat step 5.1 – 5.4 and change the catalyst dosage in step 5.3 to 0.5 and 0.6 g/L.

3.3.7 Study on the effect of initial of methyl orange pH

6.1 Prepare 600 ml of methyl orange solution at concentration of 75 mg/L in 1,000 ml beaker, and take the beaker in UV reactor with turn of UV lamp.

6.2 Adjust initial pH solution of methyl orange to 4 by hydrogen chloride and measure by pH meter.

6.3 Take sample of methyl orange solution before reaction for measure the absorbance.

6.4 Load 0.5 g/l of Fe-diatomite and 100 mg/l of hydrogen peroxide concentration in methyl orange solution. Turn on the UV lamp, and start the timer.

6.5 Take sample every 10 minutes and separate the Fe-diatomite by centrifuge for 5 minute. Measure the absorbance with wavelength at 464 nm and record the results. Do this step until the absorbance is equal to a constant.

6.6 Repeat step 6.1 – 6.5 and change the initial pH solution of methyl orange to 4, 7 and 10.

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3.3.8 Calculate the degradation efficiency

$$\text{Degradation efficiency (\%)} = \left(1 - \frac{[MO]_t}{[MO]_0}\right) x100\%$$

When $[MO]_t$ is concentration of methyl orange at reaction time t. (mg/l)

$[MO]_0$ is concentration of methyl orange at reaction time 0. (mg/)

3.3.9 Analyze the amount of iron in solution by Atomic Absorption Spectrophotometer (AAS)

8.1 Measure the amount of iron in solution before and after reaction.

8.2 Find the percent leaching of iron in solution with the below equation:

$$\text{Leaching of iron (\%)} = \left(1 - \frac{Fe_{solution}}{Fe_{catalyst}}\right) x100\%$$

when $Fe_{solution}$ is amount of iron in solution after reaction. (mg)

$Fe_{catalyst}$ is amount of iron in catalyst loading. (mg)

3.3.10 Analyze the value of total organic carbon (TOC)

9.1 Measure the amount of iron in solution before and after reaction by a TOC analyzer.

9.2 Find percent reduce of TOC in solution with below equation:

$$\text{Reduction of TOC (\%)} = \left(1 - \frac{TOC_t}{TOC_0}\right) x100\%$$

when TOC_0 is value of initial TOC in solution. (mg/l)

TOC_t is value of TOC at time t. (mg/l)

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CHAPTER IV

RESULTS AND DISCUSSION

4.1 Catalyst characterization

4.1.1 X-ray fluorescence (XRF)

The XRF analysis as shown in Table 4.1, the silica represents the major constituent of diatomite and Fe-diatomite. From the result, the percent weight of iron in diatomite was increased, when the diatomite was modified by ferric sulfate.

Table 4.1 Composition by XRF (wt/wt%) of diatomite and Fe-diatomite.

Sample	Mg	Al	Si	K	Ca	Ti	Fe
Diatomite	0.49	8.52	35.7	1.52	0.23	0.20	2.96
Fe-diatomite	0.38	6.76	31.3	1.32	0.16	0.18	5.23

4.1.2 X-ray diffraction (XRD)

Fig. 4.1 shows the XRD of diatomite, it can be observed that there was no peak. Therefore, the diatomite was amorphous.

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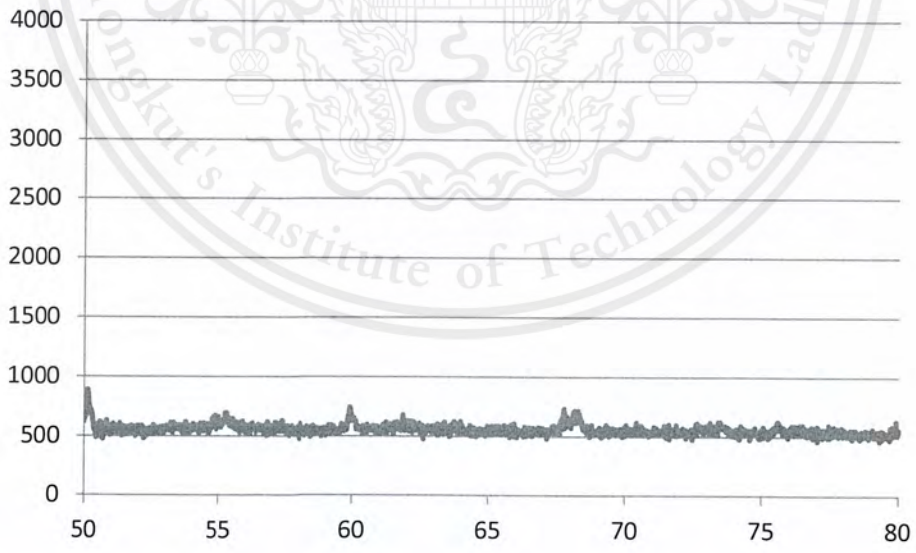

Fig. 4.1 XRD spectra of diatomite.

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4.2 Methyl orange removal process

4.2.1 Effect of hydrogen peroxide concentration

Since the concentration of hydrogen peroxide was directly related to the amount of hydroxyl radicals produced in the Fenton reaction, this parameter influences degradation efficiency. In this case, three concentration of hydrogen peroxide, i.e., 100, 300, and 500 mg/l, were selected to study on the methyl orange degradation.

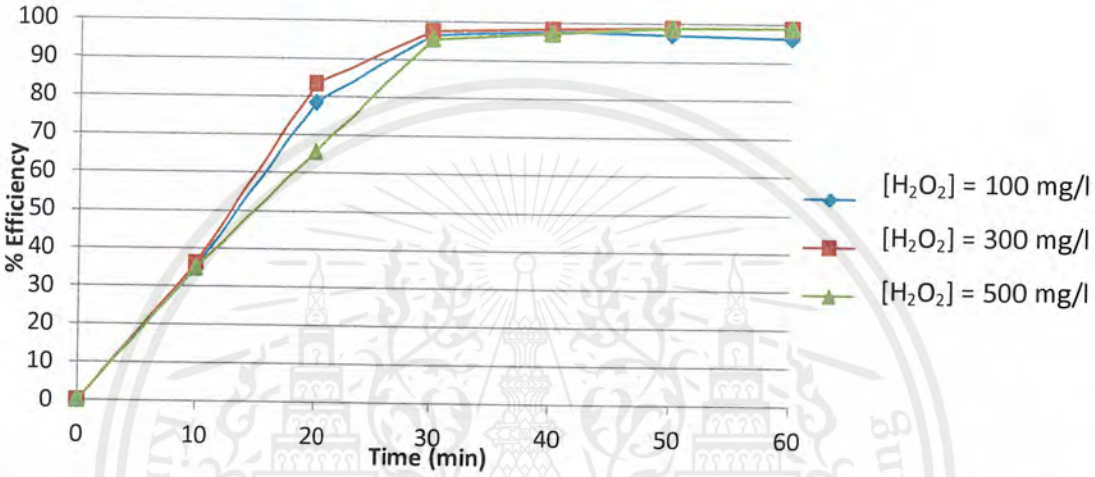

Fig. 4.2 Effect of hydrogen peroxide concentration on the degradation of methyl orange by photo-Fenton. The experimental conditions were: [MO] = 75 mg/l; Catalyst = 0.5 g/l; initial pH solution.

From the Fig. 4.2, it can be observed that increase of hydrogen peroxide concentration from 100 to 500 mg/l enhanced the degradation of methyl orange from 96% to 99% within 30 minutes of reaction. However, with a further increase of hydrogen peroxide concentration at 500 mg/l, the degradation of methyl orange was not improved but slightly decrease at 10 to 20 minutes. The decrease of the degradation efficiency of methyl orange at high concentration of hydrogen peroxide was mainly caused by the scavenging effect of excessive hydrogen peroxide to hydroxyl radical, as shown in Equation (3.1). In addition, the recombination of hydroxyl radical also contributed for the declining of the degradation efficiency of methyl orange, as shown in Equation (3.2) [7]. From the experimental results, therefore, the optimum concentration of hydrogen peroxide at 100 mg/l was selected.

$$^{\bullet}OH + H_2O_2 \rightarrow H_2O + OH_2^{\bullet} \quad (3.1)$$

$$^{\bullet}OH + OH_2^{\bullet} \rightarrow H_2O + O_2 \quad (3.2)$$

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4.2.2 Effect of catalyst dosage

Fe-diatomite was used as catalyst in the degradation of methyl orange. In this case, three concentration of Fe-diatomite, 0.4, 0.5 and 0.6 g/l, were selected to study the effect of catalyst loading on the methyl orange degradation. The catalyst has a positive influence by catalyzing hydrogen peroxide decomposition on the surface of catalyst as Equations (3.3) and (3.4), where ≡ represents the iron species bound to the catalyst surface [6].

$$\equiv Fe^{2+} + H_2O_2 \rightarrow \equiv Fe^{3+} + OH^- + {}^{\bullet}OH \quad (3.3)$$

$$\equiv Fe^{3+} + H_2O_2 \rightarrow \equiv Fe^{2+} + H^+ + {}^{\bullet}HO_2 \quad (3.4)$$

As shown in Fig. 4.3, when catalyst dosage was increased from 0.4 to 0.6 g/l, the required time to complete degradation of methyl orange were shorten using 60, 30, and 20 minutes, respectively, and the degradation efficiency of methyl orange were 95%, 96%, and 96%, respectively. The phenomenon could be explained that more active sites and active components enhanced more radicals generated in the solution. Thus, 0.5 g/l of catalyst dosage was considered to be a suitable dosage for the degradation of methyl orange.

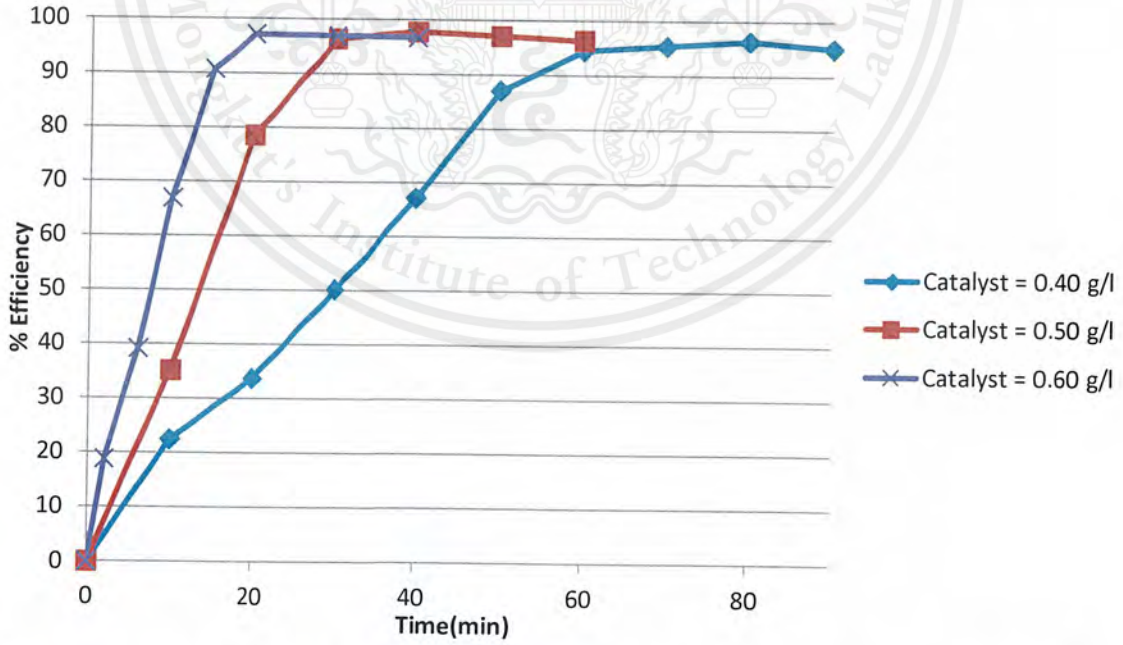

Fig. 4.3 Effect of catalyst dosage on the degradation of methyl orange by photo-Fenton. The experimental conditions were: [MO] = 75 mg/l, [H_2O_2] = 100 mg/l, initial pH solution.

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4.2.3 Effect of initial pH of methyl orange solution

In general, pH of 2 – 4 was considered as appropriate rang for Fenton's reaction, but wider pH range was desirable in this study. The effects of initial pH were investigated in the range from 3 to 10. As shown in Fig. 4.4, 96% removal efficiency of methyl orange was achieved with wide initial pH range and time required to complete degradation of methyl orange increased from 10 to 60 minutes, respectively. This phenomenon could be explained that the formations of ferrous/ferric hydroxide complexes were depended on pH of solution, which ferrous ion was main substance in Fenton reaction, as shown in equation (3.3). When amount of ferrous ion was increased, the amount of hydroxyl radical was increased. Thus, the degradation of dye was higher [8]. From the result assume that at low pH solution can generate ferrous iron better than high pH solution. Compared with the conventional Fenton use pH at 3.5, this Fe-diatomite in photo-Fenton process had a wide applicable of pH.

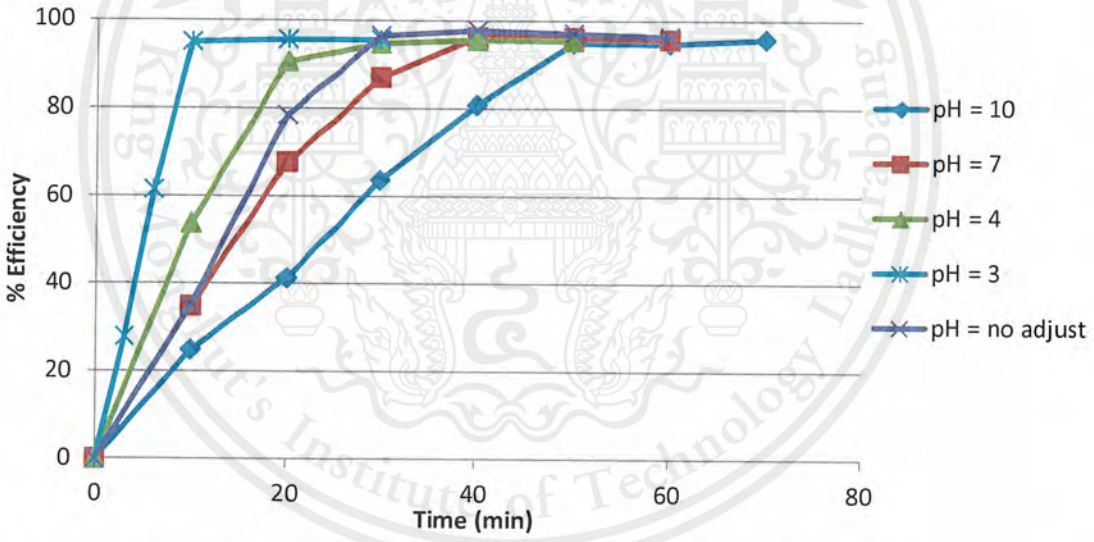

Fig. 4.4 Effect of initial pH of methyl orange solution on the degradation of methyl orange by photo-Fenton. The experimental conditions were: [MO] = 75 mg/l; [H_2O_2] = 100 mg/l; Catalyst = 0.5 g/l.

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4.3 The optimum condition for heterogeneous photo-Fenton process

The optimum condition for methyl orange degradation was 100 mg/l of hydrogen peroxide concentration, 0.5 g/l of catalyst dosage, and initial pH 3, the degradation efficiency was 96% at 10 minutes. After the reaction, the concentration of iron (Fe) in solution and total organic carbon (TOC) were determined at the optimal condition. The result showed the amount of iron was 5.28 mg that leached from the reaction which approximate about 33%. Thus, this process cannot conclude that heterogeneous process. The TOC before the experiment conducted was 35.38 mg/l and decrease to 16.76 mg/l after 30 minutes. Therefore, the reduction of TOC concentration was 47%

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CHAPTER V

CONCLUSION

5.1 Conclusion

In this work, the degradation of methyl orange in aqueous solution by heterogeneous photo-Fenton process over Fe-diatomite was studied on different experimental condition. Fe-diatomite was prepared by a dry- impregnation method with diatomite and ferric sulfate ($Fe_2(SO_4)_3$)). The characterization of diatomite was indicated the presence of an amorphous.

The degradation of methyl orange by photo-Fenton process over Fe-diatomite as heterogeneous catalyst was impacted by hydrogen peroxide concentration, catalyst dosage, and initial pH solution of methyl orange. The optimum operating condition was selected as 75 mg/l of initial concentration of methyl orange, 100 mg/l of hydrogen peroxide concentration, 0.5 g/l of catalyst dosage, and pH 3 at room temperature. In the given condition, more than 95% of degradation efficiency was achieved within 10 minutes of reaction. The amount of iron was 5.28 mg/l that leached from the reaction which approximate about 33%. The TOC before the experiment conducted was 35.38 mg/l and decrease to 16.76 mg/l after 30 minutes. Therefore, the reduction of TOC concentration was 47%. In conclusion, the Fe-diatomite catalyst has a high potential application potential in wastewater treatment.

5.2 Recommendation

1. Study on the other parameters affect to degradation efficiency of methyl orange such as temperature, pressure, and initial dye concentration.
2. Use photo-Fenton process over Fe-diatomite in other dyes solution.

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APPENDIX

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APPENDIX A

RESULTS OF PREPARE Fe-DIATOMITE

1. Prepare Fe-diatomite as a catalyst in process.

1.1 Characterize diatomite by using X-ray fluorescence (XRF)

Table A.1 Composition by XRF (wt/wt%) of diatomite and Fe-diatomite.

Sample	Mg	Al	Si	K	Ca	Ti	Fe
Diatomite	0.49	8.52	35.7	1.52	0.23	0.20	2.96
Fe-diatomite	0.38	6.76	31.3	1.32	0.16	0.18	5.23

1.2 Characterize diatomite by using X-ray diffractometer (XRD)

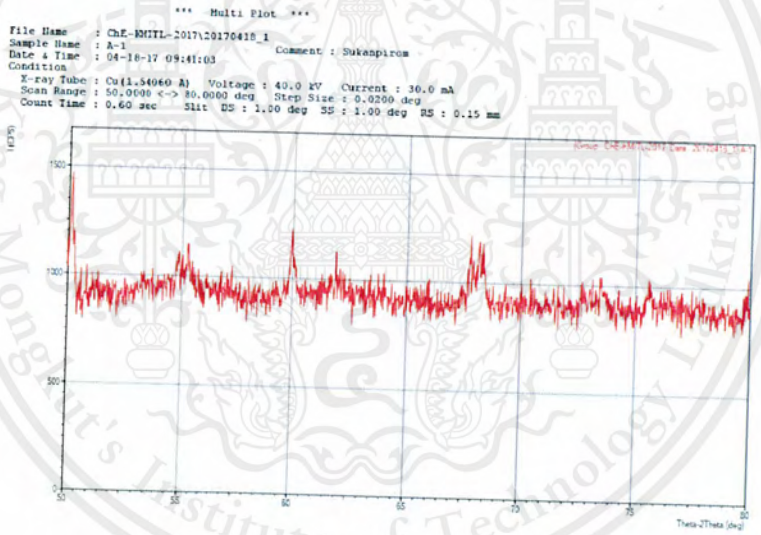

Fig. A.1 XRD spectra of diatomite.

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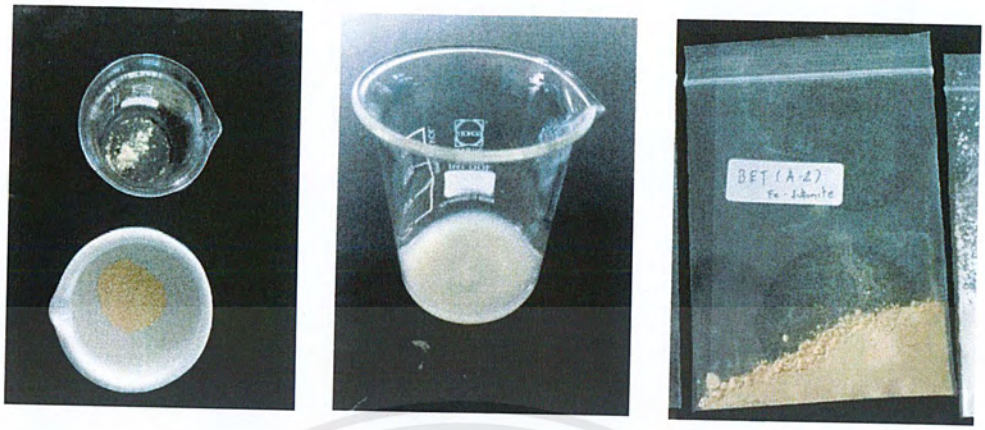
1.3 Prepare Fe – diatomite by dry-impregnation method



(a) (b) (c)

Fig A.2 Prepare Fe-diatomite by dry-impregnation method. (a) ferrous sulfate and diatomite(b) ferrous sulfate solution (c) Fe-diatomite

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APPENDIX B

RESULTS OF ACTIVITY OF CATALYST FOR DEGRADATION OF METHYL ORANGE AT DIFFERNCE PARAMETERS

2. Methyl orange removal process

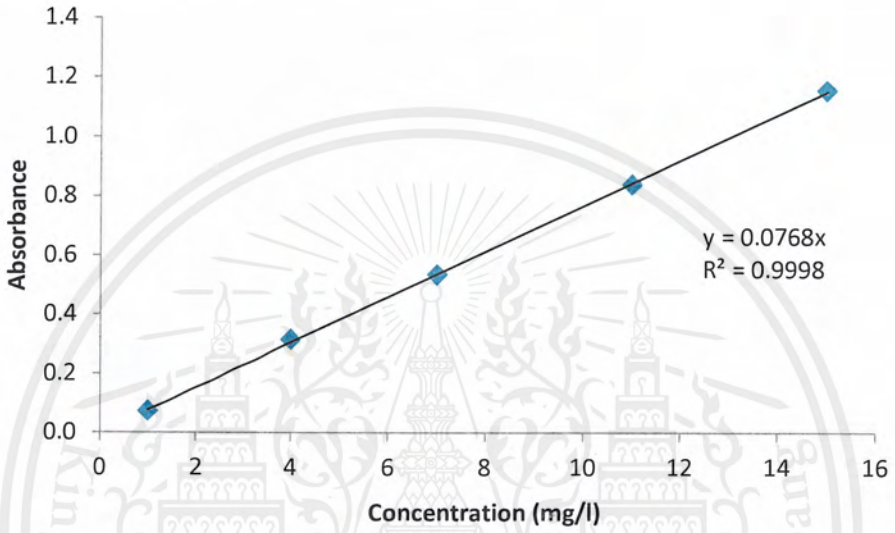

Fig. B.1 Calibration curve of methyl orange concentration.

Calculation of methyl orange concentration

Absorbance = 0.07686 X (concentration of methyl orange (mg/l))

Calculation of methyl orange degradation efficiency

$$\text{Degradation efficiency (\%)} = \left(1 - \frac{[MO]_t}{[MO]_0}\right) x100\%$$

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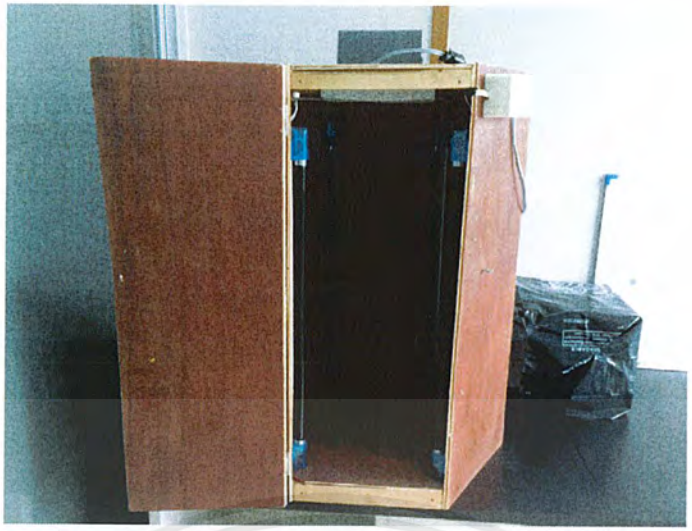

Fig. B.2 UV reactor for photo-Fenton process.

2.1 Test for methyl orange degradation of catalyst

Table B.1 Results of hydrogen peroxide to efficiency degradation of methyl orange with 75 mg/l initial concentration, 0.5 g/l of catalyst dosage and initial pH.

	No hydrogen peroxide				$[H_2O_2]$ = 100 mg/l		
Time (min)	Absorbance	[MO]	%eff.	Time (min)	Absorbance	[MO]	%eff.
0	0.936*	75.15	0.00	0	0.936*	75.15	0.00
15	0.796*	66.51	11.50	5	2.344	31.34	58.30
30	0.512*	42.75	43.11	10	2.299	30.73	59.11
45	0.428*	35.79	52.38	20	1.693	22.64	69.88
60	0.393*	32.81	56.34	30	0.381	5.09	93.23
75	0.412*	34.45	54.15	45	0.200	2.67	96.45
				60	0.131	1.75	97.67
				75	0.106	1.42	98.11

*Dilute 4 times of solution.

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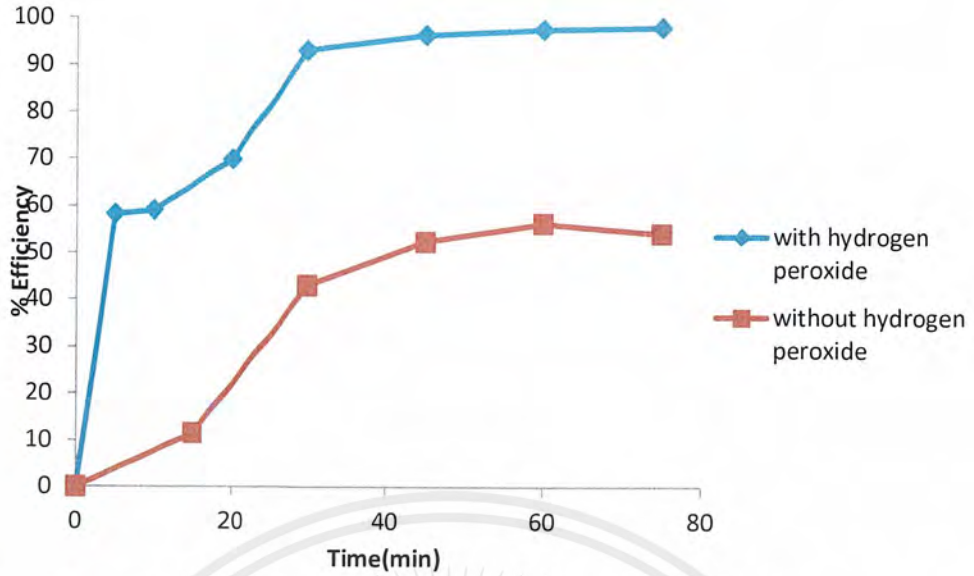

Fig. B.3 Relationship between time and efficiency degradation of dye in photo-Fenton process with hydrogen peroxide and without hydrogen peroxide.

2.2 Hydrogen peroxide concentration

Table B.2 Results of hydrogen peroxide concentration on the degradation of methyl orange by photo-Fenton. The experimental conditions were: [MO] = 75 mg/l; Catalyst = 0.5 g/l; initial pH solution.

	[H2O2] = 100 mg/l			[H2O2] = 300 mg/l			[H2O2] = 500 mg/l		
Time (min)	Abs.	[MO]	%eff.	Abs.	[MO]	%eff.	Abs.	[MO]	%eff.
0	1.111*	73.67	0.00	1.131*	75.00	0.00	1.214*	79.04	0.00
10	0.721*	47.79	35.13	0.722*	47.86	36.19	0.790*	51.43	34.93
20	0.239*	15.85	78.49	0.187*	12.40	83.47	0.417*	27.17	65.62
30	0.199	2.63	96.42	0.146	1.94	97.41	0.283	3.68	95.34
40	0.123	1.64	97.78	0.096	1.28	98.30	0.173	2.25	97.15
50	0.162	2.15	97.08	0.072	0.95	98.73	0.070	0.91	98.85
60	0.203	2.69	96.35	0.058	0.77	98.97	0.060	0.78	99.02

*Dilute 4 times of solution.

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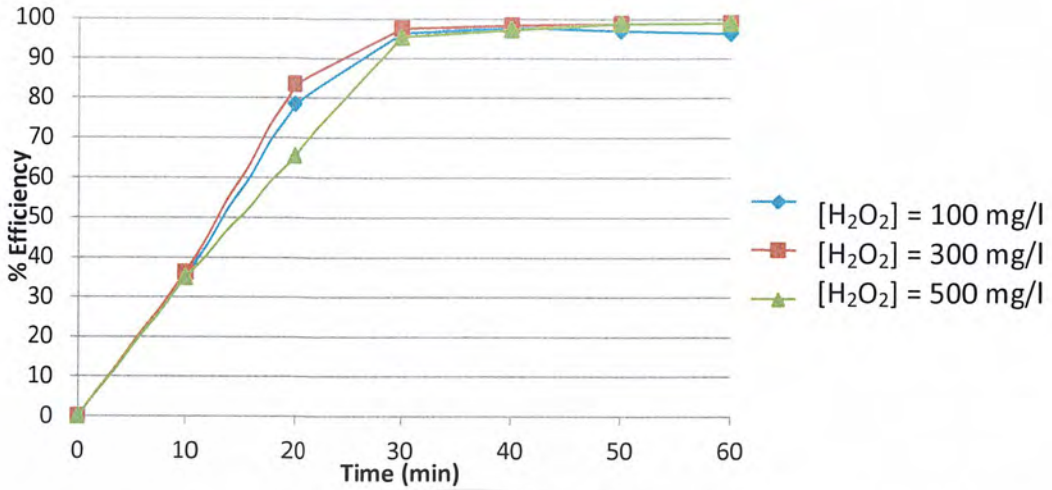

Fig B.4 Effect of hydrogen peroxide concentration on the degradation of methyl orange by photo-Fenton. The experimental conditions were: [MO] = 75 mg/l; Catalyst = 0.5 g/l; initial pH solution.

2.3 Catalyst dosage

Table B.3 Results of catalyst dosage on the degradation of methyl orange by photo-Fenton. The experimental conditions were: [MO] = 75 mg/l, [H_2O_2] = 100 mg/l, initial pH solution.

	Catalyst = 0.40 g/l			Catalyst = 0.50 g/l			Catalyst = 0.60 g/l		
Time (min)	Abs.	[MO]	%eff.	Abs.	[MO]	%eff.	Abs.	[MO]	%eff.
0	1.171*	76.24	0.00	1.111*	73.67	0.00	1.123*	73.13	0.00
2							0.912*	59.35	18.84
6							0.684*	44.51	39.14
10	0.908*	59.09	22.49	0.721*	47.79	35.13	0.371*	24.18	66.94
20	0.776*	50.52	33.73	0.239*	15.85	78.49	0.159	2.07	97.18
30	0.584*	38.00	50.16	0.199	2.63	96.42	0.169	2.20	96.99
40	0.384*	25.02	67.18	0.123	1.64	97.78	0.181	2.36	96.77
50	0.152*	9.87	87.05	0.162	2.15	97.08			
60	0.320	4.16	94.54	0.203	2.69	96.35			
70	0.267	3.47	95.45						
80	0.213	2.77	96.37						
90	0.285	3.71	95.13						

*Dilute 4 times of solution.

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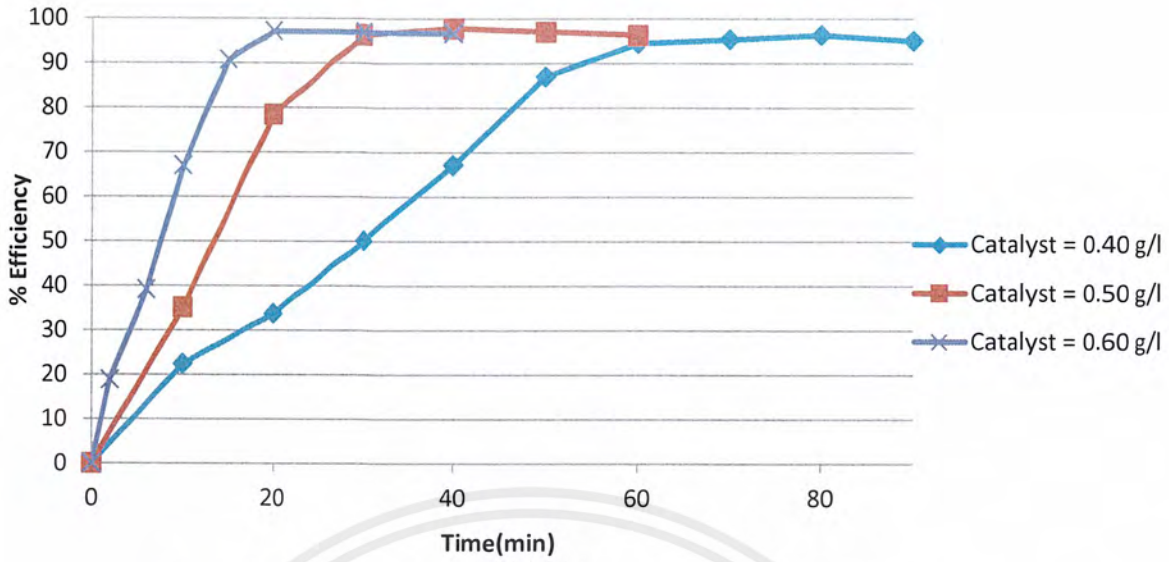

Fig. B.5 Effect of catalyst dosage on the degradation of methyl orange by photo-Fenton. The experimental conditions were: [MO] = 75 mg/l, [H_2O_2] = 100 mg/l, initial pH solution.

2.4 Initial pH of methyl orange solution

Table B.4 Results of initial pH of methyl orange solution on the degradation of methyl orange by photo-Fenton. The experimental conditions were:[MO] = 75 mg/l; [H_2O_2] = 100 mg/l; Catalyst = 0.5 g/l.

	pH = 3			pH = 4			pH = 7		
Time (min)	Abs	[MO]	%eff.	Abs	[MO]	%eff.	Abs	[MO]	%eff.
0	1.146*	74.63	0.00	1.146*	74.59	0.00	1.146*	74.59	0.00
3	0.828*	53.88	27.80						
6	0.442*	28.80	61.41						
10	0.057	8.79	94.98	0.530*	34.51	53.74	0.746*	48.59	34.86
20	0.253	2.88	95.55	0.109*	7.12	90.46	0.370*	24.11	67.68
30	0.254	3.23	95.54	0.304	3.96	94.69	0.151*	9.81	86.85
40				0.257	3.34	95.52	0.222	2.89	96.12
50				0.272	3.54	95.26	0.225	2.93	96.07
60							0.248	3.22	95.68

*Dilute 4 times of solution.

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Table B.4 (Continue) Results of initial pH of methyl orange solution on the degradation of methyl orange by photo-Fenton. The experimental conditions were: [MO] = 75 mg/l; [H_2O_2] = 100 mg/l; Catalyst = 0.5 g/l.

	pH = 10			No adjust		
Time (min)	Abs	[MO]	%eff.	Abs	[MO]	%eff.
0	1.123*	73.09	0.00	1.111*	73.67	0.00
10	0.844*	54.95	24.82	0.721*	47.79	35.13
20	0.659*	42.90	41.30	0.239*	15.85	78.49
30	0.408*	26.54	63.69	0.199	2.63	96.42
40	0.216*	14.04	80.79	0.123	1.64	97.78
50	0.287	3.73	94.89	0.162	2.15	97.08
60	0.298	3.88	94.69	0.203	2.69	96.35
70	0.240	3.13	95.72			

*Dilute 4 times of solution.

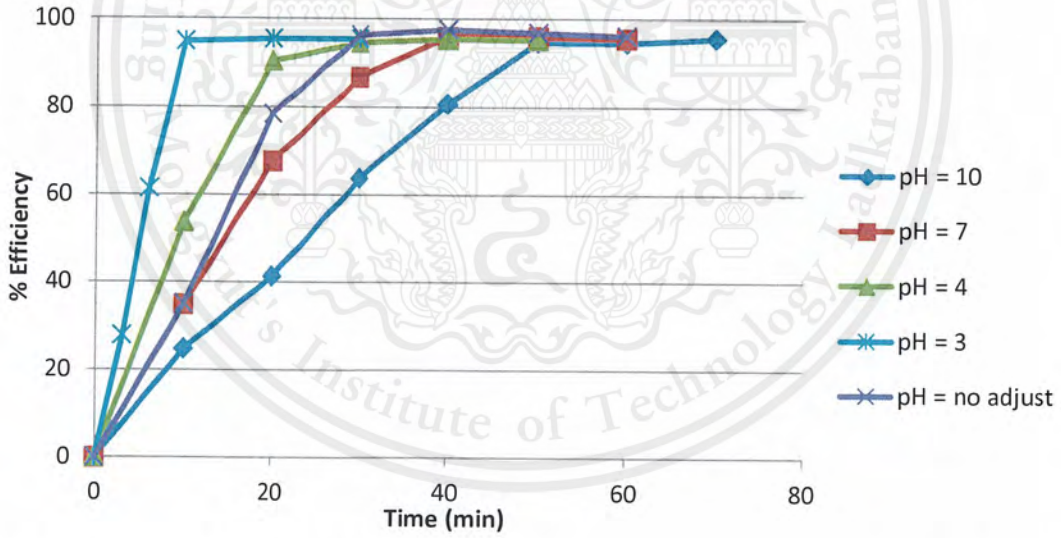

Fig. B.6 Effect of initial pH of methyl orange solution on the degradation of methyl orange by photo-Fenton. The experimental conditions were: [MO] = 75 mg/l; [H_2O_2] = 100 mg/l; Catalyst = 0.5 g/l.

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2.5 Amount of iron in solution

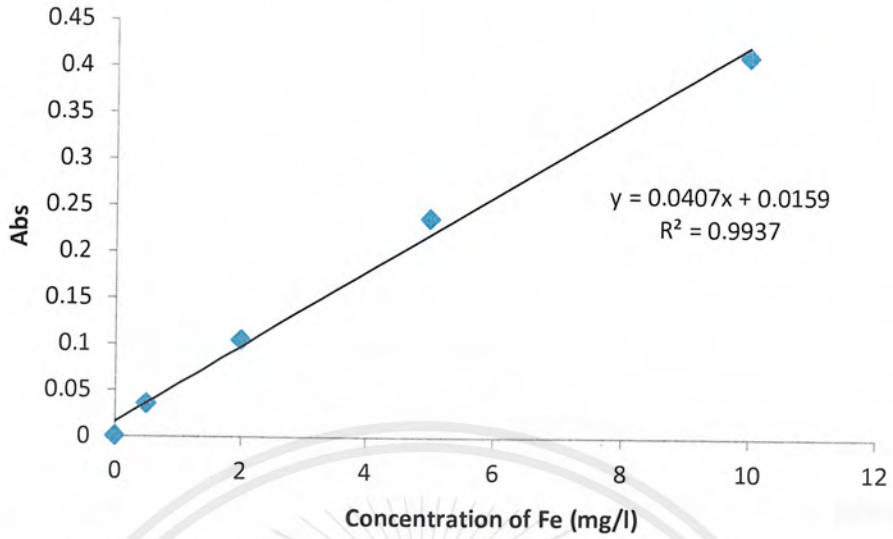

Fig. B.7 Calibration curve of Fe concentration.

Table B.5 Amount of iron in solution by Atomic Absorption Spectrophotometer (AAS).

Sample	Repeat	Abs	Concentration of Fe (mg/l)
MO, t = 0 min	1	-0.016	-0.7838
	2	-0.028	-1.0786
MO, t = 30 min.	1	0.374	8.7985
	2	0.387	9.1179

Calculation of amount of iron

Absorbance = [0.0407 X (concentration of Fe (mg/l))] + 0.0159

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2.6 Total organic carbon (TOC)

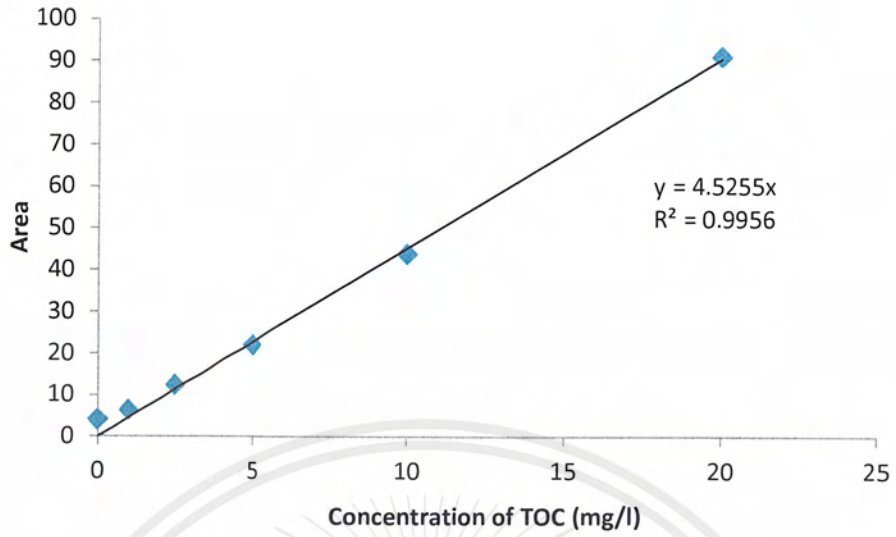

Fig. B.8 Calibration curve of TOC.

Table B.6 Total organic carbon (TOC) by TOC analyzer.

Sample	Concentration of TOC (mg/l)
MO, t = 0 min	35.38
MO, t = 30 min.	16.76

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