โครงการ

การเรียนการสอนเพื่อเสริมประสบการณ์

Title	Synthesis of MIL-88A for decolorization and COD removal in sugar industrial wastewater
Student name	Miss Chulaphorn Buakaew
Student ID	6033311323
Department	Environmental science
Academic year	2020

Academic Year 2020

Department of Environmental Science

Faculty of Science, Chulalongkorn University

Synthesis of MIL-88A for decolorization and COD removal in sugar industrial wastewater

การสังเคราะห์ MIL-88A เพื่อกำจัดสีและซีโอดีในน้ำเสียโรงงานน้ำตาล

Chulaphorn Buakaew

A Senior Project Submitted in Partial Fulfillment of the Requirement for the Degree of Bachelor of Science Program in Environmental Science, Faculty of Science, Chulalongkorn university, Academic Year 2020

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Name	Miss Chulaphorn Buakaew **ID** 6033311323
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Accepted by Department of Environmental Science, Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Degree of Bachelor of Science

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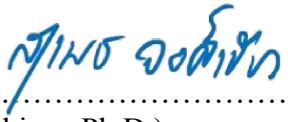

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หัวข้อ การสังเคราะห์ MIL-88A เพื่อกำจัดสีและซีโอดีในน้ำเสียโรงงานน้ำตาล

โดย นางสาวจุฬาภรณ์ บัวแก้ว **รหัสนิสิต** 6033311323

อาจารย์ที่ปรึกษา ผู้ช่วยศาสตราจารย์ ดร.วรพจน์ กนกกันฑพงษ์

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ปีการศึกษา 2563

บทคัดย่อ

งานวิจัยนี้มีวัตถุประสงค์เพื่อสังเคราะห์ MIL-88A ในการกำจัดสีและซีโอดีจากน้ำเสียโรงงานน้ำตาล ด้วยกระบวนการการดูดซับ โดยการสังเคราะห์ตัวดูดซับ (MIL-88A) ด้วยการผสมกรดฟูมาริก และ $FeCl_3 \cdot 6H_2O$ ศึกษาลักษณะโครงสร้างและสัณฐานวิทยาของ MIL-88A ด้วย กล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราดที่มีสมรรถนะสูง ชนิดฟิลด์อีมิสชัน(FESEM) และ เครื่องเอกซเรย์ดิฟแฟรกโตมิเตอร์ (XRD) จากนั้นนำ MIL-88A ที่สังเคราะห์ได้มาศึกษาประสิทธิภาพในการดูดซับน้ำเสียของโรงงานน้ำตาลในจังหวัดเพชรบูรณ์ ผลการศึกษาพบว่า ลักษณะโครงสร้างและสัณฐานวิทยาของ MIL-88A จากเครื่อง FESEM มีลักษณะเป็นแท่งหกเหลี่ยม ความยาว 100 นาโนเมตร และผลจาก XRD แสดงจุดที่มีความชัดเจนที่สุดที่ 10.8° และ 12.0° ซึ่งผลที่ได้นี้ตรงตามรูปแบบมาตรฐานของ MIL-88A และ MIL-88A นี้ สามารถกำจัดสีและซีโอดีได้สูงสุดที่ร้อยละ 74.9 และร้อยละ 85.0 ตามลำดับ โดยใช้เวลาในการเข้าสู่สมดุลที่ 30 และ 60 นาที ตามลำดับ ในส่วนจลนศาสตร์การดูดซับสีและซีโอดีนั้น สอดคล้องกับสมการอัตราเร็วปฏิกิริยาอันดับสองเทียม โดยมีค่าสัมประสิทธิ์สหสัมพันธ์ของการกำจัดสีเท่ากับ 0.9976 และการกำจัดซีโอดีเท่ากับ 0.9270 อย่างไรก็ตาม เมื่อพิจารณามาตรฐานน้ำทิ้งจากโรงงานอุตสาหกรรมพบว่า ยังไม่สามารถลดค่าสีและซีโอดีให้อยู่ในเกณฑ์มาตรฐานได้

คำสำคัญ: ตัวดูดซับ, การบำบัดน้ำเสีย, การดูดซับ, การกำจัดซีโอดี

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ABTRACT

This research aimed to synthesize MIL-88A for color and COD removal in sugar factory wastewater by adsorption process. The sorbent (MIL-88A) was produced by mixing of fumaric acid and $FeCl_3 \cdot 6H_2O$. The structure and morphology of MIL-88A were studied with Field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD). The as-prepared MIL-88A was then study for the treatment efficiency of sugar industry wastewater in Phetchabun Province. The results showed that structural and morphological characteristics of MIL-88A performed by FESEM was hexagonal rod-like morphology with uniform size distribution and the length was 100 nm while the peaks from XRD were found at 10.8° and 12°. The as-prepared MIL-88A pattern met with standard MIL-88A pattern. The maximum treatment efficiencies of color and COD by as-prepared MIL-88A were 74.9% and 85.0%, respectively. The equilibrium times of color and COD adsorption were 30 and 60 minutes, respectively. The adsorption kinetics of decolorization and COD were consistent with the pseudo-second order model. The correlation coefficient of color removal was 0.9976 and the COD removal was 0.9270. When considering the effluent standards from industrial plants, it was found that the color and COD values could not be reduced to comply the standard.

Keywords: Adsorbent, Wastewster treatment, Adsorption, COD removal

ACKNOWLEDGMENTS

First, this research would not have been achievable without the guidance and kind support. I take the opportunity to express my sincere thanks to all of them.

I would like to express my special thanks of gratitude to my advisor, Asst. Prof. Dr. Vorapot Kanokkantapong for helped me with consulting, supporting, and constant encouragement throughout this research and providing knowledge about so many new things. He has taught me the method to carry out the research and present the research work as clearly as possible. I am really thankful. I am thankful to the research committee chair; Asst. Prof. Dr. Sarawut Srithongouthai, and my committees; Dr. Sumeth Wongkiew and Dr. Jatuwat Sangsanont for their kindness and valuable suggestions.

I would like to thank the staff of the laboratory of environmental science department, Chulalongkorn University; Mrs. Ketsaraporn Kankaew for their help in offering the resources to do the experiment and suggestions.

Last, I would like to thank Miss Kwanruedee suwannasung, Miss Ratchamol Withuwatthana, my family, my all friends, and whoever to helped me and supported me with this research. Thank you

Chulaphorn Buakaew

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Chapter 1

Introduction

1.1 Background and rationale

The sugar industry is great importance to industrial sectors as it generates revenues from exports into the country. Thailand is the second-largest exporter of sugar in the world. However, this factory generates highly polluted wastewater, especially COD (chemical oxygen demand) and color. COD in the sugar industry wastewater presents approximately 2000-6000 mg/L. It can wreak havoc downstream if not treated as it contains high difficulty to degraded organic. In the past, the standard value of the color in the effluent was set as "not despicably", however, the standard nowadays is set to not more than 300 ADMI (Ministry of Industry, 2017). This means the factories have to pay more awareness to these two parameters and find an approach to manage wastewater.

Wastewater treatment plant is a unit that removes contaminated water produced from industrial production processes. Several treatment techniques include the electrochemical method, advanced oxidation processes (AOPs), biological method, anaerobic digestion, and membranes separation. Anywise, these have some deficiencies, for example, the electrochemical method and AOPs may release by-products which can cause secondary pollution. Metal-organic frameworks (MOFs) are a class of compounds consisting of metal ions or clusters coordinated to organic ligands to form one-, two-, or three-dimensional structures should be one of the interesting and effective methods.

MOFs have attracted considerable interest in many applications because of their high surface areas which highlighted them with superior adsorption capacity resulting in solving industrial wastewater problems (Yuan et al., 2016). These materials have a series of characteristics like chemical and physical properties, unique texture, tunable but uniform cavities, including inherent large surface areas, and functionalized easily using different ligands (Wang et al., 2018). In addition, several MOFs can be produced as adsorbents and catalysts with high stability in an aqueous solution (Wang et al., 2016). MIL-88A is one type of MOFs that can easily prepare in low synthesis temperature, short time, and effectively reduces energy consumption and stability in water, making it usable in humid environments. Besides, this structure provides high porosity and a large specific surface area, which enables pollutants to absorb efficiently.

Due to the interesting properties of MIL-88A as it can be produced in room temperature which reduces energy and cost in preparation step, it is expected to solve the problem of industrial wastewater better than other methods. Hence, the work aims to use synthesized MIL-88A to treat wastewater from the sugar industry via the adsorption process.

1.2 Objectives

1) to synthesize MIL-88A for use in the adsorption process.

2) to remove the color and COD in sugar industry wastewater by MIL-88A.

1.3 Benefit

1) Apply the knowledge to treat the sugar factory wastewater in real situations

2) Provides useful information for product (MIL-88A) development for industrial wastewater treatment.

Chapter 2

Theory and literature review

2.1 Theory

2.1.1 Sugar industry wastewater

The sugar industry is very important for agriculture and industry as it generates income from exports into the country. The main sources of wastewater from sugar industries are cooling water and floor wash water, which is 12% of the total wastewater emitted from sugar industries (Yadav et al., 2021). The sugar production process is illustrated in Figure 2.1. The sugar industry requires a lot of water use in the production process and generates quite low quelity wastewater. The characteristics of sugar industry wastewater are pH 6-10, COD 5,000-9,000 mg/L, BOD_5 3,000-5,000 mg/L, Total Hardness 2,000-4,000 mg/L, Total suspended solids 6,000-9,000 mg/L, Turbidity 40-100 NTU and Oil and Grease 10-15 mg/L (Yadav et al., 2021).

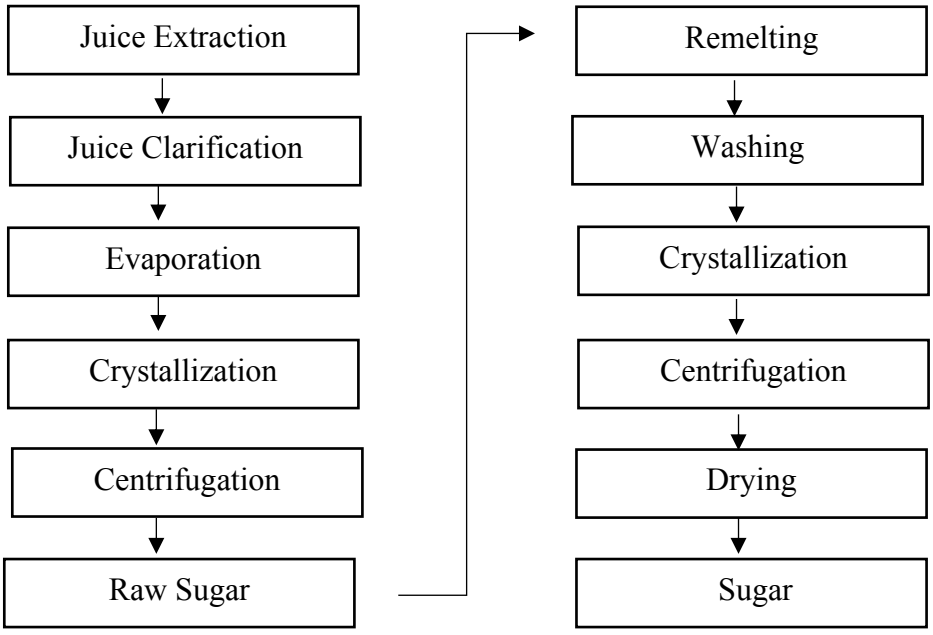

Figure 2.1 Production process diagram (Ministry of Industry, 2017)

Normally, wastewater treatment system used in sugar industry is a stabilization pond that relies on nature to treat the organic matter in wastewater. This can be divided into 3 types of behavior i.e., anaerobic pond, facultative pond and aerobic pond, and if there are many

consecutive ponds the last pond will act as a maturation pond to improve the quality of effluent before draining into the environment. Stabilization ponds involve natural treatment processes that take time because removal rates are slow. So, it requires a large land area for treatment processes. The effluent has high concentrations of suspended solids, resulting from algal production, and ponds have low efficiencies in the removal of organic matter and low capacities for removing nitrogen and phosphorus. Therefore, stabilization ponds with additional stages of post-treatment should be included.

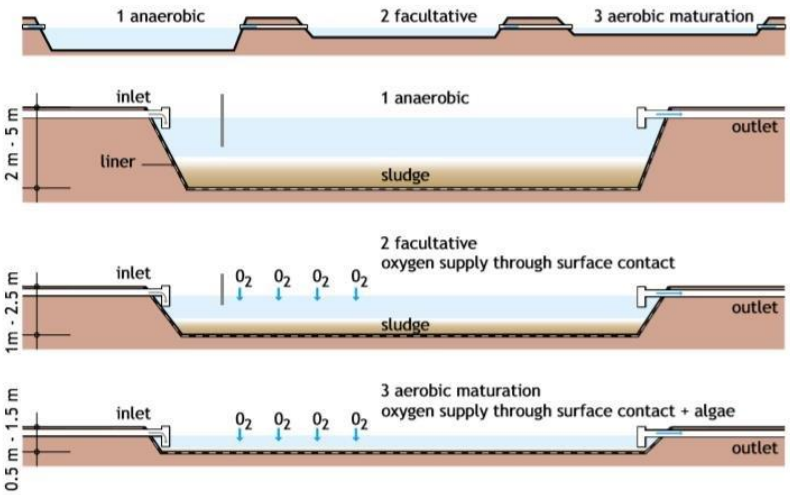

Figure 2.2 Stabilization Pond (Kone et al., 2008)

2.1.2 Adsorption

Adsorption is the ability of certain substances to extract molecules or colloids which are in liquid or gas to stick on the solid surface. The solid material that uses to absorb pollutants is called adsorbent, whereas, molecules or colloids was absorbed are called adsorbate. There are two processes of adsorption i.e., physical adsorption and chemical adsorption. Both processes occur when a molecule in a liquid bind to the surface of a solid resulting from the attraction of the solid surface.

2.1.2.1 Physical adsorption

Physical adsorption is the simplest immobilization method. The adsorbate molecules are held by physical forces like Van der Waals forces, electrostatic force. The heat of absorption is very low, reversible, and more pronounced at a temperature below the boiling point of absorbate. This adsorption is always multilayer and is almost non-specific.

2.1.2.2 Chemical adsorption

Chemical adsorption occurs when the absorbate molecule is held on the adsorbent surface by chemical forces as short covalent chemical bonding occurs by the sharing of electrons. The heat of chemical absorption is relatively higher than physical adsorption. Chemical adsorption is more pronounced usually at a high temperature, always monolayer, and is highly specific. It has a characteristic function of both adsorbent and adsorbate.

2.1.2.3 Adsorption kinetics

The adsorption kinetics could estimate the adsorption rate and adsorption type. Adsorption kinetics is a curve that describes the rate of retention or release of a solute from an aqueous environment to a solid-phase interface at a given adsorbents dose, temperature, flow rate, and pH. It can occur in these two models,

- **Pseudo-first-order model**

  The equation of the pseudo-first-order model:

$$ln(q_e - q_t) = ln\, q_e - k_1 t \qquad \text{Eq. (2.1)}$$

In equation: q_e and q_t are the amounts of adsorbate uptake per mass of adsorbent at equilibrium and at any time t (min), respectively, and k_1 (min^{-1}) is the rate constant of the Pseudo-first-order model equation.

- **Pseudo-second-order model**

  The equation of the pseudo-second-order model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad \text{Eq. (2.2)}$$

In equation: q_e (mg/g) and q_t (mg/g) are the adsorbate amount adsorbed at equilibrium and any t(min), respectively and k_2 (g/mg min) is the pseudo-second-order equation constant rate.

2.1.3 Metal-Organic Frameworks (MOFs)

MOFs were first introduced in the mid-1990s by Omar Yaghi. MOFs are compounds of metal ions and organic molecules that form structured frameworks. MOFs are organic-inorganic hybrid crystalline porous materials that consist of a regular array of positively charged metal ions surrounded by organic 'linker' molecules. MOFs have a high surface area, high porosity, unique structure, variable functional groups, stability in various environments as well as, a low-cost preparation process. Pores in MOFs are highly ordered, their size and shape can be adjusted by variation in linkers and metal ions (Design et al., 2003). This

structure provides high porosity and a large specific surface area, which enables pollutants to absorb efficiently. This may be due to diverse porosity and large surface area which has access through the adsorption site to capture the contaminants through the MOFs framework.

The water purification over MOFs is mainly decided by the four principal factors including stability, the adsorption capacity of MOF, interaction ability, and regenerative ability of MOF. Water pollutants are primarily divided into two distinct categories as organic pollutants and inorganic pollutants. MOFs as adsorbents or photocatalysts should be related to the specific kind of pollutant for the separation purpose. MOFs can be categorized into four categories: (Li et al., 2019)

1. **IRMOF (Isoreticular metal-organic framework) series**

IRMOF is synthesized from inorganic $[Zn_4O]^{6+}$ and various aromatic carboxylic acid ligands to form octahedral crystalline structures uniform and high porosity but lacks the stability of water For example, MOF-5 can be used for extraction, separation, and gases storage, it is the most famous MOFs reported by Yaghi's group (Furukawa et al., 2013)

2. **MIL (Materials of Institute Lavoisier) series**

MIL series are made from various transition metals and dicarboxylic acid ligands, succinic acid and glutaric acid or use trivalent metals such as chromium, vanadium, aluminum and iron in the synthesis with terephthalic acid and tribenzoic acid, which MIL is stable in water, making it usable in humid environments. For example, MIL-88A is stable in the water and having a large pore size.

3. **ZIF (Zeolitic imidazolate framework) series**

These types of MOFs are stable in water and solvents. They can be synthesized from Zn (II) or Co (II) and imidazole ligands. The zeolite structure is a tetrahedron structure and is chemically stable in boiling alkaline solutions. It can be differentiated by organic solvents, so ZIF materials are widely used, such as ZIF-8, used for the detection of alkanes in petroleum-based fuels and human serum (Chang et al., 2011).

4. **UiO (University of Oslo) series**

They are zirconium-based MOFs due to their high physical-chemical stability (Kutzscher et al., 2016). They are very useful sorbents for extracting compounds from biological samples such as UiO-66.

2.1.4 MIL (Materials of Institute Lavoisier)

MIL is an important class of MOFs. These materials are being used to treat wastewater and have proven to be very efficient because of their exceptionally large surface area and porous nature. MIL-88A generated from Fe^{3+} and fumaric acid is a good candidate for the scale. It is synthesized via the solvothermal method at room temperature (Fu et al., 2020). It is propitious to adsorb organic pollutants from water because of their chemically and thermally stable super tetrahedral cells, easy preparation method, low synthesis cost (low prices of organic ligands), and possible abundant binding sites but also excellent adsorption performance (Zhang et al., 2021). Furthermore, flexible MIL-88A(Fe) 's breathing effect is propitious to adsorb organic pollutants from water.

The morphology and particle size of MIL-88A(Fe) as illustrated in Figures 2.3 and 2.4, the MIL-88A(Fe) particles exhibit hexagonal rod-like and the lengths of MIL-88A rods are nanometer-scale, ranging from 100 to 800 nm. (Lin et al., 2015)

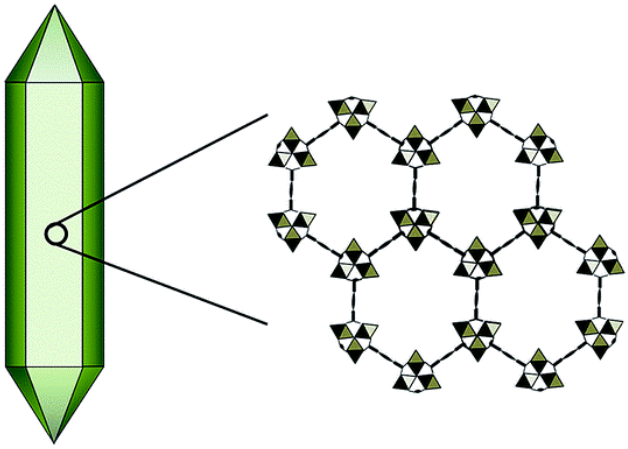

Figure 2.3 Structure of MIL-88A (Lin et al., 2015)

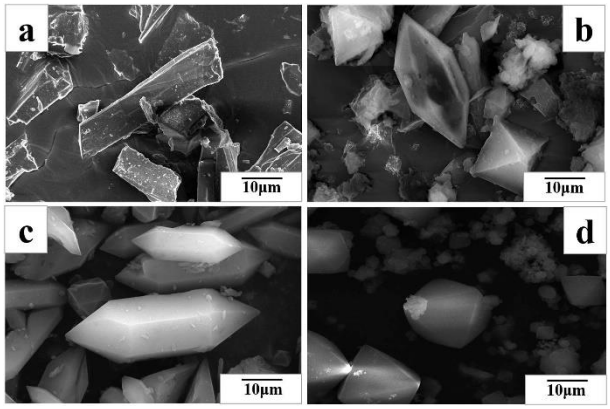

Figure 2.4 FESEM image of MIL-88A (Pang et al., 2020)

The XRD patterns of the synthesized Fe-based MOFs indicate that pure products with Fe-based MOFs topologies were successfully synthesized. The crystallographic structure of the as-prepared Fe-based MOFs samples was examined by XRD. As shown in Figure 2.5 that MIL-88A(Fe) exhibits a high crystallinity.

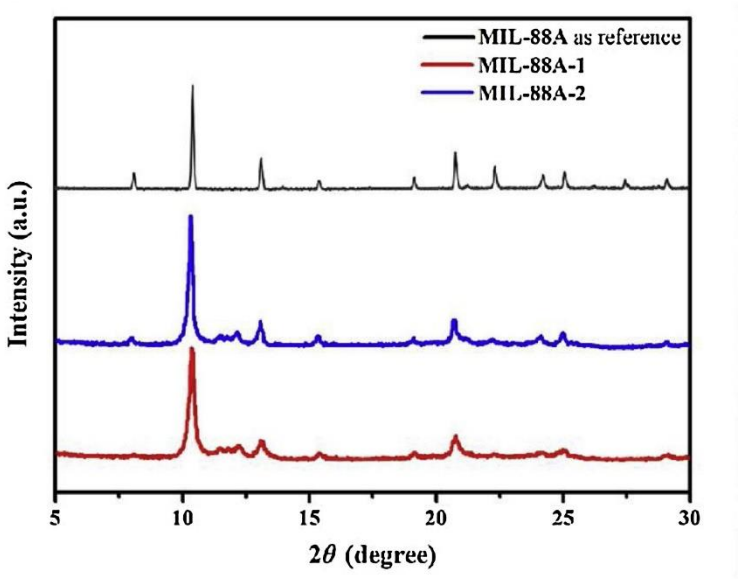

Figure 2.5 XRD of MIL-88A (Fu et al., 2020)

2.2 Literature review

2.1.5 Synthesis of Fe-type of MOFs

Wang et al. (2016) synthesized MIL-88A that was performed as follows: 8.4 mmol of fumaric acid and 8.4 mmol $FeCl_3 \cdot 6H_2O$ were added to a beaker with D.I. water. It was stirred for an hour at magnetic stirrers into a 100 mL Teflon-lined steel autoclave and heated. After that until drops to the room temperature, the precipitates were recovered by centrifugation at 9,000 rpm for 10 min. The as-synthesized solids should be washed by ethanol and water repetitively. The final precipitates were dried in a vacuum oven at 100 °C for no less than 10 h after centrifugation.

Fu et al. (2020) produced MIL-88A with 10 mmol fumaric acid and 10 mmol $FeCl_3 \cdot 6H_2O$ with dissolved in 75 mL ethanol and 75 mL ultrapure water, respectively. The mixed solutions stirred for 24 h at room temperature. The products were washed by ethanol and centrifugation.

Paiman et al. (2020) generated non-functionalized MOF labelled as MOF-Fe, 2.45 mmol of $FeCl_3 \cdot 6H_2O$ and 1.24 mmol of Benzene dicarboxylic acid with dissolved in 30 mL of DMF and transferred into a 250 mL Teflon bottle and placed in an oven for the solvothermal process at 120 °C for 24 h. After that cooled down to room temperature and

collected orange solid powder by centrifugation and purified with DMF and ethanol and dried at 60 °C for 24 h.

Alipanah et al. (2021) prepared MIL-88A (Fe) nanoparticles by mixed fumaric acid and 5 $FeCl_3.6H_2O$ in 100 ml deionized water. Then, the homogeneous solution with orange-like color was put into an autoclave and heated at 65 °C for 12 h. After cooling to room temperature and washed product with a dilute NaOH solution to neutralize free acids and dried in an oven at 65 °C after centrifugation.

2.1.6 Wastewater treatment by MOFs

Wang et al. (2016) synthesized MIL-88A for degrading Orange Gelb (OG) through persulfate activation and tested at a temperature of 25 °C. MIL-88A produced at the synthesis temperature of 85 °C and in the crystallization time of 2 h (85 °C/2 h) was the best one with a removal rate of 96.4% mainly due to high SBET and much greater leach-out of Fe. The solution pH < 4 could show a high degradation effect without the help of temperature. Comparing two different methods in the recycling experiment, the removal rate of OG decreased after the fourth run in both. Loss of active catalytic sites for Fe (III) in MIL-88A in the process of separating and sampling was responsible for activity decay.

Yilmaz et al. (2016) synthesized MIL-53 (Fe) and did adsorption experiment on interaction between this MOF and methyl red (MR) in an aqueous solution. the adsorption kinetics obeyed the pseudo-second-order kinetic model and an intraparticle diffusion model was also applied to understand the adsorption mechanism and Langmuir and Freundlich adsorption isotherm models. The adsorption of MR by selected MOF was a spontaneous and exothermic process.

Yu et al. (2019) used MIL-53(Fe) and MIL-53(Fe) series to investigate the effects of initial pH values co-existed ions, and humic acid on the adsorption performance of functionalized MIL-53(Fe). The adsorption kinetics fitted well with the pseudo-second-order model and the adsorption isotherms matched the Langmuir model, which suggested that the adsorption process was dominant by chemisorption and the adsorption surface was homogenous. Br-MIL-53(Fe) had the highest maximum adsorption capacity of 309.6 mg/g.

Fu et al. (2020) prepared MIL-88A with different sizes at room temperature with exhibited excellent photo-Fenton catalytic performance towards rhodamine B and bisphenol A removal under visible light irradiation (LED). Furthermore, the as-prepared MIL-88A displayed good reusability, and there was no obvious decline in degradation performance after five cycles.

Table 2.1 Synthesis of Fe-type of MOFs

MOF	Mixing Reagent	Stirring time	Reactor	Reaction Temperature	Chemical Washing	Centrifugation	Dry	Ref.
MIL-53 (Fe)	16 mmol BDC and 16 mmol $FeCl_3 \cdot 6H_2O$ in 40 mL of DMF	-	Teflon-lined autoclave	15 h at 150 °C	ultrapure water	/	60 °C for 24 h.	Zhang et al. (2021)
MIL-88A	8.4 mmol $FeCl_3 \cdot 6H_2O$ 8.4 mmol fumaric acid ($C_4H_4O_4$)	1 h	Teflon-lined steel autoclave	2 h at 85 °C	DMF and ethanol (3 times)	/	60 °C 24 h	Zhang et al. (2021)
MIL-101(Fe)	1.242 mmol BDC and 2.497 mmol $FeCl_3 \cdot 6H_2O$ in 15 mL of DMF	-	Teflon-lined autoclave	20 h at 110 °C	DMF and ethanol	/	60 °C for 24 h	Zhang et al. (2021)
MIL-88A	10 mmol fumaric acid 10 mmol $FeCl_3 \cdot 6H_2O$	24 h at room temperature	-	room temperature	Ethanol	/	-	Fu et al. (2020)
MIL-101(Fe)	0.675 g $FeCl_3 \cdot 6H_2O$ 0.206 g H_2BDC 25 mL DMF	room temperature 10 min	25 mL Teflon autoclave	383 K for 20 h.	DMF and ethanol (several times)	/	80 °C overnight	Li et al. (2020)

MOF	Mixing Reagent	Stirring time	Reactor	Reaction Temperature	Chemical Washing	Centrifugation	Dry	Ref.
MIL-101(Fe)	2.45 mmol of $FeCl_3 \cdot 6H_2O$ and 1.24 mmol of BDC 30 mL of DMF		250 mL Teflon bottle	120 °C for 24 h.	DMF and ethanol	/	60 °C for 24 h	Paiman et al. (2020)
MIL-53 (Fe)	$FeCl_3.6H_2O$, 1.35 g, 5 mmol H_2BDC 0.83 g,5 mmol 25 mL DMF	-	Teflon-lined autoclave	150 °C for 12 h	ethanol (multiple times)	-	110 °C	Tran et al. (2020)
MIL-88A	$FeCl_3 \cdot 6H_2O$ fumaric acid in equimolar amounts (1:1)	/	-	-	DMF and ethanol (2 times)	9000 rpm for 10 min	85 °C overnight	Amaro-gahete et al. (2019)
MIL-88A	1.352 g $FeCl_3 \cdot 6H_2O$ 0.580 g fumaric acid	/	Teflon reaction kettle	4 h at 65 °C	DMF/deionized water (4 times)	/	60 °C	Liao et al. (2019)
MIL-53(Fe)	$FeCl_3 \cdot 6H_2O$ (0.674 g) 1, 4-H_2BDC (0.415 g) 56 mL DMF	1 h at room temperature	100 mL Teflon-lined stainless-	170 °C for 24 h	DMF and ethanol	/	100 °C for	Yu et al. (2019)

MOF	Mixing Reagent	Stirring time	Reactor	Reaction Temperature	Chemical Washing	Centrifugation	Dry	Ref.
			steel autoclave				several hours	
MIL-53(Fe)	$FeCl_3.6H_2O$, 1 mmol terephthalic acid 1 mmol HF (1 mmol) DMF, 5 m	-	Teflon lined stainless steel autoclave	150 °C for 3 days	Methanol water (1 g of MIL-53 in 0.5 l of water)	-	dried naturally	Yılmaz et al. (2016)

Table 2.2 Decolorization and COD removal by several treatment processes

Treatment process	Wastewater	Pollutant	Initial COD (mg/L)	Initial color	COD removal efficiency	Decolorization efficiency	Ref.
Adsorption: ultrasound and combined ultrasound/activated carbon	textile	rifacion yellow HE4R	160	-	99.9%	85.22%	Enes. (2006)
Coagulation	yeast wastewater	secondary yeast wastewater	1200±200	2.2-2.5 abs/cm	72%	90%	Zhou et al. (2008)
Adsorption: bamboo-based activated carbon	cotton textile wastewater.	cotton textile wastewater.	200–260	450–650 Pt/Co	75.21%	91.84%	Ahmad et al. (2009)
Et aFluidized-bed Fenton process: fluidized-bed reactor (FBR)	synthetic dye wastewater	Reactive Black 5 (RB5), Reactive Orange 16 (RO16) and Reactive Blue 2 (RB2) dyes	160	6500 ADMI	34% 47% 49%	99% 99% 96%	Su et al. (2011)
Electrocoagulation: Combining fluidized metal-impregnated granular activated carbon	cotton textile wastewater	real cotton textile wastewater	685 ± 50	-	97.01 ± 0.18%	99.13 ± 0.21%	Jung et al. (2015)

Table 2.3 Efficiency of pollutant removal

Type of MOFs	Pollutant	pH range (optimum pH)	Adsorption kinetics	Adsorption isotherm	Adsorption abilities	Reusability	Removal efficiency	Ref.
MIL-53(Fe)	Methyl red	Low pH (3.0)	pseudo-second-order model	Langmuir model	excellent	3 cycles	83.3%	Yılmaz et al. (2016)
MIL-53(Fe)	Tetracycline antibiotics	3.0-10.0 (3.32)	pseudo-second-order model	Langmuir model	excellent	4 cycles		Yu et al. (2019)
MIL-88A	inorganic and organic arsenic pollutants	8.0 -11.0 (11.0)	pseudo-second-order model	Langmuir isotherm model	excellent	good	92.6%	Pang et al. (2020)
MIL-101(Fe)	Tetracycline hydrochloride	3.0-8.0	pseudo-second-order model	Langmuir model	MIL-101 (Fe)> MIL-88A (Fe) > MIL-53 (Fe)	3 cycles	MIL-101 (Fe)> MIL-88A (Fe) > MIL-53 (Fe)	Zhang et al. (2021)
MIL-88A								
MIL-53(Fe)								

It can be concluded in the literature review that there are several procedures to synthesize MIL-88A(Fe). Two based chemicals used in MIL-88A(Fe) preparations are $FeCl_3 \cdot 6H_2O$ and fumaric acid with vary a condition, for example, the temperature was in the range of room temperature to 85°C. The products were recovered by centrifugation and washed with DMF and/or ethanol 2 or 4 times and then drying at 60 - °C for 24 hours or overnight. The efficiency of MIL in treating wastewater with adsorption mechanism was in the range of around 83 - 93%. Lower pH values were found to be more favorable for adsorption. The kinetics data and adsorption capacity almost fitted well with the pseudo-second-order kinetic model and Langmuir isotherm model, respectively.

Chapter 3

Materials and methods

3.1 Materials

3.1.1 Equipment

1) Field Emission Scanning Electron Microscope (FESEM): JEOL JSM-7610F, Oxford X-Max 20, Japan
2) X-Ray Diffractometer (XRD): Model D8 Advance: Bruker AXS, Germany
3) Spectrophotometer: Spectroquant Prove 600, Germany
4) COD reactor: Hach DRB 200
5) Reciprocal shaker: Gerhardt brand, Scientific Promotion Co., LTD.
6) Hotplate Stirrer: C-MAG HS7 model, S/N. 08.112991, Kittisit Enterprise CO., LTD.
7) Desiccator
8) Laboratory glassware

3.1.2 Chemicals

3.1.2.1 For synthesis of absorbent

1) Fumaric acid ($C_4H_4O_4$)
2) Iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$)
3) Ethanol (CH_3CH_2OH)

3.1.2.2 For COD test

1) Potassium dichromate ($K_2Cr_2O_7$)
2) Conc. sulfuric acid 98% (H_2SO_4)
3) Mercury (II) sulfate ($HgSO_4$)
4) Silver sulfate (Ag_2SO_4)
5) Ammonium ferrous (II) sulfate hexahydrate ($Fe(NH_4)_2(SO_4)_2.6H_2O$)
6) 20% Ferrous sulfate (20% $FeSO_4.7H_2O$)
7) 1,10-Phenanthroline monohydrate ($C_{12}H_8N_2.H_2O$)

3.2 Experimental procedure

The experiment was conducted as illustrated in Figure 3.1

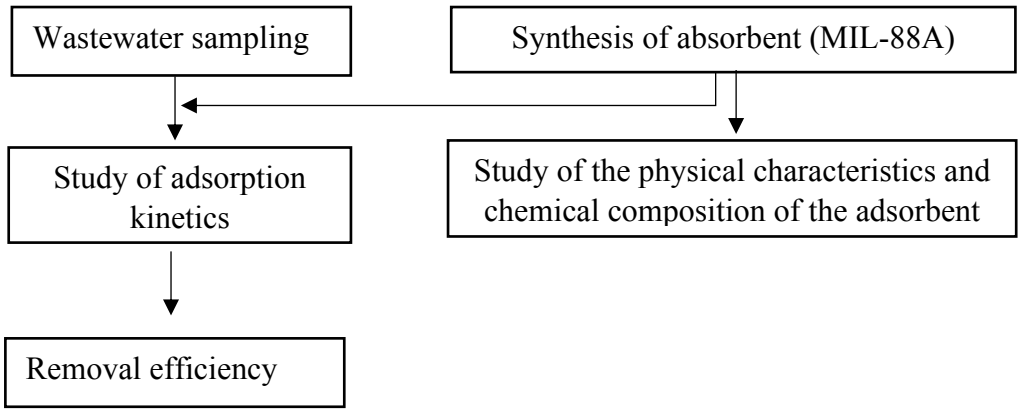

Figure 3.1 Flowchart of experiment

3.1.3 Wastewater sampling

Wastewater was collected from a sugar factory in Phetchabun, Thailand. All samples were stored at 4 ˚C in the refrigerator. Wastewater characteristics before the experiment including COD and color were analyzed follows the method as shown in Table 3.1.

Table 3.1 Analytical Methods

Parameter	Analytical Methods	Unit
COD	Closed Reflux Method	mg/L
Color	Spectrophotometer	ADMI

3.1.4 Synthesis of absorbent (MIL-88A) (Fu et al., 2020)

1) Mixed 10 mmol fumaric acid, 10 mmol $FeCl_3 \cdot 6H_2O$, 38 mL ethanol, and 38 mL ultrapure water in a beaker.

Figure 3.2 wighted fumaric acid and $FeCl_3 \cdot 6H_2O$

2) Stirred the solution with a magnetic stirrer for 24 h at room temperature.

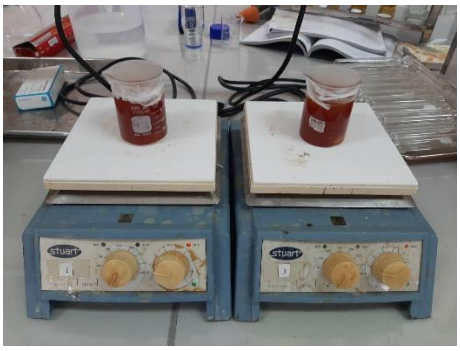

Figure 3.3 Stirred the solution with a magnetic stirrer

3) Washed the products (MIL-88A) with ultrapure water three times and ethanol two times and separated with centrifugation at 6500 rpm for 5 min and was dried in a vacuum oven at 60 °C overnight. The as-prepared MIL-88A was orange powder.

Figure 3.4 The as-prepared MIL-88A

4) Confirmed synthetic MIL-88A with SEM and XRD

Synthetic MIL-88A received from this step was used to treat wastewater.

3.1.5 Adsorption kinetics

1) Added 0.2 g MIL-88A to 50 mL sugar factory wastewater in the flask.
2) Shaked the solution with a shaker at 100 rpm for 10, 20, 30, 60, 120 and 180 minutes.
3) Analyzed color with Spectrophotometer and measure COD.

* Repeating three times and control one sample

3.2.4 Treatment Efficiency

The removal efficiency (%) was calculated via Eq. (3.1)

$$\text{Removal } \% = \frac{C_i - C_f}{C_i} \times 100 \qquad \text{Eq. (3.1)}$$

In equation: C_i is the initial concentration

C_f is the concentration after treatment

3.3 Data analysis

The data analysis was conducted using SPSS 23.0 statistical package. Statistical significances of means were tested with a model of One-Way ANOVA followed by Tukey's tests with 95% ($p < 0.05$)

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Wastewater characteristic

Wastewater was collected from a sugar industry in Phetchabun, Thailand. All samples were stored at 4 ˚C in the refrigerator. Initial color and COD were 12,600 ADMI and 2,240 mg/L, respectively.

4.2 Structural and morphological characteristics

MIL-88A was produced via a reaction between an aqueous solution of an alcohol solution of fumaric acid and $FeCl_3$ at room temperature. It was affirmed by the FESEM images and XRD patterns. MIL-88A was prepared according to the previous literature of Fu et al. (2020).

4.1.1 SEM images

To investigate the surface morphology of the MIL-88A, it was characterized by FESEM images with 30,000 magnification. The FESEM pattern of the obtained MIL-88A showed that the as-prepared MIL-88A was a crystalline solid. The MIL-88A particles exhibited hexagonal rod-like morphology with uniform size distribution that length of MIL-88A rods were 300-500 nm as shown in Figure 4.1. It was matched well with the standard MIL-88A pattern as reported by Lin et al. (2015).

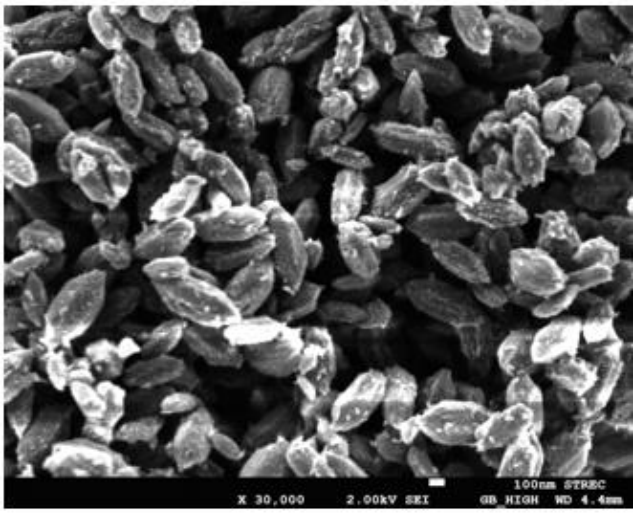

Figure 4.1 FESEM images of prepared MIL-88A

4.1.2 XRD analysis

The XRD pattern of the obtained products shows that the as-prepared MIL-88A is a crystalline solid, as showed in Figure 4.2. The XRD characteristic diffraction appeared main peaks of the MIL-88A at 10.8° and 12.0° corresponded well with the previous literature of Fu et al. (2020). Moreover, the XRD analysis clearly revealed that the obtained products were single-phase MIL-88A MOFs and a large number of free water molecules existed in the channels and cages of MIL-88A and the MIL-88A flexible structures were all in a closed pore configuration by Xu et al. (2014)

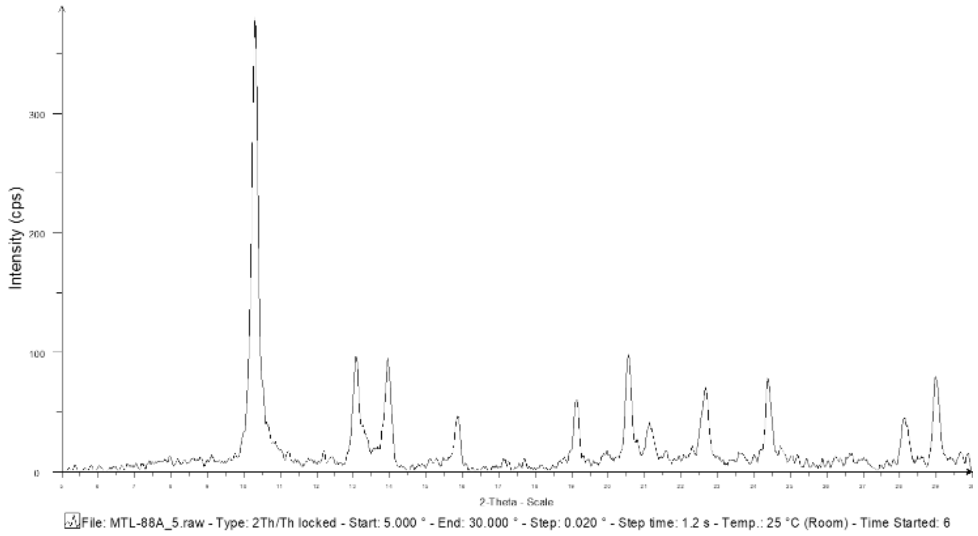

Figure 4.2 XRD patterns of as-prepared MIL-88A

4.3 Efficiency of decolorization and COD removal by as-prepared MIL-88A

The result of sugar industry wastewater treatment by adsorption process with as-prepared MIL-88A 0.2 gram and contact time of 10, 20, 30, 60, 120, 180 min is showed in Figure 4.3

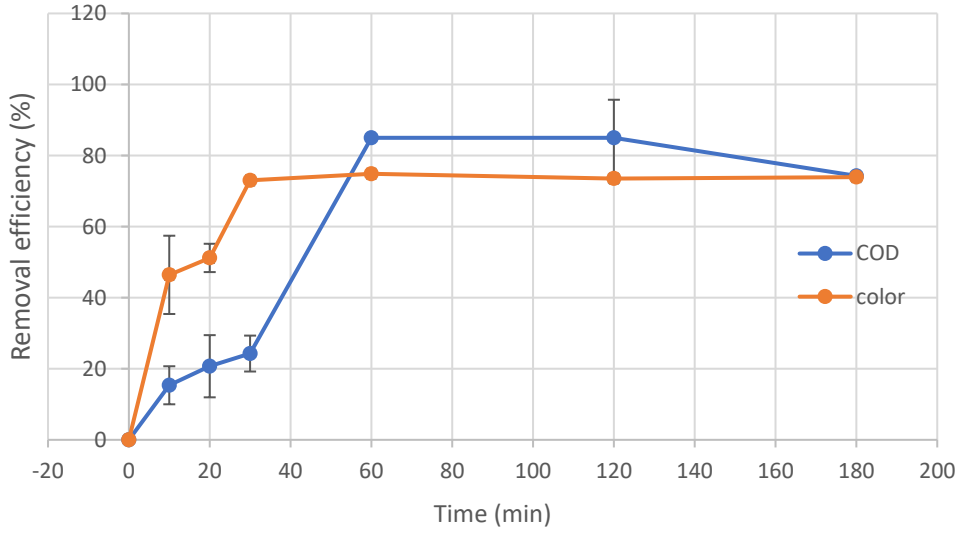

Figure 4.3 Efficiency of color and COD removal by as-prepared MIL-88A

Color removal efficiency increased dramatically from 0 to 30 minutes and remained steady from 30 to 180 minutes, this means the equilibrium time was 30 minutes. The maximum color removal efficiency was 74.9 % at approximately 60 minutes. In addition, the equilibrium time of COD removal was around 60 minutes. It showed highest COD removal efficiency was 85.0% at that time as the analysis from one-way ANOVA (at $p < 0.05$) revealed that COD removal efficiencies at 60, 120, and 180 minutes were no significant difference. Note that this is not too long equilibrium time compared to the study of Zhang et al. (2021) which required 10 hours to adsorb TCH with MIL-88A.

The color and COD of treated sugar industry wastewater was 336 mg/L and 3,166 ADMI, respectively. This means, both parameters were not complied the standard requirement set by Ministry of Industry (2017) (color $\leq$ 300 ADMI and COD $\leq$ 120 mg/L) and needed to study the appropriate amount of adsorbent or pH range to provide more adsorption capacity.

4.4 Adsorption kinetics

The adsorption kinetics is the measure of the adsorption uptake with respect to time at a constant pressure or concentration and is employed to measure the diffusion of adsorbate in

the pores (Saha & Grappe, 2017). It can occur in these two models, pseudo-first-order model and pseudo-second-order model.

The result of adsorption kinetics which pseudo-first-order model was showed in Figure 4.4. For decolorization, it showed coefficient r^2 value of 0.9086 and 0.9976 in the pseudo-first order and pseudo-second order, respectively. For COD removal, the pseudo-first- and pseudo-second-order models had coefficient r^2 value of 0.9176 and 0.9270, respectively. The linear equations (y = mx+c) can be used to find the slope (m). The resulting slope is the rate constant (k). For decolorization, it showed k value of -0.0085 in pseudo-first-order and 0.0004 in pseudo-second-order. For COD removal, the pseudo-first-order had k value of -0.0056 and 0.0014 in the pseudo-second-order. The k value of pseudo-first-order was negative and therefore did not indicate the velocity of the reaction.

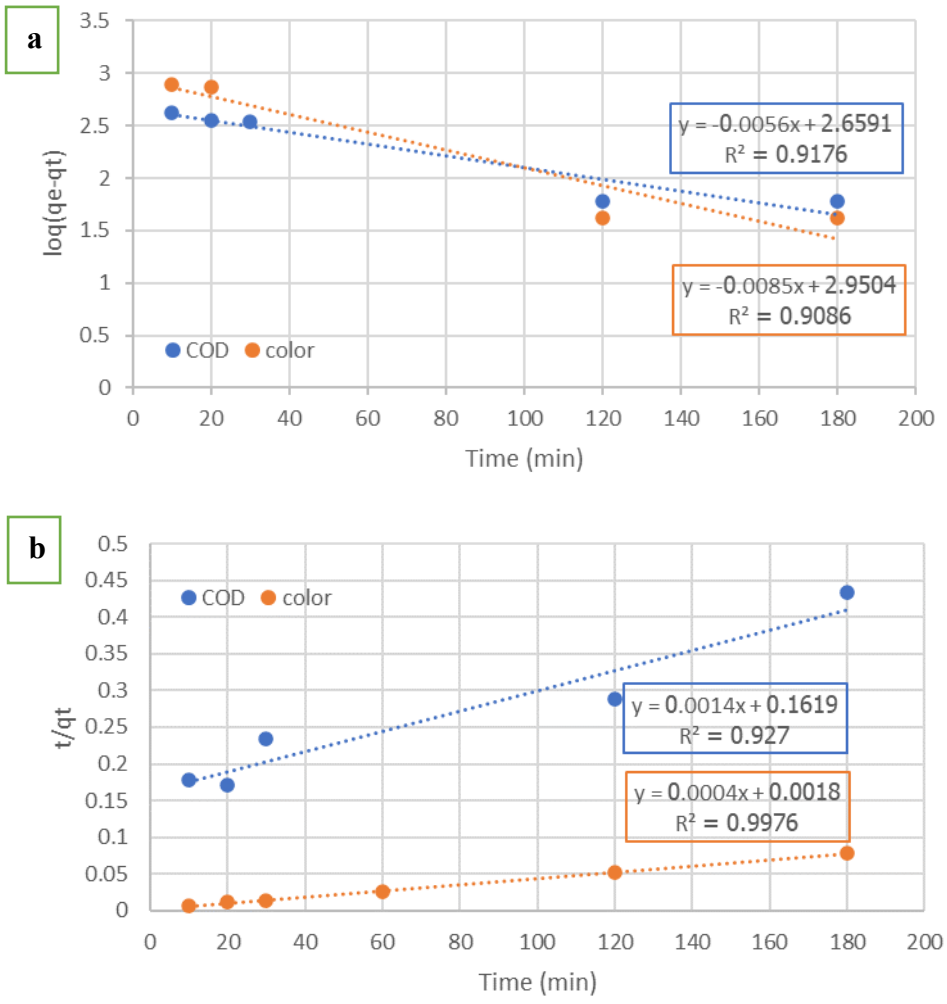

Figure 4.4 (a) pseudo-second-order model and (b) pseudo-second-order model

This work revealed the best fitted of color and COD removal with the pseudo-second order model. Several researches (as shown in Table 2.4) also performed that adsorption kinetics of color and COD by MOFs were preferable on pseudo-second order. It indicated that adsorption mechanism is caused by a chemical mechanism by forming a bond between the absorbent and the adsorbed substance that share electrons or exchange electrons.

CHAPTER 5

CONCLUSION & RECOMMENDATIONS

5.1 Conclusion

This study focused on synthesis of MIL-88A and use this as-prepared MIL-88A for removal of color and COD in sugar industry wastewater by adsorption process. The conclusion can be summarized as follows:

1) The synthetic MOFs can be confirmed as MIL-88A by FESEM images with surface morphology as hexagonal rod-like and 100 nm lengths, and XRD patterns with diffraction peaks at about 10.8° and 12°.
2) As-prepared MIL-88A could reduce color and COD in sugar industry by adsorption process. The color and COD removal efficiency were 74.9% and 85.0%, respectively. The adsorption kinetic was fitted with pseudo-second order model.

5.2 Recommendations

This research studied about synthesis of MIL-88A for decolorization and COD removal in sugar industrial wastewater which can be is a guideline for development of wastewater treatment process. The further research can be conducted as follows:

1. Analysis of MIL-88A by FTIR analysis to identify functional unit.
2. Synthesis of MIL-88A in the larger scale for more product.
3. Variation of pH in the decolorization and COD removal process, that might increase treatment efficiency.

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APPENDICES

Table 1 Efficiency of the COD removal for different time at $p < 0.05$ by one-way ANOVA

ANOVA

Color

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	2545.715	5	509.143	14.557	.000
Within Groups	419.721	12	34.977		
Total	2965.436	17			

Post Hoc Tests

Multiple Comparisons

Dependent Variable: color

	(I) time	(J) time	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
						Lower Bound	Upper Bound
Tukey HSD	10.00	20.00	-4.76333	4.82885	.914	-20.9831	11.4564
		30.00	-26.58667*	4.82885	.001	-42.8064	-10.3669
		60.00	-28.44000*	4.82885	.001	-44.6597	-12.2203
		120.00	-27.11333*	4.82885	.001	-43.3331	-10.8936
		180.00	-27.51000*	4.82885	.001	-43.7297	-11.2903
	20.00	10.00	4.76333	4.82885	.914	-11.4564	20.9831
		30.00	-21.82333*	4.82885	.007	-38.0431	-5.6036
		60.00	-23.67667*	4.82885	.004	-39.8964	-7.4569
		120.00	-22.35000*	4.82885	.006	-38.5697	-6.1303
		180.00	-22.74667*	4.82885	.005	-38.9664	-6.5269
	30.00	10.00	26.58667*	4.82885	.001	10.3669	42.8064
		20.00	21.82333*	4.82885	.007	5.6036	38.0431
		60.00	-1.85333	4.82885	.999	-18.0731	14.3664
		120.00	-.52667	4.82885	1.000	-16.7464	15.6931
		180.00	-.92333	4.82885	1.000	-17.1431	15.2964
	60.00	10.00	28.44000*	4.82885	.001	12.2203	44.6597
		20.00	23.67667*	4.82885	.004	7.4569	39.8964
		30.00	1.85333	4.82885	.999	-14.3664	18.0731
		120.00	1.32667	4.82885	1.000	-14.8931	17.5464
		180.00	.93000	4.82885	1.000	-15.2897	17.1497
	120.00	10.00	27.11333*	4.82885	.001	10.8936	43.3331

		20.00	22.35000*	4.82885	.006	6.1303	38.5697
		30.00	.52667	4.82885	1.000	-15.6931	16.7464
		60.00	-1.32667	4.82885	1.000	-17.5464	14.8931
		180.00	-.39667	4.82885	1.000	-16.6164	15.8231
	180.00	10.00	27.51000*	4.82885	.001	11.2903	43.7297
		20.00	22.74667*	4.82885	.005	6.5269	38.9664
		30.00	.92333	4.82885	1.000	-15.2964	17.1431
		60.00	-.93000	4.82885	1.000	-17.1497	15.2897
		120.00	.39667	4.82885	1.000	-15.8231	16.6164

Table 2 Efficiency of the decolorization for different time at $p < 0.05$ by one-way ANOVA

ANOVA

COD

	Sum of Squares	**df**	**Mean Square**	**F**	**Sig.**
Between Groups	12661.355	5	2532.271	11.114	.001
Within Groups	2506.301	11	227.846		
Total	15167.656	16			

Post Hoc Tests

Multiple Comparisons

Dependent Variable: COD

			Mean			95% Confidence Interval	
	(I) time	(J) time	Difference (I-J)	Std. Error	Sig.	Lower Bound	Upper Bound
Tukey HSD	10.00	20.00	-5.35833	13.77938	.999	-52.3509	41.6343
		30.00	-8.92833	13.77938	.984	-55.9209	38.0643
		60.00	-69.64500*	13.77938	.004	-116.6376	-22.6524
		120.00	-58.93167*	13.77938	.012	-105.9243	-11.9391
		180.00	-44.64833	13.77938	.066	-91.6409	2.3443
	20.00	10.00	5.35833	13.77938	.999	-41.6343	52.3509
		30.00	-3.57000	12.32465	1.000	-45.6015	38.4615
		60.00	-64.28667*	12.32465	.003	-106.3181	-22.2552
		120.00	-53.57333*	12.32465	.011	-95.6048	-11.5419
		180.00	-39.29000	12.32465	.071	-81.3215	2.7415
	30.00	10.00	8.92833	13.77938	.984	-38.0643	55.9209
		20.00	3.57000	12.32465	1.000	-38.4615	45.6015
		60.00	-60.71667*	12.32465	.005	-102.7481	-18.6852
		120.00	-50.00333*	12.32465	.018	-92.0348	-7.9719

		180.00	-35.72000	12.32465	.112	-77.7515	6.3115
	60.00	10.00	69.64500*	13.77938	.004	22.6524	116.6376
		20.00	64.28667*	12.32465	.003	22.2552	106.3181
		30.00	60.71667*	12.32465	.005	18.6852	102.7481
		120.00	10.71333	12.32465	.946	-31.3181	52.7448
		180.00	24.99667	12.32465	.386	-17.0348	67.0281
	120.00	10.00	58.93167*	13.77938	.012	11.9391	105.9243
		20.00	53.57333*	12.32465	.011	11.5419	95.6048
		30.00	50.00333*	12.32465	.018	7.9719	92.0348
		60.00	-10.71333	12.32465	.946	-52.7448	31.3181
		180.00	14.28333	12.32465	.847	-27.7481	56.3148
	180.00	10.00	44.64833	13.77938	.066	-2.3443	91.6409
		20.00	39.29000	12.32465	.071	-2.7415	81.3215
		30.00	35.72000	12.32465	.112	-6.3115	77.7515
		60.00	-24.99667	12.32465	.386	-67.0281	17.0348
		120.00	-14.28333	12.32465	.847	-56.3148	27.7481

BIOGRAPHICAL DATA

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