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ชื่อโครงการ Treatment of Wood Adhesives Wastewater from Lumber Mill via Fe^{0}/air Modified Fenton using Iron Waste from Auto Parts Manufacturing

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Abstract

Iron waste or used shot blast, which received from auto parts manufacturing, comprises zero-valent iron (Fe^0) with can transfer to ferrous iron (Fe^{2+}). In this experiment, used shot blast in aeration condition called Fe^0/air modified Fenton was applied to treat wood adhesives wastewater from lumber mill with contained high organic content (approx. COD of 32,000 mg/L). The optimum conditions were carried out at different time (5-120 min), pH (2.0-4.0), air flow rate (0.5-2.0 L/min), and shot blast dosage (10-40 g/L). The results found that maximum COD removal efficiency from Fe^0/air modified Fenton reaction at time 60 min., pH 3.0, air flow rate 1.5 L/min, and shot blast 20 g/L was 79.33 %. At this condition, treatment efficiencies of turbidity, total suspended solids and BOD were 84.78, 13.28 and 73.68 %, respectively. Biodegradability (BOD/COD) increased from 0.08 to 0.11. Even though effluent from this treatment process did not comply with the industrial effluent standard, Fe^0/air modified Fenton reaction is especially suitable for treating wastewater in the first process in order to reduce burden of wastewater treatment in the next processes.

Keywords: modified Fenton, shot blast, COD, Fe^0/air, Urea-formaldehyde wastewater

หัวเรื่อง	การบำบัดน้ำกาวจากโรงงานไม้แปรรูปผ่านกระบวนการเฟนตันประยุกต์ โดยการทำงานร่วมกันของเหล็กประจุศูนย์ในสภาวะที่มีอากาศโดยใช้เศษเหล็กจากการผลิตชิ้นส่วนรถยนต์
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บทคัดย่อ

เศษเหล็กหรือช็อตบลาสท์เหลือทิ้งที่มาจากกระบวนการผลิตชิ้นส่วนรถยนต์ ประกอบไปด้วยเหล็กประจุศูนย์ที่สามารถเปลี่ยนรูปไปเป็นเหล็กเฟอรัส ในการทดลองนี้ได้นำช็อตบลาสท์เหลือทิ้งในภาวะเติมอากาศที่เรียกว่า กระบวนการเฟนตันประยุกต์โดยการทำงานร่วมกันของเหล็กประจุศูนย์ มาประยุกต์เพื่อบำบัดน้ำเสียกาวยูเรียฟอร์มาลดีไฮด์จากโรงงานไม้แปรรูปซึ่งมีสารอินทรีย์ปนเปื้อนสูง โดยมีค่าซีโอดีในน้ำเริ่มต้นประมาณ 32,000 มิลลิกรัมต่อลิตร ศึกษาหาสภาวะที่เหมาะสมในการทดลอง ได้แก่ ระยะเวลาในการบำบัด 5-120 นาที ค่าความเป็นกรด-ด่าง 2.0-4.0 อัตราการไหลของอากาศ 0.5-2.0 ลิตรต่อนาที และปริมาณช็อตบลาสท์เหลือทิ้ง 10-40 กรัมต่อลิตร ผลการทดลองพบว่า สภาวะที่เหมาะสมได้แก่ ช่วงเวลาในการบำบัด 60 นาที ค่าความเป็นกรด-ด่าง 3.0 อัตราการไหลของอากาศ 1.5 ลิตรต่อนาที และปริมาณช็อตบลาสท์เหลือทิ้ง 20 กรัมต่อลิตร จะให้ประสิทธิภาพในการลดค่าซีโอดีสูงถึงร้อยละ 79.33 ภายใต้สภาวะที่เหมาะสมนี้ ยังมีประสิทธิภาพในการลดค่าความขุ่น ค่าของแข็งแขวนลอย และค่าบีโอดี เท่ากับร้อยละ 84.78, 13.28 และ 73.68 ตามลำดับ ค่าอัตราส่วนระหว่างบีโอดีต่อซีโอดีที่มีผลต่อการย่อยสลายทางชีวภาพมีค่าเพิ่มขึ้นจาก 0.08 ไปถึง 0.11 แม้ว่าน้ำหลังจากผ่านกระบวนการบำบัดน้ำเสียด้วยวิธีนี้จะยังไม่ได้ผ่านค่ามาตรฐานน้ำทิ้งอุตสาหกรรม แต่การบำบัดน้ำเสียด้วยกระบวนการเฟนตันประยุกต์โดยการทำงานร่วมกันของเหล็กประจุศูนย์ มีความเหมาะสมอย่างมากในการบำบัดน้ำเสียเป็นกระบวนการแรก เพื่อเป็นการลดภาระของการบำบัดน้ำเสียในกระบวนการถัดไป

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Yanisa Deesanuwat

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Abbreviation	Meaning
AOPs	Advanced oxidation processes
BOD	Biochemical oxygen demand
B/C ratio	BOD/COD ratio
COD	Chemical oxygen demand
DO	Dissolved oxygen
MDF	Medium density fiberboard
TDS	Total dissolved solids
TSS	Total suspended solids
WAUF	Wood adhesive Urea-formaldehyde
XRF	X-Ray Fluorescence
ZVI	Zero-valent iron

CHAPTER 1
INTRODUCTION

1.1 Background and rationale

From the rapid growth of industrialization and modernization, it causes the development of lumber mill industry. One of the lumber mill industrials is wood-based panel, which products applied by residual of wood in order to reduce the use of expensive, rare, and large wood. Urea-formaldehyde (UF) resin is the most important type of adhesive resins for the wood-based panel productions (Dunky, 1998). In the end of process, it discharges wastewater contaminated with wood adhesive urea-formaldehyde (WAUF). WAUF wastewater consists mainly of formaldehyde and ammonia nitrogen. It contains very high COD values and low BOD_5/COD ratio (Kowalik, 2011). This means it is not suitable for biological wastewater treatment process.

Advanced Oxidation Processes (AOPs) are an alternative wastewater treatment refer to chemical processes that employ ozone (O_3), hydrogen peroxide (H_2O_2) and ultraviolet (UV). Fenton process is one of AOPs that often used because it has a high efficiency in short time treatment and no odor problem also (Lim, 2009). The Fenton process uses hydrogen peroxide and catalyst with ferrous iron (Fe^{2+}) to generate hydroxyl radical (HO•) and then this radical oxidizes organic pollutant into CO_2 and H_2O. However, the main disadvantage of Fenton is high operating cost of chemical used (ferrous iron and hydrogen peroxide). Hence, modified Fenton, which refers to the process that uses other activated agents instead of ferrous iron, has been applied to solve apparent limitation in the Fenton process. In addition, aeration system can improve organic removal efficiency in wastewater treatment and replace of H_2O_2 in order to reduce using chemical agent and save operating costs (Zhang et al., 2019)

Auto parts manufacturing in Thailand has several production steps and also generates numerous industrial wastes. Shot blasting is one of the auto parts production processes, which produces the residues called used shot blast that composes mainly of iron (Fe^0). Used shot blast continuously increases every year and it normally disposes by landfilling method. Therefore, utilization of used shot blast should be the better approach. Due to it comprises of Fe^0, this means it is likely to be a catalyst in modified Fenton process because Fe^0 in water has iron oxide surrounded around surface and transfers to Fe^{2+} in aeration condition (O_2) and acid condition (H^+) then it forms H_2O_2 and generates HO• for oxidize pollutants in wastewater. Thus, the purpose of this project is to use used shot blast with aeration system (called Fe^0/air modified Fenton process) to treat WAUF wastewater.

1.2 Objectives

1. To determine treatment efficiency of WAUF wastewater via Fe^0/air modified Fenton process.
2. To optimize the conditions (pH, air flow rate, shot blast dosage and reaction time) for WAUF wastewater treatment.

1.3 Scope of study

1. WAUF wastewater sampling was from lumber mill factory
2. Treatment time of WAUF wastewater for Fe^0/air modified Fenton reaction were 5, 15, 30, 45, 60, 90 and 120 minutes
3. pH was adjusted in acidic condition range from 2.0 to 4.0
4. Aeration System (O_2) generated from air pump and adjusted air flow rate (0.5, 1.0, 1.5, and 2.0 L/min) with air flow meter
5. Fe^0 obtained from used shot blast in auto part manufacturing with concentration of 10, 20, 30, and 40 g/L

1.4 Benefits

1. Increase the capability and efficiency of WAUF wastewater treatment
2. Increase the value of iron waste (used shot blast) from industry as apply to treat wastewater
3. Apply the optimum condition of Fe^0/air modified Fenton process in laboratory to design for real industrial wastewater treatment plant

CHAPTER 2

THEORY AND LITERATURE REVIEW

2.1 Fundamental of Lumber wood

Lumber is a raw material used in many industries. It can be used as construction or decorative materials such as door and window frames etc. In general, Lumber mill processing can be divided into two types of products, which are sawn timber and wood-based Panel.

1. Sawn timber is the process of converting large log pieces in order to produce the desired size and quality. Next, they are compressed and baked in a chemical solution to maintain quality before selling products. Sawn Timber can be produced from many types of perennials, including hardwoods such as teak, Pradu wood, rosewood and softwood such as rubber wood. In the past, furniture manufacturers used Sawn Timber as the main raw material for furniture production. Until the forest areas of the world are rapidly decreasing and becoming forest conservation around the world. Therefore, it often uses wood-based panel in order to make the best utilization of various wood resources (Kijchai, 2016).

2. Wood-based panel is a product that is applied from knowledge and technology to be able to reduce using large log pieces which are rare and expensive. It can be divided into different three products such as plywood, particleboard, and fiberboard (Nuryawan, Park, and Singh, 2014). All three products have different manufacturing processes that depend on the objective of utilization.

Fiberboard is made up of branches and then taken the wood fibers to compress into wood plates by heating. The chemical adhesive resin (urea-formaldehyde) is bonded together to create fiberboard. In Thailand, most of the raw materials are used from rubber and eucalyptus trees as the main raw materials. Medium density fiberboard or MDF is a wood-based panel that has similar properties to natural wood and able to be used for a variety of purposes especially in the production of furniture.

2.2 Lumber mill processing

The processes of lumber mill production are follows:

1. Crushing wood is passed to the refiner to grind the lumber into wood fibers by using Urea-Formaldehyde, which connects wood fibers together until becoming a wood fiber mixed with glue (Kijchai, 2016).

2. Baking process, which is the steaming process by transporting through the dryer, absorbs water and reduces moisture.

3. Forming process, wood fibers mixed with glue that has been baked and it will be sent to the fiber spreading machine. They are made into a layer of thickness according to the production formula specified to get the desired thickness and density of wood.

4. Compressing sheets wood fibers mixed with glue that is made into a thick layer will be compressed using heat and high pressure in order to become a solid wood board with the specified density example medium density fiber board or MDF. This step is the last step in the main processing. It is important and takes the longest to produce. When the sheet wood fibers have been pressed, the cutter is installed at the end of the main machine and left the production to be a wood board. Later, the productions will be packing for the next step of transportation (Kijchai, 2016).te

From the above processing, it shows that urea-formaldehyde is used as a binder in wood production resulting in wood adhesive urea-formaldehyde wastewater.

2.3 Wood Adhesive Urea-formaldehyde (WAUF)

2.3.1 Characteristic of WAUF wastewater

Figure 2.1 characteristic of WAUF wastewater

Urea-formaldehyde (UF) resin is produced from the main raw material such as urea and formaldehyde. It is the thermo-setting resin, which is received heating to convert solid phase. Characteristic is as a milky white liquid (as shown in Figure 2.1) which has the formaldehyde odor leftover from the reaction and has a pH between 7-9 (Eternal resin, 2002). UF is commonly used to make plywood board and MDF board. It still resists moisture, but it does not resist water. Researchers revealed that WAUF wastewater has a high chemical oxygen demand (COD) reached around 0.4–4.0 g/L (Garrido, Mendez, and Lema, 2000).

2.3.2 Reaction of UF resin

1) Addition reaction or methylolation (Suranard, 2007)

Reaction between urea and formaldehyde generate methal-urea in base condition

$$NH_2COONH_2 + CH_2O \longrightarrow NH_2CONHCH_2OH$$

Urea + formaldehyde ⟶ methal-urea

2) Condensation reaction or polymerization reaction

Reaction of two methal-urea compounds generate urea-formaldehyde resin and water in acid condition

$$2NH_2CONHCH_2OH \longrightarrow NH_2CONH\text{-}CH_2NHCONH_2CH_2OH + H_2O$$

2 methal-urea ⟶ **urea-formaldehyde resin** + water

There are several methods that can treat wood adhesive urea-formaldehyde wastewater. Advanced Oxidation Processes (AOPs) is one of the alternative wastewater treatments.

2.4 Advanced oxidation processes (AOPs)

Advanced oxidation processes (AOPs) often oxidize the organic compounds by using hydroxyl radicals (HO•) which is characterized as a short-lived, powerful oxidant with a standard reduction potential (2.8V) that is higher than many other strong oxidants. The most reducing agents are hydrogen peroxide (H_2O_2), titanium dioxide (TiO_2), ozone (O_3) and UV (Boonrung, 2010).

During the AOPs treatment of wastewater, hydroxyl radicals or sulfate radicals is generated to remove refractory organic matters, traceable organic contaminants, and certain inorganic pollutants. AOPs show many advantages including the transformation of organic compounds into simpler and less dangerous pollutants to CO_2 and H_2O, and no sludge production (Mikhak, 2019). Fenton process which is one of the AOPS is often used.

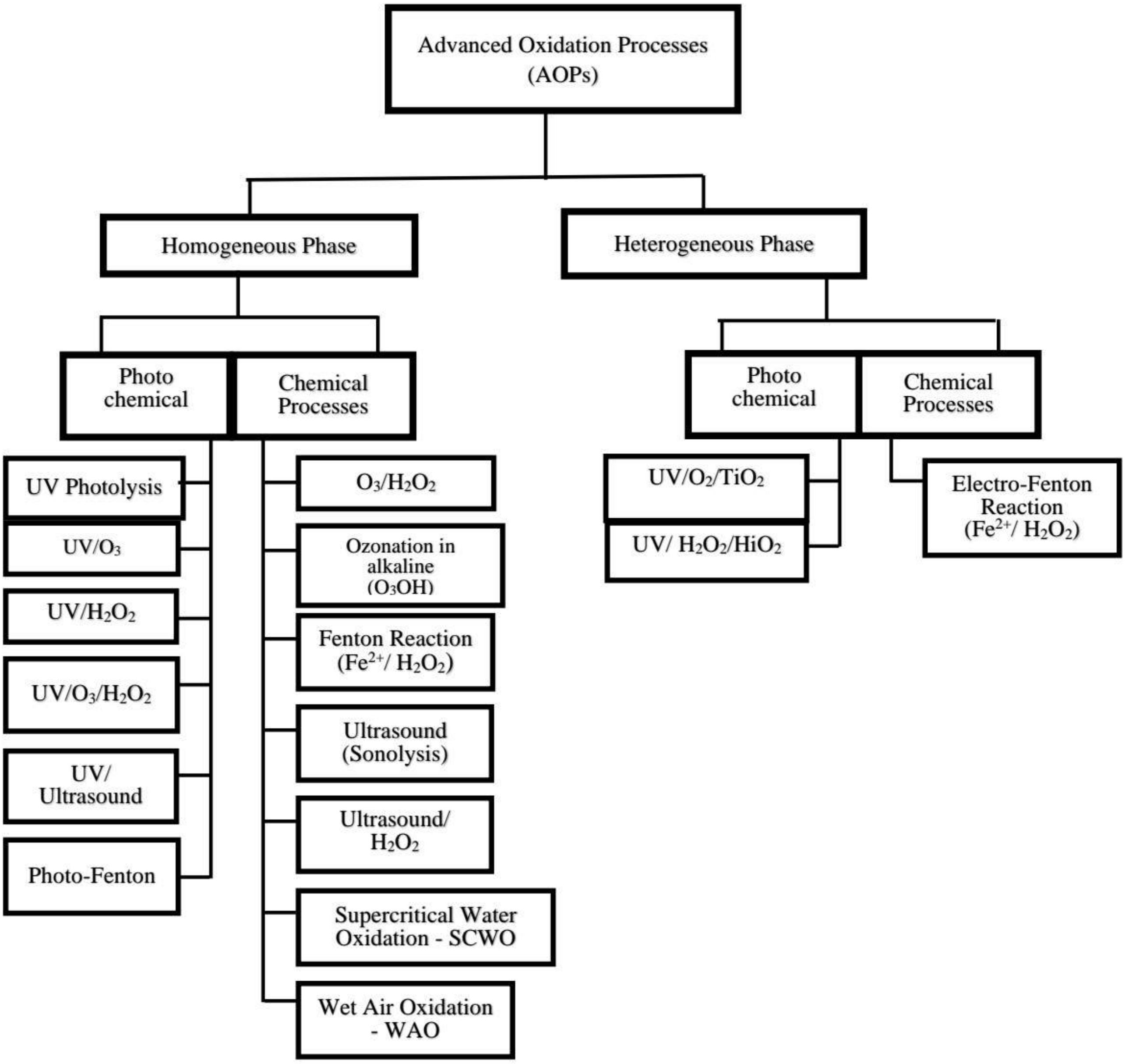


Figure 2.2 Type of Advanced Oxidation Processes (AOPs) (Bin A.K., 2012)

2.5 Fenton Process: Ferrous ion

The Fenton process is commonly used in wastewater treatment. It uses hydrogen peroxide and ferrous iron in the reaction. The effectiveness of degradation has been proved that it can treat many different types of wastewater (Bautista et al., 2008). Due to the rapid reaction between ferrous iron and hydrogen peroxide, the activation of them and the generation of HO• are done in the shortest time (Babuponnusami and Muthukumar, 2013) and mineralization let the transformations of organic pollutants into carbon dioxide and water. The limitation is high operating cost such as ferrous ion (Fe^{2+}), hydrogen peroxide

(H_2O_2) and high acid chemical agent (H^+) (Zhang et al., 2019). The Modified Fenton process has been applied in solving apparent limitation in the Fenton process.

2.6 Modified Fenton Process

2.6.1 Modified Fenton

Modified Fenton is used in the treatment of wastewater using other catalysts instead of ferrous ion. These methods have efficiency and adjust limitation of Fenton process. The choice of alternative zero-valent metals with higher efficiency of producing ROS depends on the transfer of electrons to oxygen and the stability of the dissolved metal species in wide pH range (Bokare and Choi, 2009). Zero-valent metal (ZVM) have many types example for ZVAI, ZVNi, ZVZn, and ZVI etc. ZVI is quite popular in wastewater treatment.

2.6.2 Zero-Valent Iron (ZVI)

Zero-Valent Iron (ZVI) is one of the most promising materials of wastewater treatment, due to its low operating cost-effective and non-toxicity. It has ability to degrade or transform various pollutants in wastewater (Crane, 2012).

$$Fe^0 (s) + 2H_2O (aq) \rightarrow Fe^{2+} (aq) + H_2(g) + 2OH^- (aq) \quad (2.1)$$

$$Fe^0 (s) + O_2(g) + 2H^+ \rightarrow Fe^{2+} (aq) + H_2O_2 (aq) \quad (2.2)$$

$$Fe^0 (s) + H_2O_2 (aq) \rightarrow Fe^{2+} (aq) + 2OH^-(aq) \quad (2.3)$$

$$Fe^{2+} (aq) + H_2O_2 (aq) \rightarrow Fe^{3+} (aq) + OH^-(aq) + HO\bullet \quad (2.4)$$

$$HO\bullet + \text{refractory compounds} \rightarrow H_2O + CO_2 + \text{inorganic compounds} \quad (2.5)$$

(Raman, 2016)

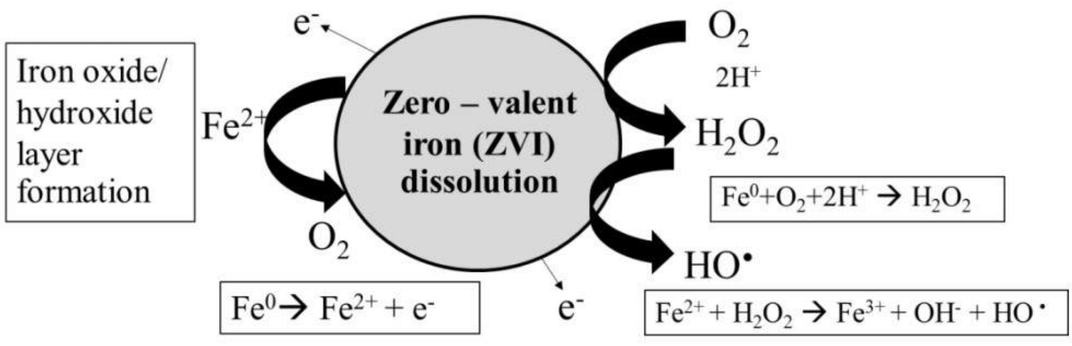


Figure 2.3 The OH radical generation related with iron dissolution (Harada et al., 2016)

When ZVI (Fe^0) combined with oxygen (aeration system), it forms ferrous ion (Fe^{2+}) and hydrogen peroxide (H_2O_2) in acid condition and then become ferric ion (Fe^{3+}), hydroxide ion (OH-), and hydroxyl radical (HO•) (as shown in Figure 2.3). Hydroxyl radical will transform pollutants into CO_2 and water. In acid condition, it has accelerated corrosion of iron oxide or iron hydroxide layer surrounded around Fe^0 in presence of oxygen (O_2). Furthermore, using aeration system (O_2) instead of adding H_2O_2 reduces operating costs and uses less chemical agent.

2.6.3 Aeration System

Aeration system in Fenton process could improve the mass transfer rate to active site of zero-valent iron (ZVI or Fe^0) and oxygen in air or air pump could be dissolved into solution. Sufficient air flow rate should be provided to improve the mass transfer rate and dissolved oxygen (DO). DO from air flow could accept electron released from the corrosion of Fe^0 and form into H_2O_2. It reacts with Fe^{2+} and generates hydroxyl radical (Yuan et al., 2016). When combined modified Fenton process and aeration system together (Fe^0/air), COD removal efficiencies is higher than Fenton process. Therefore, using aeration system is interesting for wastewater treatment.

2.7 Factors affecting Modified Fenton reaction

1. Effect of the initial pH: Lower pH accelerates the corrosion of Fe^0, which electron released. Fe^0 will transfer rapidly to Fe^{2+} (Teixeira et al., 2015).

2. Effect of used Fe^0 dosage: It increases surface area and active sites in order to favor of Fenton-like reaction.

3. Effect of air flow rate: Sufficient air flow rate should be provided to improve the mass transfer rate, DO and corrosion products. DO from air flow could accept electron released from the corrosion of Fe^0 and form into H_2O_2.

4. Reaction time: The reaction time depends on types of wastewater and its concentration (Pimonporn, 2014).

Fe^0 can be found from residual of manufacturing process in Auto parts manufacturing. Utilization of industry waste will reduce the amount of waste that is treated or disposed in secure landfill.

2.8 Auto parts manufacturing

2.8.1 Fundamental of Auto parts manufacturing process

Auto parts manufacturing has high quality control started from casting to machining process and contributes significantly to the growth of demands of automobile and motorcycles in Thailand. Products can be classified into main three types. When passing through many processes, it will cause increasing industry wastes resulting in many wastes that can be recycled or treated before landfill. Utilization of industry waste is interesting because properties of some of industry waste can be used.

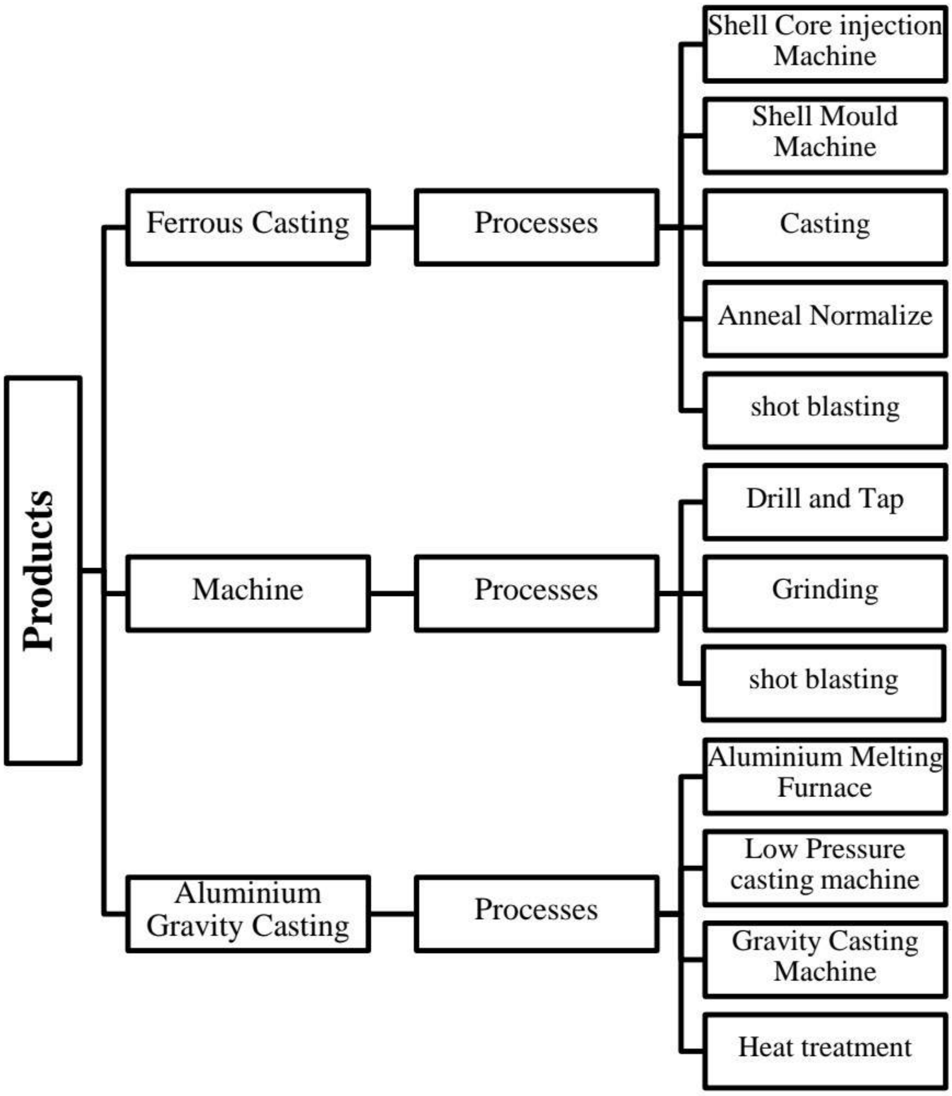


Figure 2.4 Flowchart of products and processes of Auto parts manufacturing (YAMAHA motor parts manufacturing Thailand, 2011)

2.8.2 Shot Blasting

Shot blasting is the process of forming a work piece by polishing products with a high-speed spherical material, which used usually shot blast grains (Fe^0). This process is carried out in different ways in a limited space to be reused and to limit the amount of dust. The most of shot blasting is based on the wind through the shot blasting nozzle, which creates a vacuum. Shot blast grains will through pass of surface products (Tidtanon, 2015). The purpose of shot blasting is

1. Polish the steel or cleaning the surface before coating, plating various substances or spraying products
2. Decorate of auto products
3. Reduce magnetism

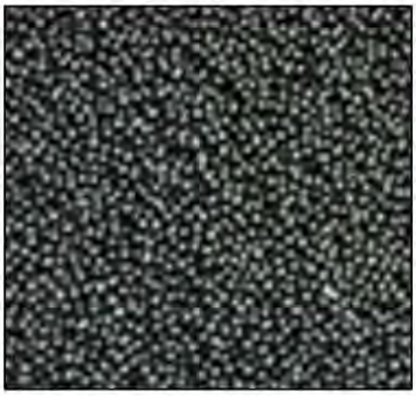


Figure 2.5 Characteristic of shot blast

The residual of shot blast generates from shot blasting process. Property of shot blast is zero-valent iron and then it can be used in wastewater treatment.

2.9 Literature review

Li et al. (2009) studied treatment of triazophos pesticide wastewater. The initial COD of synthesized wastewater and industrial wastewater were 3,242 and 3,418 mg/L, respectively. The optimum condition of synthesized wastewater was at pH 4.0, treatment time 1.30 hours, 2.5 g/L of $FeSO_4.7H_2O$ and 100 mL/L of 30% H_2O_2. The removal efficiency of COD was 96.3 %. The optimum reaction of actual industrial wastewater was at pH 4.0, treatment time 1.30 hours, 5.0 g/L of $FeSO_4.7H_2O$ and 75 mL/L of 30% H_2O_2. The removal efficiency of COD was 85.4%. When higher pH than 4.0, H_2O_2 decomposed slowly and generated less hydroxyl radical but the flocculation by ferric hydroxide supported the little removal of COD at high pH. When pollutants are degraded via Fe^{2+} transferred to Fe^{3+} in Fenton reaction. H_2O_2 dosage consumed and then hydroxyl radical decreased. Fenton reaction can treat high COD value and high toxic of wastewater.

Shimizu et al. (2012) studied phenol wastewater treated by combined zero-valent iron and aeration system (Fe^0/air). Phenol wastewater consists of phenol, hydroquinone, and catechol. The optimum reaction was at a pH 3.0, treatment time 23 hours, air flow rate 0.5 L/min, and 1 g/L of Fe^0 dosage. The removal efficiency of COD was 91% and TOC value was 24%, respectively. Advantages of Fe^0 are reducing agent, non-expensive, reactive in water (electron donor), produce strong oxidants etc. Removal of organic contaminants come from reductive transformation and adsorption/precipitation. Fenton reaction slightly occurred adsorption/precipitation on Fe^0 surface for little removal of pollutants in wastewater.

Xiong et al. (2015) studied P-nitro phenol (PNP) wastewater by Fe/Cu bimetallic and ZVI under optimal conditions such as initial pH 6.7, Fe^0 dosage 20 g/L, treatment time 60 minute, and air flow rate 1.5 L/min. Catalyst was Fe/Cu. COD removal efficiency and TOC efficiency reached about 83.8 % and 83.2%, respectively. In this study, comparative capacity of biodegradability PNP followed the trend that Fe/Cu (air)>Fe/Cu (N_2: 0–30min, air: 30–120min)>control-Fe (air)>Fe/Cu (without aeration)>Fe/Cu (N_2)>control-Fe (N_2). Therefore, DO will improve the mineralization of PNP and Cu enhance the reactivity of Fe^0.

Yuan et al. (2016) [a] studied the dinitrodiazophenol (DDNP) industry wastewater that was treated by combined Fe^0/air and Fenton process (1st Fe^0 /air - 2nd Fenton -3rd Fe^0/air). Under the optimum conditions of Fe^0/air such as initial pH 2.0, Fe^0 dosage 40 g/L, treatment time 30 minutes, air flow rate 1.5 L/min. Initial pH in Fenton process was pH 3.0, and treatment time 60 minutes. COD removal efficiency from 66.1 %,61.0 % and 78 %

respectively. In COD removal efficiency of 2nd Fenton process was lower than 1st Fe^0 /air Because $Fe(OH)_2$/$Fe(OH)_3$ formed in first step adsorbed pollutants but they would be dissolved and released them when pH was adjusted to 3.0. Fe^0 in 3rd Fe^0 /air can promote the decomposition of the residual H_2O_2. It has been proved ZVI can intensify Fenton process. Moreover, chromaticity removal efficiency reached about 98% and BOD_5/COD ratio reached about 0.27. Improvement of biodegradability was mainly resulting from the synergistic reaction between Fe^0/air and Fenton process.

Yuan et al.(2016) [b] studied ammunition wastewater by combined ZVI (Fe^0) /air and Fenton process under optimal conditions such as initial pH 2.5, Fe^0 dosage 10 g/L, treatment time 60 minutes, air flow rate 1.0 L/min and initial pH in Fenton process that was pH 3.0 and treatment time 120 minutes. COD removal efficiency was around 94.6%. The generated Fe^{2+}/Fe^{3+} in Fe^0/air could be used as the catalyst of Fenton reaction which decompose residual intermediates and pollutants. In this study, 1st Fe^0 /air - 2nd Fenton -3rd Fe^0/air can be considered as a cost-effective, feasible and efficiency for ammunition wastewater treatment.

It can be concluded in the literature review in Table 2.1 that many researchers used Fe^0 as catalysts in Fenton reaction. The conditions used in the experiment of initial pH, initial Fe^0 dosage, optimum air flow rate, and treatment time were in range of 2.0-4.0, 10 and 40 g/L, 0.5 - 1.5 L/min, 0.5 - 1 hour. The efficiencies of COD removal were in the range around 70% to 95%.

Table 2.1 Summarization of the literature review

Researcher (year)	Type of wastewater	Process	Parameters	Efficiency Removal (%)	Optimal condition in research				
					Initial pH	Initial dosage (g/L)	Air flow rate (L/min)	Time (hours)	Catalyst
Li et al. (2009)	Triazophos industrial wastewater	Fenton Process	Triazophos pesticide	85.4	4.0	5.0	-	1.30	$FeSO_4.7H_2O$
Shimizu et al. (2012)	Phenol	Fe^0/air	Phenol, hydroquinone, catechol	91	3.0	1	0.5	23	Fe^0
			TOC	24					
Xiong et al. (2015)	P-nitrophenol (PNP)	Fe/Cu bimetallic and ZVI	COD	83.8	6.7	20	1.5	1	Fe/Cu
			TOC	83.2					
Yuan et al. (2016) [a]	Dinitrodiazo-phenol industry	Combined ZVI (Fe^0) /air and Fenton process	COD	78	2.0	40	1.5	0.5	Fe^0
			Coloration	98					
			Nitro, Benzene, Azo group	99.83					
Yuan et al. (2016) [b]	Ammunition	Combined ZVI (Fe^0) /air and Fenton process	COD	94.6	2.5	10	1.0	1	Fe^0

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

3.1.1 Equipment for

3.1.1.1 modified Fenton process

1) DWYER model RMA-26-SSV flow meter 2sacle 0.5-5 LPM Air
2) Air pump: Resun LP-100
3) Flexible silicone tube, plastic joints, air stone bubble
4) Parafilm
5) Erlenmeyer flask 125 mL

3.1.1.2 COD

1) Digestion vessels
2) COD reactor: Hach DRB 200
3) Oven: WTB BINDER FD115
4) Glass wares
5) Distilled water
6) Analytical Balance: Mettler Toledo
7) Burette
9) Pipette

3.1.1.3 BOD

1) BOD bottle
2) BOD incubator
4) Glass wares
5) Distilled water
7) Burette
9) Pipette

3.1.1.4 Total iron

1) Spectrophotometer
2) Hot plate
3) Volumetric flask 50 mL

3.1.1.5 parameter of wastewater

1) Lutron pen pH meter
2) DO meter: Hach 51850-11 Sension 6
3) Conductivity meter: Hach 5465010 Sension 156 PH
4) Turbidity Meter: HACH 2100P
5) Vacuum pump
6) Glass microfiber filters GF/C™: Whatman™
7) Evaporating Dish
8) Water bath: Memmert

3.1.2 Chemical agents for

3.1.2.1 modified Fenton reaction

1) Shot blast
2) Sulfuric acid (H_2SO_4)
3) Sodium Hydroxide (NaOH)

3.1.2.2 COD

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
6) 20% Ferrous sulfate (20% $FeSO_4.7H_2O$)
7) 1,10-Phenanthroline monohydrate ($C_{12}H_8N_2$.H2O)

3.1.2.3 BOD

1) Potassium dihydrogen phosphate (KH_2PO_4)
2) Sodium hydrogen phosphate heptahydrate ($Na_2HPO_4.7H_2O$)
3) Dipotassium hydrogen phosphate (K_2HPO_4)
4) Ammonium chloride (NH_4Cl)
5) Magnesium sulfate heptahydrate ($MgSO_4.7H_2O$)
6) Anhydrous calcium chloride ($CaCl_2$)
7) Iron(III) chloride hexahydrate ($FeCl_3.6H_2O$)
8) Manganese(II) Sulfate Monohydrate ($MnSO_4$.H2O)
9) Sodium Hydroxide (NaOH)
10) Sodium iodide (NaI)
11) Sodium azide (NaN_3)

12) Conc. sulfuric acid 98% (H_2SO_4)
13) Starch
14) Salicylic acid
15) Sodium Thiosulfate Pentahydrate ($Na_2S_2O_3.5H_2O$)
16) Potassium dichromate ($K_2Cr_2O_7$)
17) Potassium iodide (KI)

3.1.2.4 total iron

1) Conc. HCI
2) Hydroxylamine solution
3) Ammonium acetate buffer solution
4) Sodium acetate solution
5) Phenanthroline
6) Stock standard solution

3.2 Experimental procedure

Wood adhesives urea-formaldehyde (WAUF) wastewater samples were collected from Lumber Wood factory in Pathumthani province. It was measured pH, DO, turbidity, conductivity, BOD, COD, TSS, TDS, B/C ratio, and total iron (Table 3.1) before experiment. WAUF was treated via modified Fenton process with used shot blast. Several optimum conditions were varied such as reaction time, pH, air flow rate, and amount of used shot blast for COD removal. Treatment with maximum COD removal efficiency was selected to measure pH, DO, turbidity, conductivity, BOD, TSS, TDS, BOD/COD, and total iron. The flow chart of experimental procedure was shown in Figure 3.1.

Flowchart of experiment

1. Collected WAUF wastewater from lumber mill factory and measured pH, DO, conductivity, turbidity BOD, COD, TDS, TSS, B/C ratio, and total iron before experiment.

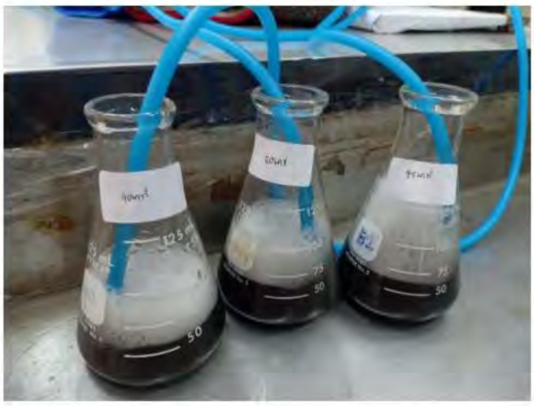
⇩

Setup the experiment

Air pump

Air flow meter

Added shot blast in 75 mL of WAUF wastewater in Erlenmeyer flask125 mL



⇩

2. Determined the optimum conditions for COD removal

⇩

2.1 Determined the optimum reaction time of COD removal

Sample No.	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Time (min)	5	15	30	45	60	90	120
pH	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Air flow rate(L/min)	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Shot blast (g/L)	20	20	20	20	20	20	20

⇩

2.2 Determined the optimum pH of COD removal

Sample No.	**1**	**2**	**3**	**Control**
Time (min)	Optimum time			
pH	2.0	3.0	4.0	-
Air flow rate(L/min)	1.5	1.5	1.5	1.5
Shot blast (g/L)	20	20	20	20

⇩

2.3 Determined the optimum Air flow rate of COD removal

Sample No.	**1**	**2**	**3**	**4**	**Control**
Time(min)	Optimum time				
pH	Optimum pH				
Air flow rate(L/min)	0.5	1.0	1.5	2.0	-
Shot blast (g/L)	20	20	20	20	20

⇩

2.4 Determined the optimum amount of used shot blast of COD removal

Sample No.	1	2	3	4	Control
Time(min)	Optimum time				
pH	Optimum pH				
Air flow rate(L/min)	Optimum Air flow rate				
Shot blast (g/L)	10	20	30	40	-

⇩

3. The only optimum condition was selected to measure pH, DO, conductivity, turbidity BOD, COD, TDS, TSS, total iron and B/C ratio after experiment.

Figure 3.1 Flow chart of experimental procedure

The procedure to determine optimum condition of WAUF wastewater treatment via Fe^0/air modified Fenton process was done as follows:

3.2.1 Determined the optimum reaction time

1) Adjusted pH to 3.0 using H_2SO_4 or NaOH

2) Poured 75 mL of the sample WAUF wastewater in the Erlenmeyer flask 125 mL and added 20 g/L of used shot blast

3) Aerated with air flow rate 1.5 L/min for 5, 15, 30, 45, 60, 90 and 120 minutes

4) Measured COD for all flasks

The optimum time of COD removal was used in the next section.

3.2.2 Determined the optimum pH

1) Adjusted pH to 2.0, 3.0, and 4.0 using H_2SO_4 or NaOH

2) Poured 75 mL of the sample WAUF wastewater in the Erlenmeyer flask 125 mL and added 20 g/L of shot blast

3) Aerated with air flow rate 1.5 L/min with the optimum reaction time received from 3.2.1

4) Measured COD for all flasks

The optimum pH of COD removal was used in the next section.

3.2.3 Determined the optimum air flow rate

1) Adjusted the optimum pH received from 3.2.2

2) Poured 75 mL of the sample WAUF wastewater in the Erlenmeyer flask 125 mL and added 20 g/L of shot blast

3) Aerated with air flow rate 0.5, 1.0, 1.5, and 2 L/min with the optimum reaction received from 3.2.1

4) Measured COD for all flasks

The optimum air flow rate of COD removal was used in the next section.

3.2.4 Determined the optimum of used shot blast

1) Adjusted the optimum pH received from 3.2.2

2) Poured 75 mL of the sample WAUF wastewater in the Erlenmeyer flask 125 mL and added amount of used shot blast 10, 20, 30, and 40 g/L respectively

3) Aerated with air flow rate received from 3.2.3 with the optimum reaction time received from 3.2.1

4) Measured COD for all flasks

Every experimental steps from 3.2.1 - 3.2.4 had the control group and all studies were performed in triplicate.

a b

Figure 3.2 Measured a) pH and b) DO (before and after WAUF wastewater treatment)

Figure 3.3 Setup experiment

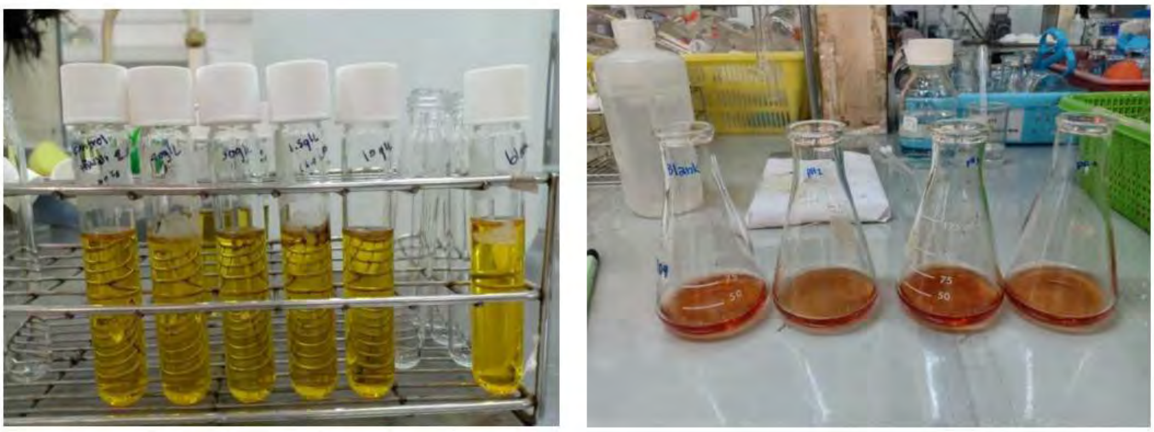


Figure 3.4 Measured COD for COD removal efficiency after WAUF wastewater treatment

Figure 3.5 WAUF wastewater before and after treatment via Fe^0/air modified Fenton reaction

3.3 Analytical methods

The removal efficiency (%) will be calculated via Eq. (3.1)

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

Where C_i is the initial concentration

C_f is the concentration after treatment

Table 3.1 Analytical Methods

Parameter	Analytical Methods	Unit
COD	Closed Reflux Method	mg/L
TDS	Total Dissolved Solids Dried at 180°C	mg/L
TSS	Total Suspended Solids Dried at 103–105°C	mg/L
pH	Electrometric Method	-
Conductivity	Laboratory Method	µs/cm
DO	Membrane electrode	mg/L
Turbidity	Nephelometric Method	NTU
BOD	5-Day BOD Test	mg/L
Total iron	Atomic Absorption Spectrometric	mg/L

3.4 Statistical analysis

The data analysis was conducted using SPSS 22.0 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

The studies were conducted by sampling of wood adhesives urea-formaldehyde (WAUF) wastewater from lumber mill factory. Physical properties of WAUF were murky white and white sediment. Chemical properties i.e., COD, BOD, pH, conductivity, turbidity, TSS, TDS, total iron, and BOD/COD ratio were 32,000 mg/L, 2,850 mg/L, 3.0, 1,770 μs/cm, 9.99 NTU, 226 mg/L, 6,140 mg/L, 0 mg/L, and 0.08 respectively. The results from the treatment of WAUF wastewater with Fe^0/air-Fenton process (used shot blast (Fe^0) in aeration system (O_2)) included control samples were investigated in triplicate. WAUF wastewater by varied treatment time, pH, air flow rate, and used shot blast were described as follows:

4.1 Characteristic of used shot blast

Used shot blast generated from shot blasting process in auto parts manufacturing was used as a catalyst in Fe^0/air-Fenton process. The result from Energy Dispersive X-Ray Spectroscopy (EDS) showed that used shot blast consists of Fe 80.05 % which reasonable to treat wastewater with modified Fenton process.

4.2 Effect of the treatment time

Treatment time can affect to pH, DO, and COD removal efficiency. 75 mL of WAUF wastewater was adjusted pH to 3.0 and added 20 g/L of used shot blast, and aerated with air flow rate 1.5 L/min for 5, 15, 30, 45, 60, 90 and 120 min. pH, DO and COD of all samples were then measured. The optimum time that provided highest COD removal efficiency would be used in the next section. Note that in control experiments, two identical experiments were carried out: in one of them, the treatment with only used shot blast was applied whereas in the other group, the treatment with only aeration system was tested. The result is illustrated in Figure 4.1.

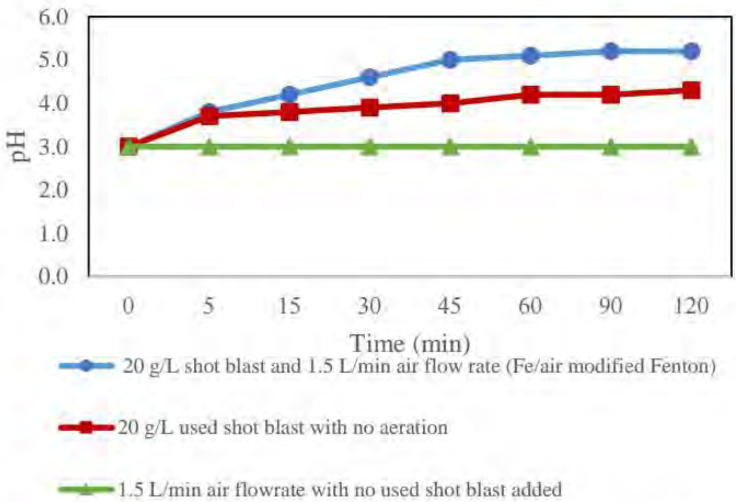


Figure 4.1 pH of WAUF wastewater at different time after treated via Fe^0/air modified Fenton reaction

Figure 4.1 illustrates that pH after WAUF wastewater treatment via Fe^0/air modified Fenton reaction increased rapidly from 3.0 to 5.2 because Fe^0 transformed into Fe^{2+} and significantly generated hydroxide ion following Eqs. 2.1, 2.3, and 2.4. pH increased along the experiment. pH after WAUF treatment at different time via used shot blast alone rise steadily from 3.0 to 4.3. This causes corrosion from iron oxide surrounded of shot blast and Fe^{2+} generated in system resulting in increasing of OH^- after treatment. pH of sole aeration remained stable at 3.0 throughout the experiment because there was no shot blast in order to convert Fe^0 into Fe^{2+}.

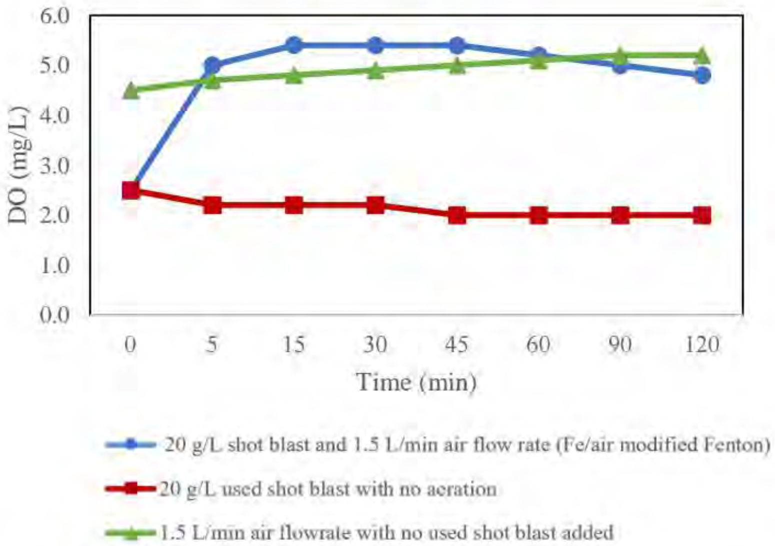


Figure 4.2 DO of WAUF wastewater at different time after treated via Fe^0/air modified Fenton reaction

Figure 4.2 shows initial DO via Fe^0/air modified Fenton reaction was 2.5 mg/L and DO after WAUF wastewater treatment remained steady at 15 to 45 min and then slightly decreased from 60 to 120 min. This means it had enough DO for the reaction to removal pollutants. In contrast, initial DO of used shot blast alone was 2.5 mg/L and DO after WAUF treatment decreased slowly and remained constant at 2.0 mg/L from 45 to 120 min. This causes no air added in the reaction. DO consumption in the reaction was slightly treated pollutants in wastewater. Initial DO from aeration system was 4.5 mg/L and DO after WAUF treatment increased slowly. This can be concluded that DO still did not react with Fe^0 in control experiment. Note that this experiment was done in atmospheric temperature, it can increase DO intake efficiency by control at low temperature.

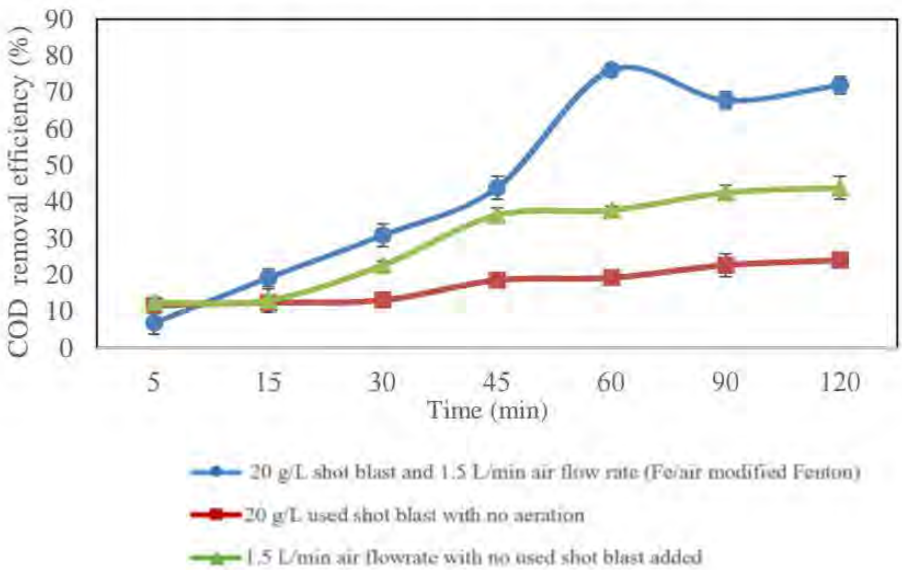


Figure 4.3 COD removal efficiency at different time from Fe^0/air modified Fenton and control groups at $p < 0.05$ by the one-way ANOVA

In Figure 4.3, Fe^0/air modified Fenton reaction (pH 3.0, air 1.5 L/min and Fe^0 20 g/L) displayed maximum COD removal efficiency of 76.03% at 60 min. At treatment time of 90 and 120 min, COD removal efficiencies were 67.81% and 71.92%, however; result from analysis of one-way ANOVA (at $p < 0.05$) revealed that COD removal efficiencies were not statistical difference among 60, 90 and 120 min. This means that the optimum time should be 60 min because shorter time can save treatment cost. From Equations 2.1 to 2.5, when Fe^0 is filled in the WAUF wastewater, it can be transformed to Fe^{2+} which dissolution in acidic condition. It then forms H_2O_2 from the presence of dissolved oxygen and change to OH·. This OH· can oxidize organic in WAUF wastewater resulting in COD removal.

COD removal efficiency from used shot blast alone (pH 3.0 and Fe^0 20 g/L), in this study, continuously increased with increasing time and showed the highest efficiency 23.97 % with treatment time 120 min. The efficiency of WAUF treatment via only used shot blast was much lower than via Fe^0/air modified Fenton. The mechanisms of used shot blast to remove COD in wastewater were adsorption and precipitation of organic pollutants onto the Fe^0 surface (Huang et al., 2018).

The result from aeration system (pH 3.0 and air 1.5 L/min), in this experiment, found that COD removal efficiency continuously increased with increasing time and displayed maximum efficiency of 43.84% with treatment time 120 min. The extravagant oxygen can remove pollutants gradually by repulse Urea-formaldehyde volatile from wastewater.

From the result above, it can be concluded that optimum time of WAUF wastewater treatment via Fe^0/air modified Fenton reaction was 60 min. This reaction time will be used in further investigation.

4.3 Effect of initial pH

WAUF wastewater was adjusted pH to 2, 3 and 4, added 20 g/L of used shot blast and aerated with air flow rate (O_2) 1.5 L/min for 60 min. pH, DO, and COD were measured at the end of reaction. Note that the control sample was WAUF wastewater with no pH adjustment (pH = 3.4). Table 4.2 shows that pH after WAUF wastewater treatment via Fe^0/air modified Fenton reaction significantly increased. Due to transformation of Fe^0 to Fe^{2+} and generated hydroxide ion, pH was higher than before treatment. DO after treatment dropped gradually because Fe^{2+} reacted with oxygen to form H_2O_2 and generated hydroxyl radical to treat organic pollutants.

Table 4.1 pH and DO after WAUF treatment at different initial pH via Fe^0/air modified Fenton reaction

Initial pH	**Final pH**	**DO (mg/L)**
2.0	2.8	5.4
3.0	4.9	5.2
3.4 (control)	5.1	5.2
4.0	5.8	5.1

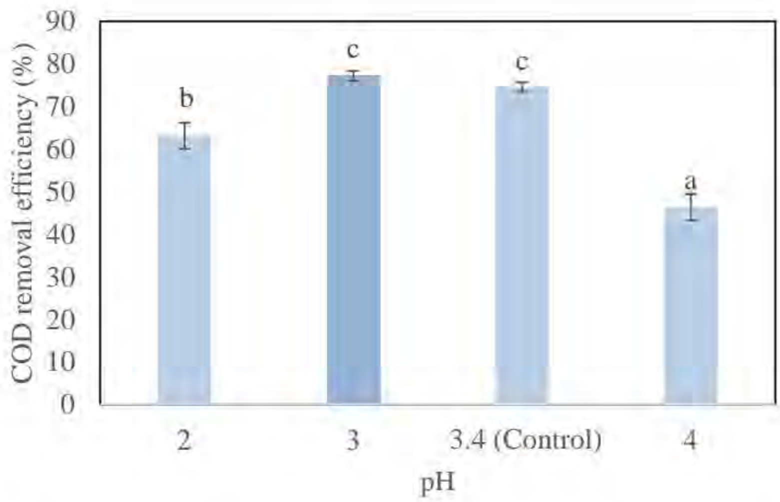


Figure 4.4 COD removal efficiency at different pH from Fe^0/air modified Fenton at $p < 0.05$ by the one-way ANOVA

The optimum pH for COD removal was studied by varying initial pH from 2 to 4 and control experiment (no adjusted pH). The experiments were carried out with air flow rate 1.5 L/min and used shot blast 20 g/L. The results from Figure 4.4 found that the highest COD removal for Fe^0/air modified Fenton was 77.18 % at pH 3.0. Moreover, COD removal efficiency of control experiment (pH 3.4) was 74.50 %. For statistical analysis, the effects of pH 3.0 and control pH 3.4 showed no significant difference in the WAUF treatment at $p < 0.05$ by the one-way ANOVA.

There are several reasons for explanation the highest COD removal via modified Fenton reaction. Firstly, the lower pH is favor for the degradation of pollutants. Acidic condition would accelerate the corrosion of layer surrounded of Fe^0 (or used shot blast in this study) which electron released from Fe^0 and more transferred into Fe^{2+} (Chang et al., 2009 and Yuan et al., 2016). Secondly, pH 2.0 has excess H^+ in system resulting in H_2O_2 tends to form to oxonium ion ($H_3O_2^+$) instead of hydroxyl radical (OH·). As the fact that $H_3O_2^+$ has lower oxidation potential than OH·, hence, extremely low pH condition reduces COD removal efficiency (Kwon et al., 1999). Thirdly, normally, high efficiency of Fenton reaction should continuously transform Fe^{3+} back to Fe^{2+} for productive reaction with H_2O_2 or O_2. However, higher pH (pH 4.0 in this study) obstruct Fe^{3+} converting to Fe^{2+} resulting in less producing free radical and treating efficiency (Pimonporn, 2014; Walling,1975; Sailumpore, 1998; Jeong, and Yoon, 2005).

From the result in this section, pH 3.0 was an optimum pH for WAUF wastewater treatment via Fe^0/air modified Fenton and would be used in further investigation.

4.4 Effect of air flow rate

75 mL WAUF wastewater was adjusted pH to 3.0 and added 20 g/L of used shot blast. Then aerated with air flow rate (O_2) 0.5 – 2.0 L/min for 60 min. pH, DO, and COD were measured at the end of experiment. Note that the control sample was WAUF wastewater with 20 g/L of used shot blast and no aeration. Table 4.3 shows that pH and DO of WAUF wastewater treatment via Fe^0/air modified Fenton reaction increased at the end of experiment.

Table 4.2 pH and DO after WAUF treatment at different of air flow rate via Fe^0/air modified Fenton reaction

Air flow rate (L/min)	pH	DO (mg/L)
0 (Control)	4.2	2.0
0.5	5.0	5.0
1.0	5.1	5.1
1.5	5.2	5.3
2.0	5.3	4.8

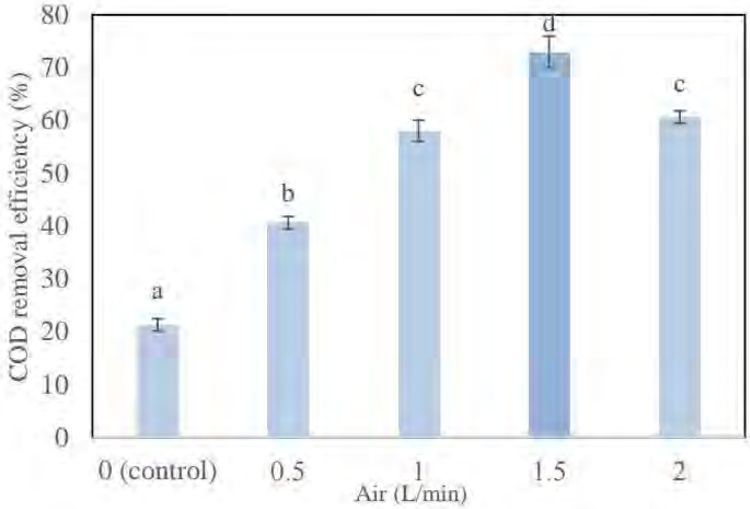


Figure 4.5 COD removal efficiency at different air flow rate from Fe^0/air modified Fenton at $p < 0.05$ by the one-way ANOVA

Figure 4.5 shows that COD removal efficiency from air flow rate 0 to 1.5 L/min increased dramatically and then decreased at 2.0 L/min. The maximum COD removal efficiency was 72.94 % at 1.5 L/min. As mentioned in Equation 2.4, hydroxyl radical generated from air and catalyst (Fe^0) removed the organic pollutant in wastewater. Enough air flow rate induces the improvement of mass transfer rate and corrosion products (Shimizu et al., 2012; Chang et al., 2009 and Yuan et al., 2016). The interesting point is that COD removal efficiency of air flow rate 2.0 L/min found lower than air flow rate 1.5 L/min. This might be due to a large amount of air flow rate produce excessively bubbles and then small bubbles will form larger bubbles. These large bubbles have lower surface area resulting in decrease of dissolved oxygen (Bochholz, 1978). Control sample (air flow rate 0 L/min) provided lowest COD removal efficiency (21.33 %) because removal mechanism is only adsorption (no oxidation mechanism occurred).

The result from this section concluded that optimum air flow rate of WAUF wastewater treatment via Fe^0/air modified Fenton reaction was 1.5 L/min and this flow rate would be used in further investigation.

4.5 Effect of used shot blast

75 mL WAUF wastewater was adjusted pH to 3.0, added 10 to 40 g/L of used shot blast and aerated with air flow rate (O_2) 1.5 L/min for 60 min. pH, DO, and COD were analyzed. Note that the control sample was WAUF wastewater and aeration with no used shot blast added. The increase of used shot blast in the reaction led to an increase of pH and

a decrease of DO. As mentioned in Equations. 2.1, 2,3 and 2.4, solid Fe^0 transfers to dissolved Fe^{2+} and produces OH^-. In addition, O_2 was used in reaction to react with Fe^{2+} and, finally, generated hydroxyl radical to treat contaminants. In control sample, after treatment had pH 3.0 which almost equaled to the initial pH.

Table 4.3 pH and DO after WAUF treatment at different number of used shot blast via Fe^0/air modified Fenton reaction

Shot blast (g/L)	pH	DO (mg/L)
0 (Control)	3.0	5.0
10	4.9	5.3
20	5.2	5.1
30	5.6	4.8
40	6.0	4.5

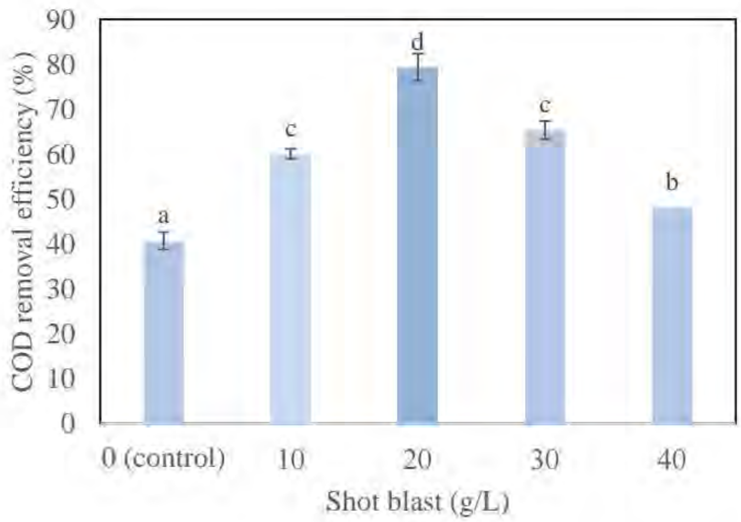


Figure 4.6 COD removal efficiency at different number of used shot blast from Fe^0/air modified Fenton at $p < 0.05$ by the one-way ANOVA

In Figure 4.6, the maximum COD removal efficiency was 79.33% at 20 g/L used shot blast. Increasing amount of used shot blast provided more active site of Fe^0 layer resulting in improved pollutant removal. In contrast, the results at high dosage of used shot blast at 30 g/L and 40 g/L found lower COD removal efficiency. In fact, Fenton reaction is limited by mass transportation rate of intermediates, corrosion products, and pollutants in wastewater. Excess Fe^{2+} might induce HO• to be a self-scavenging and form less hydroxyl radical (Chang et al., 2009 and Yuan et al., 2016) resulting in lower COD removal efficiency. Control sample (no used shot blast added) provided lowest COD removal efficiency (40.67 %). Air bubbles might removal organic pollutant by volatilization.

From this study, it can be concluded that optimum condition of WAUF wastewater treated via Fe^0/air modified was treatment time 60 min, pH 3.0, air flow rate 1.5 L/min, and number of used shot blast 20g/L that provided maximum COD removal efficiency 79.33%.

4.6 Wastewater parameters before and after treatment by Fe^0/air modified Fenton reaction

The results from treatment of WAUF wastewater treatment via Fe^0/air modified Fenton reaction with used shot blast revealed that COD decreased from 32,000 mg/L to 6,613 mg/L or 79.33% removal efficiency, whereas BOD reduced from 2,850 mg/L to 750 mg/L or 73.68 % removal efficiency. BOD/COD ratio increased from 0.08 to 0.11 means this wastewater has more biodegradability. Total iron increased to 1.35 mg/L because excess total iron released from shot blast in system. However, total iron has no effluent quality standards. Moreover, turbidity and TSS decreased from 9.9 NTU to 1.52 NTU and from 226 mg/L to 196 mg/L, respectively. Slightly increased of TDS was found in Fe^0/air modified Fenton reaction might due to dissolve of Fe^0. In conclusion, almost all the wastewater parameters did not comply with the effluent quality standard (except pH). It needs other wastewater treatment units follows Fe^0/air modified Fenton unit for treating wastewater.

Table 4.4 Wastewater parameters before and after treatment by Fe^0/air modified Fenton reaction

Parameters	Treatment with used shot blast			
	Before	After	Industrial Effluent Quality Standards*	Removal Efficiency (%)
COD (mg/L)	32,000	6,613	120	79.33
BOD (mg/L)	2,850	750	20	73.68
Conductivity (μs/cm)	1,770	3,110	-	-
pH	3.0	5.2	5.5-9.0	-
Turbidity (NTU)	9.99	1.52	-	84.78
TSS (mg/L)	226	196	50	13.28
TDS (mg/L)	6,140	6,426	3,000	-
Total iron (mg/L)	0.00	1.35	-	-
B/C ratio	0.08	0.11	-	-

Remark: * Notification of the Ministry of Industry: Factory effluent control standard 2017

4.7 Comparison of this study with other studies

Due to moderate COD removal efficiency (79.33%) from Fe^0/air modified Fenton in this experiment, the researchers tried to compare this result with others. From literature reviews, initial COD of triazophos pesticide, p-nitrophenol (PNP), ammunition wastewater and dinitrodiazophenol (DDNP) wastewater in several experiments was 3,418, 500, 518, and 1,250 mg/L, respectively and their COD removal efficiency was 85.4%, 83.8%, 94.6%, and 78% respectively. Interestingly, all experiments above had lower initial COD compare with this study (initial COD of WAUF wastewater was 32,000 mg/L). This should be main reason behind the different COD removal efficiency. Moreover, many researches were investigated to treat pollutants via combined several processes e.g. combined of Fe^0 and Fe/Cu bimetallic, and combined of Fe^0/air with original Fenton process.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

1. Characteristics of wood adhesives Urea-formaldehyde (WAUF) wastewater from lumber mill i.e., COD, BOD, pH, conductivity, turbidity, TSS, TDS, total iron, and BOD/COD ratio were 32,000 mg/L, 2,850 mg/L, 3.0, 1,770 μs/cm, 9.99 NTU, 226 mg/L, 6,140 mg/L, 0 mg/L, and 0.08 respectively.

2. Maximum COD removal efficiency from Fe^0/air modified Fenton with used shot blast at optimum condition of time 60 min, pH 3.0, air flow rate 1.5 L/min, and shot blast 20 g/L was 79.33 %.

3. At optimum condition, treatment efficiencies of turbidity, TSS, and BOD were 84.78, 13.28 and 73.68 %, respectively. Biodegradability (BOD/COD ratio) increased from 0.08 to 0.11.

4. Wastewater treatment via Fe^0/air modified Fenton reaction with used shot blast had high pollutants removal efficiency and was cost effective than original modified Fenton reaction (with added H_2O_2).

5.2 Recommendations

Fe^0/air modified Fenton reaction with used shot blast is a wastewater treatment process that have lower operating cost compared to original modified Fenton reaction. Although this process exhibited satisfactory organic treatment efficiency (approx. 79%), BOD and COD from effluent still did not comply with the effluent quality standard. Three recommendations are approached. Firstly, due to wastewater after treating via Fe^0/air modified Fenton improved BOD/COD ratio (biodegradability), it increases opportunity to treat in activated sludge subsequent. Secondly, it should analyze shot blast by X-ray diffraction (XRD) analysis for characterizing crystalline structure. Thirdly, the smaller sizes of used shot blast and air bubble increase contact area in reaction that might increase treatment efficiency.

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APPENDICES

Table I.1 Determined the optimum reaction time via Fe^0/air modified Fenton

Time (min) (pH 3.0, shot blast 20g/L, and air 1.5 L/min)	COD removal efficiency (%)			Average	STDEV
	1	2	3		
5	3.41	7.53	9.50	6.8133	3.10761
15	17.80	17.80	21.92	19.1733	2.37868
30	30.14	28.08	34.25	30.8233	3.14125
45	44.52	40.41	46.58	43.8367	3.14125
60	75.34	77.40	75.34	76.0267	1.18934
90	69.18	69.18	65.07	67.8100	2.37291
120	69.18	73.29	73.29	71.9200	2.37291

Table I.2 Determined the optimum reaction time via used only shot blast (control group)

Time (min) (pH 3.0 and shot blast 20g/L)	COD removal efficiency (%)			Average	STDEV
	1	2	3		
5	13.70	11.64	9.50	11.6133	2.10013
15	11.64	11.64	13.70	12.3267	1.18934
30	13.70	13.70	11.64	13.0133	1.18934
45	17.80	17.80	19.86	18.4867	1.18934
60	19.86	17.80	19.86	19.1733	1.18934
90	21.92	19.86	26.03	22.6033	3.14125
120	23.97	21.92	26.03	23.9733	2.05500

Table I.3 Determined the optimum reaction time via used only aeration (control group)

Time (min) (pH 3 and air 1.5 L/min)	COD removal efficiency (%)			Average	STDEV
	1	2	3		
5	11.64	13.70	11.64	12.3267	1.18934
15	13.70	9.50	15.75	12.9833	3.18604
30	21.92	23.97	21.92	22.6033	1.18357
45	38.36	34.25	36.30	36.3033	2.05500
60	38.36	36.30	38.36	37.6733	1.18934
90	42.47	44.52	40.41	42.4667	2.05500
120	44.52	46.58	40.41	43.8367	3.14125

Table I.4 Determined the optimum of pH via Fe^0/air modified Fenton

Condition pH	COD removal efficiency (%)			Average	STDEV
	1	2	3		
2	63.76	59.73	65.77	63.0866	3.075782
3	75.84	77.85	77.85	77.1800	1.160474
3.4 (control)	73.83	75.84	73.83	74.5000	1.16047
4	49.66	45.64	43.62	46.3067	3.07469

Table I.5 Efficiency of the COD removal for different values of pH at $p < 0.05$ by the one-way ANOVA

pH		N	Subset for alpha = 0.05		
			a	b	c
Tukey HSD[a]	4	3	46.3067		
	2	3		63.0867	
	3.4 (control)	3			74.5000
	3	3			77.1800
	Sig.		1.000	1.000	.526

Table I.6 Determined the optimum of air flow rate via Fe^0/air modified Fenton

Condition Air (L/min)	COD removal efficiency (%)			Average	STDEV
	1	2	3		
control	20.00	22.00	22.00	21.3300	1.15470
0.5	40.00	42.00	40.00	40.6667	1.15470
1.0	60.00	56.00	58.13	58.0433	2.00141
1.5	72.84	76.00	70.00	72.9467	3.00142
2.0	62.00	60.00	60.00	60.6667	1.15470

Table I.7 Efficiency of the COD removal for different values of air flow rate at $p < 0.05$ by the one-way ANOVA

Air (L/min)		N	Subset for alpha = 0.05			
			a	b	c	d
Tukey HSD[a]	control	3	21.3333			
	0.5	3		40.6667		
	1.0	3			58.0433	
	2.0	3			60.6667	
	1.5	3				72.9467
	Sig.		1.000	1.000	.453	1.000

Table I.8 Determined the optimum of shot blast via Fe^0/air modified Fenton

Condition Shot blast (g/L)	COD removal efficiency (%)			Average	STDEV
	1	2	3		
control	40.00	42.00	40.00	40.6667	1.15470
10	62.00	60.00	58.13	60.0433	1.93536
20	80.00	80.00	78.00	79.3333	1.15470
30	68.00	66.00	62.00	65.3333	3.05505
40	50.00	46.00	48.00	48.0000	2.00000

Table I.9 Efficiency of the COD removal for different values of shot blast at $p < 0.05$ by the one-way ANOVA

Condition Shot blast (g/L)		N	Subset for alpha = 0.05			
			a	b	c	d
Tukey HSD[a]	control	3	40.6667			
	40	3		48.0000		
	10	3			60.0433	
	30	3			65.3333	
	20	3				79.3333
	Sig.		1.000	1.000	.052	1.000

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