長岡技術科学大学

大学院工学研究科

博士論文

COD REMOVAL FROM WASTEWATER USING ELECTROCOAGULATION

電気凝集法を用いた廃水からの有機物除去

指導教員　中山　忠親　教授

著者

学籍番号 17701386

氏名 NGUYEN HO QUE

専攻　材料工学専攻

DECLARATION

I declare that this thesis has been conducted by myself in the Extreme Energy-Density Research Institute (EDI), Nagaoka University of Technology. Now, it is submitted for assessment on the program of study leading to the award of a Ph.D. The thesis was carried out under the Prof. Nakayama Tadachika supervisor and has not been submitted in whole or part to this or any other academic organization for any degree.

Date: Signed:

ACKNOWLEDGMENT

This thesis was conducted at the Extreme Energy-Density Research Institute (EDI) and Department of Civil and Environmental Engineering in the Nagaoka University of Technology (NUT) during the period from September 2017 to July 2020.

I would like to express my sincere gratitude to Prof. Nakayama Tadachika for his supervision, encourage, invaluable guidance and inspiration provided over the course of 3 years of this research, and immediately adaptation of my requirements that relation to necessary equipment for experiment. I really appreciate for everything that he has done for me.

I wish to thank to the Ministry of Education, Culture, Sports, Science and Technology of Japanese Government for giving me the scholarship which the complete financial support for this research.

I am grateful to the Prof. Suematsu Hisayuki for his academic consultant, guidance as well as have given many suggestions to me during researching. Without his support, my research cannot reach what it is now.

I deeply thank Prof. Takashi Yamaguchi and Assoc. Prof. Masashi Hatamoto for giving the opportunity and facilities to conduct experiment in Department of Civil and Environmental Engineering. I have my gratitude to Dr. Takahiro WATARI who always supported me as I had any trouble in research.

I wish to acknowledge Dr. Wiff Verdugo Juan Paulo from Chile. He is very enthusiastic to encourage me during studying time.

I wish to express my appreciation to Dr. Do Thi Mai Dung for her helpful comments and assistance during meeting report in laboratory.

I would also like to thank the laboratory member in the Extreme Energy-Density Research Institute (EDI) and Department of Civil and Environmental Engineering for their laboratory assistance.

The last word of acknowledgment, I would like to express my deepest thanks to my wife, Nguyen Thi Cam Nhung, who is the best thing happened to me, and my sons, my world, Nguyen Ho Minh Khoi and Nguyen Ho Minh Quang and my parent as well as the relative who have strong supported me to continue studying and make me most comfortable to study and indeed for my entire life.

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1. INTRODUCTION

1.1. BACKGROUND

In the 21st century, the big challenge is to provide enough clean water. If the water is polluted, it is difficult to clean as well as the cost of this process is expensive. Until now, around 80 % of wastewater in the word are not treated and directly discharged to natural environment, including waste from human and wastewater from industries that is toxic. The nature water and concentration of pollutants in freshwater that determines the using purpose such as drinking, bathing as well as for agriculture purpose. Moreover, the habitat and fish life and other wildlife are affected by water pollution. The pollutants in the water can include pathogens, organic materials, chemicals and salinity [1]. Therefore, cleaning wastewater is becoming urgent issue of word communities. Therefore, from this state there are many studies on wastewater treatment technologies to find the technologies that is simple, cheap and highly efficiency to remove pollutants from water. That is not only using in development countries but also ability application in many developing/poor countries. It is opportunity for many poor people in the world have ability to approach a clean drinking water.

The wastewater treatment technology involves reduction the pollutants from wastewater, suitable operation and maintenance to obtain the desired performance. Wastewater treatment technologies are crucial for urban water systems. Nowadays, the wastewater treatments technology can divide 2 types: biological and chemical methods. The biological technology is effective, friendly but treatment time is long, large treatment facilities and quite expensive. In addition, for using biology technology, the optimally favourable environment has to create. Furthermore, during operation the system requires management and maintenance of the microorganisms and/or physicochemical pre-treatment. Typically, the ecology technology is inefficient with the wastewater included non-degradable compounds or toxic compounds. The chemical technology, during process the chemicals need to add in solution. This technology is effective to remove pollutant. However, after finishing of treatment, there is large of by-product. Moreover, if the wastewater with concentration of metal ions, this method is not effective or requires an oxidation step if the metals are complexed [2, 3]. At that time, electrocoagulation is considered as one of the most effective approaches.

Electrochemical technologies (electrocoagulation, electroflotation and electrooxidation) have attractive again during the past two decades. There are some applications of this technology to remove metal from wastewater as well as application for treating drinking water or process water and various industrial wastewaters. Nowadays, electrochemical technologies can be competition with the other technologies since low cost, efficiency, and compact [4]. Where, electrocoagulation is one of typical of electrochemical that can get rid of pollutants from water using electricity. It does need to add any chemical. The process uses electricity and sacrificial plates to combine with contaminants in a waste stream, producing insoluble oxides and hydroxides - floc - that are easily separated from the water by precipitation or flotation. Electrocoagulation (EC) technology is potential method. It requires short treatment times and low sludge production.

1.2. HISTORY OF ELECTROCOAGULATION

The electrocoagulation was first used as well as got US patent in 1880. In this year, based on this patent the electrocoagulation was used to clean municipal wastewater in Salford (UK). This technology continued improving until in 1909 when a new patent was invented with Al and Fe electrodes [5, 6]. The treatment of sludge was difficult and high operating cost. Therefore, by 1930s all sludge was generated from treatment plant that had been abandoned. The electrocoagulation was potential technology for dealing with this problem [7].

In this period, the electrocoagulation was novel technology. Therefore, it was attached by many scientists. To understand how the electrocoagulation process works, it was continued to study and discussed the mechanism of water electrolysis as well as other chemical reactions that occurred during electrolysis time. Especially, electrocoagulation reactor with Al electrodes was more precise in 1946. The comparison between electrocoagulation and electrochemical begun investigating. The researches in this period showed that electrocoagulation was more advantage than electrochemical process about pollutants removal efficiency as well as economic [8].

To enhance the pollutants removal efficiency as well as more understanding about electrocoagulation. The other electrodes materials were investigated. Namely, Mg electrodes combine sea water were applied to disinfect wastewater by electrocoagulation. This study gave the conclusion that Cl ions in sea water were oxidized at the anode into hypochlorous ions. The colloidal in solution that was adsorb on the $Mg(OH)_2$ and precipitate. Furthermore, the hydrogen bubbles generated from cathodes were also observed that enhanced electroflotation and it was one way to remove pollutants from medium [9]. The electrocoagulation was invented that was breakthrough in environmental technology. It was promoted to study that aimed more understand about mechanism during electrocoagulation. During period from 1970s to 1980s, the researches about electrocoagulation were applied to clean various many wastewaters. However, in this period the high electricity cost that restricted electrocoagulation for application in industry [6]. Until late twentieth century, there are many electricity sources were invented that led to reduce the cost of electrocoagulation operation. Moreover, discharging from industry to natural environmental has been becoming strict also causing to re-study electrocoagulation. Therefore, electrocoagulation becomes necessary to develop to enhance pollutants removal efficiency from many type of wastewaters.

1.3. ADVANTAGE AND DISADVANTAGE OF EC

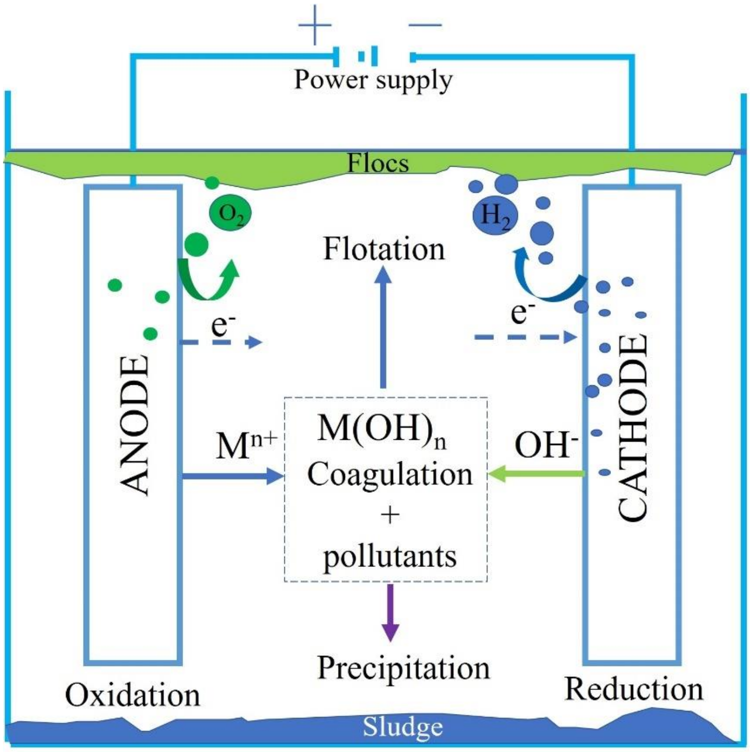

Fig 1.1. Electrocoagulation process during experiment

Technology itself is always to have a pros and cons. Depending on purpose and the way to use the technology, which can promote advantage up to maximum and cutting down disadvantage to a minimum. Electrocoagulation is an electro-chemical process that can remove heavy metals, suspended solids, emulsified organics and many other contaminants from wastewater by applying electricity through electrodes instead of expensive chemical reagents and reducing generated sludge to a minimum.

The recently studies have proved that electrocoagulation was more advantageous than conventional coagulation. The simple designed and the easy automation of the electrocoagulation that is conspicuous among the main advantages. This method does not need to add any chemicals, and the quantity of coagulant generated in solution can control by current density or applied voltage. Therefore, if the wastewater has a high current density, which need a low current density or applied voltage. As a result, it can be used with green energy as windmills, solar panels, and fuel cells, etc [10]. Hence, the electrocoagulation can be applied in isolation area such as rural or mountain areas. Those areas can used by the other technology; however, they meet a lot of problems that relation with electricity. Furthermore, if the design of electrocoagulation cell is proper, it can control both coagulation and flotation process. Consequently, it can gain destabilization of pollutants in solution, and their aggregation. Finally, they will be separate in a single-compartment reactor [11, 12].

Whereas, regarding conventional coagulation. There are three consecutive stages that have to conduct [13]: The first period needs to force turbulence to gain mixing of the coagulant and pollutant; the second period a lightly mix is used to favour flocculation of the destabilized pollutants; and the final period, separation of the precipitation based on gravity or dissolved air to make flotation process. Moreover, conventional method is more expensive than electrocoagulation method [10, 14].

Furthermore, there are some studies have pointed out that electrocoagulation process is cheaper than other methods of treatment such as ultraviolet (UV) and ozone. Besides, the electrocoagulation is also more advantageous than biological technology, which needs to specific conditions. Therefore, if the wastewater is high concentration of toxics, xenobiotic compounds, and pH, the biology technology will not effective. Whereas, electrocoagulation method can be used to treat many wastewaters, including agricultural, industrial, and domestic. Furthermore, the biological methods require more treatment time than the EC process to achieve these results from municipal wastewater. EC was also evaluated that it is more versatile and feasible than biological methods [15, 16].

Fig 1.1 shows the process of electrocoagulation during voltage supply. Basically, electrocoagulation can be divided 3 phases. Firstly, the dissolution will occur in medium during electrocoagulation. In this phase, the metal ions will be released from anode, and at the same time the hydroxide ion releases from cathode. Secondly, they all to be in the solution, then combine to generated metal hydroxide. The metal hydroxide active as coagulant. It is easy to adsorb particle as well as colloidal particles in medium. Under van der Walls forces the colloids come together and form the flocs from micro flocs to macro flocs in the thirdly phase. As the result, the flocs will become bigger, then sedimentation by gravity force or flotation due to hydrogen bubbles. Finally, they will be separated from medium by filter.

Table 1.1. Advantages and disadvantages of EC[17]

Advantages	The design is simple and easily operation
	During EC is controlled electrically with no moving parts. Therefore, EC cell requires little maintain and it can be long life.
	Treated wastewater is acceptable, pleasant, clear, colorless and odorless.
	Reducing sludge generated during EC process comparison with the conventional methods. Furthermore, the sludge is mainly composed of metallic oxides/hydroxides. Therefore, it is sedimentation and easy to subtract from medium.
	EC does not require adding chemical. So, there is less rick of secondary pollution comparison with chemical coagulation.
	The EC can be used renewable energy as solar, wind, etc. Therefore, in isolation area such as rural and mountain can use EC for cleaning wastewater since a solar panel can be enough to operate EC.

	Hydrogen bubbles are generated from cathode, which can bring pollutants up to top from medium by flotation. They are easily collected and removed.
	EC can remove smallest colloidal particle. Since the electric field promotes their vivacious, increasing of coagulation
Disadvantages	The anode is dissolved during EC process due to oxidation. Therefore, after a while it have to change.
	The high electrical conductivity of wastewater is required to reduce the energy consumption as well as operation time
	Passivation can reduce the efficiency of EC process.

1.4. REMOVE OF COD FROM WASTEWATER

COD removal from wastewater is investigated in many studies and in a long time. COD is not most important parameter; however, it is considered as a traditional parameter. When the COD value is determined, which can provide an index to assess the effect discharged wastewater to water bodies. Higher COD concentration that means a greater amount of oxidizable organic and inorganic material inside water. Consequently, it will reduce dissolved oxygen (DO) levels. The DO in water decreased as a reason for enhancing the anaerobic conditions, which is not good to aquatic life forms. The COD test is often used instead of BOD parameter because of shorter time. The COD removal efficiency from wastewater by electrocoagulation can give the different results. It cannot remove, removing a part or higher removing in COD. The detail was described in somewhere [18].

- The concentration of COD is not reduced: the soluble materials and miscible compounds do not contact at all with metal hydroxide that activates as a coagulant during electrocoagulation process. Therefore, they cannot be removed, remaining in medium. The substances in this case such as glucose, lactose, isopropyl alcohol, phenol, sucrose, etc.

- The concentration of COD is partially reduced: if in wastewater, there are sodium oxalate and similar organic salts, which prefer to stay in medium during electrocoagulation process. Therefore, there is only low percentage of acetate and similar ions will be got rid of from solution. For the other compounds such as citric, salicylic, tartaric and oxalic acids that tend to form insoluble in solution. They will be partially removed depend on the final pH of wastewater sample.

- The concentration of COD is highly reduced: The compounds in water such as suspended solid and liquids, turbidity, fecal coliforms, milk, fats oil and grease, TSS will easily contact with metal hydroxide to form insoluble compounds in solution. Finally, they will be almost completely removed from solution after finishing electrocoagulation experiment.

Table 1.2. Recent electrocoagulation studies to remove COD from wastewater

No.	Type of wastewater	Model of operation	Cathode /Anode	Power supply	COD removal	References
2	Textile dye	Batch	Al, Fe	DC	Al (65) Fe (77)	M.Bayramoglu et al./ Sep. Purif. Technol 37 (2004) 117-125
3	Olive oil mill	Continuous	Al, Fe	DC	Al (52) Fe (42)	H.Inan et al./ Sep. Purif. Technol 36 (2004) 23-31
4	Metal cutting fluids	Batch	Al, Fe	DC	Al (93) Fe (92)	M.Kobya et al./ Sep. Purif. Technol 60 (2008) 285-291
5	Livestock	Batch	Al	DC	97.9	B.-y.Tak et al/J.Ind.Eng.Chem 28 (2015) 307-315
6	Textile	Batch	Al, Fe	DC	Al (63) Fe (65)	M.Bayramoglu et al./Chem.Eng.J 128 (2007) 155-161
7	Biodiesel	Batch	Al	DC	55.43	O.Chavalparit et al./ J. Environ. Sci 21 (2009) 1491-1496.
8	Restaurant	Batch	Al, Fe	DC	Al (90) Fe (90)	X.Chen et al./ Sep. Purif. Technol 19 (2000) 65-76

No.	Type of wastewater	Model of operation	Cathode /Anode	Power supply	COD removal	References
9	Landfill leachate	Batch	Al-Fe	DC	94	L.K.Erabee et al./J.Environ.Sci.Health, Part A 0 (2017) 1-7
10	Textile	Batch	Al	DC	78	O.T.Can et al./Chemosphere 62 (2006) 181-187
11	Dairy industry	Batch	Al-Fe	DC	40	Ana L. Torres-sánchez et al./ Int. J. Electrochem. Sci 9 (2014) 6103-6112
12	Textile	Batch	Al-Fe	DC	87	F.Ghanbari et al./Environ. Process 1 (2014) 447-457.
13	Paint manufacturing	Batch	Al, Fe	DC	Al (94) Fe (93)	A.Akyol./Desalination 285 (2012) 91-99
14	Petroleum refinery	Batch	Al	DC	92	D.Bhagawan et al./Desalin.Water.Treat 57 (2016) 3387-3394
15	Textile	Batch	Al	DC	92.6	A.Samir Naje et al./ Int. J. Electrochem. Sci 10 (2015) 5924-5941
16	Pulp and paper industry	Batch	Fe	DC	85	P.Asaithambi./Desalin.Water. Treat 57 (2016) 11746-11755
17	Biodiesel	Batch	Al, Fe	DC	Al (90.94) Fe (91.74)	N.Pinar Tanatti et al./ Appl. Water Sci (2018) 8: 58
18	Spent coolant	Batch	Al	DC	68	W.Pantorlawn et al./J.water.Reuse.Desal 8 (2017) 497-506
19	Food industry	Batch	Al	DC	79.18	S.veli et al./ Global NEST journal 20 (2018) 551-557
20	Imidacloprid Pesticide	Batch	Stainless steel-Fe	DC	94	N.Ghalwa et al./J Environ Anal Chem 2 (2015)

No.	Type of wastewater	Model of operation	Cathode /Anode	Power supply	COD removal	References
21	Bilge	Batch	Al	DC	90.3	K.Ulucan et al./Int. J. Electrochem. Sci 9 (2014) 2316-2326

The last studies have shown that achieving of COD removal efficiency from 40 – 94%, the EC need to consume around 5 kWh/m^3 of specific energy consumption. The values depend on the type of wastewater. Furthermore, all studies have used DC as a main power supply. That is one of reason lead to higher energy consumption. Therefore, NSP could be ideally choice to reduce specific energy consumption.

1.5. OBJECTIVE

The objective of this study is comparison between nanosecond pulse (NSP) and direct current (DC) as main power supply to remove COD from municipal and textile wastewater. The specific objectives are:

- To design and set up a batch electrocoagulation and evaluate the COD removal efficiency.
- To investigate the effect of varying parameters to COD removal efficiency with a view to optimize input conditions.
- Appling NSP to reduce specific energy consumption and increased COD removal efficiency
- To understand the reason of NSP is better than DC to remove COD from municipal and textile wastewater.

1.6. SCOPE OF THE STUDY

This study includes six chapters. The first chapter is an introduction. This part includes background, objectives, and scope of the study. The second chapter is using electrocoagulation to remove COD from artificial wastewater. The third chapter is using an nanosecond pulse to enhance COD removal efficiency from municipal wastewater. Chapter fourth is application nanosecond pulse for electrocoagulation to remove COD from textile wastewater at low specific energy consumption. Whereas fifth chapter is comparison between NSP and DC for removing COD from municipal wastewater using Fe electrodes. Chapter sixth is final conclusions.

CHAPTER 2. USING ELECTROCOAGULATION TO REMOVE COD FROM ARTIFICIAL WASTEWATER

2.1. ABSTRACT

This work studies the influences of parameter such as pH, treatment time, applied voltage, and distance between electrodes on the chemical oxygen demand (COD) removal efficiency from an artificial wastewater using electrocoagulation process. The material of electrodes was fabricated by using commercial Al plates. The results show that at the initial pH of 4.1 value the COD removal efficiency from the standard artificial wastewater can be up to 51%. On the other hand, results reveal that pH parameter is most effect on the COD removal efficiency from artificial wastewater during electrocoagulation process when it was compared with other parameters in this study. The study also show that as initial pH was low, insoluble compounds were formed and predominant in solution. This was reason to enhance the COD removal efficiency from artificial wastewater after electrocoagulation process. In contrast, when initial pH of artificial wastewater was high, soluble compounds were predominant formation, Reducing of COD removal efficiency from artificial wastewater. Moreover, the correlation between the different sizes of hydrogen bubbles generated from cathode during electrocoagulation and COD removal efficiency from artificial wastewater was observed at various initial pH values. The results recommend that the hydrogen bubble-size fluctuation of around 42 μm can enhance the COD removal efficiency from artificial wastewater after electrocoagulation process due to the enhancement of the flotation process efficiency during electrocoagulation process. Furthermore, in this work the methods of X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS) were used to analyze characteristics of flotation and precipitation. The results show that flotation process was better performance during electrocoagulation than precipitation process.

2.2. INTRODUCTION

Chemical oxygen demand (COD) is not most important in are of environment. However, COD is a traditional parameter and it is large used as an indicator of water quality in general, and wastewater before discarding to waterbody in particular. Based on the concentration of COD in water, the quality of water can be evaluated. COD is the amount of oxygen that is used for the chemical oxidation of inorganic and organic substances existing in the wastewater. The factors to enhance COD in water in general include biodegradable organic, non-biodegradable, and inorganic oxidizable compounds [18].

Electrocoagulation (EC) has been proposed as a potential wastewater treatment technology due to EC is simple design and in operation. However, in the first time, the energy was scarce that led to the high cost of electricity has been the main reason for limiting of using electrocoagulation in industries [17, 19]. In that period, the world was developing era. There were no more energy sources. Therefore, the method using an electricity in general and electrocoagulation in particular were not attractive. However, recently there are many renewable energy sources such as solar, wind, and tide that has mad reducing the energy costs, generating new attractive applying electrocoagulation process to clean industrial wastewater. Furthermore, the combination between electrocoagulation technology and renewable energy can promote electrocoagulation process becomes an eco-friendly method for wastewater treatment technology.

To the extent of my knowledge, newly, electrocoagulation process has been re-started to apply in some industries, such as: rose processing wastewater, textile wastewater, landfill leachate, chemical mechanical polishing wastewater, poultry manure wastewater, municipal wastewater, etc. [20]. However, there are still some unclearly questions and challenges that relation to scale up for using in real industries.

Recently, many researches have been focusing to apply electrocoagulation process to clean wastewater. However, there are no above researches using electrocoagulation to remove COD from artificial wastewater under Organization for Economic Cooperation and Development (OECD) standards. Furthermore, during electrocoagulation process, the relationship between investigation parameters and COD removal efficiency is not enough attention such as the relation between initial pH values, treatment time, applied voltage, etc. and COD removal efficiency. In this study, these relations will made more clearly. To the best my knowledge, investigation hydrogen bubbles size and COD removal efficiency from wastewater during electrocoagulation is little or no discussion. Therefore, in this study, above relation will be investigated to more understand about this relationship. Moreover, there are very few studies have considered the characterization of precipitation and flotation by using the energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD) until now, after electrocoagulation process when aluminum electrodes is used to remove COD from wastewater in general. In this work, the performance of precipitation and flotation process to remove COD was compared based on their characteristic.

By using electric current passes to the electrodes during electrocoagulation process, promoting aluminum hydroxide formation as a coagulant from electrolytic oxidation. Therefore, the electrocoagulation process can reduce the amount of the formation of sub-products and sludge during wastewater treatment. Furthermore, generated sludge during electrocoagulation process is less toxic than other chemical methods. Finally, the flocs during electrocoagulation are easy to get rid of by precipitation process or flotation process [21].

For the material electrodes, Fe and Al are usually used as electrodes comparison with platinum, gold, graphite, zinc, etc. due to their commercially available at a low cost and because their hydroxides show low toxicity and a high valence after precipitation, increasing their pollutant removal ability [22]. However, to compare between aluminum and iron materials, there are some research have pointed out that Al is preferred, because it is stable, easily handled, and readily soluble [23]. However, concluding the Al is better material than Fe, which depend on the type of wastewater as well as the type of power supply.

For power supply, during electrocoagulation can use alternating current (AC), direct current (DC), or some researchers used alternating pulsed current (APC) as the main power supply. Metal ions are generated via oxidation from the anode, and hydroxides (OH^-) are generated by reduction from the cathode. They will combine each other in the medium, promoting to produce metal hydroxides with a high ability for physical adsorption [24, 25].

The main reactions as using Al material for electrodes as follows:

At the anode, Al is priority to oxidize releasing Al^{3+} cations [22].

$$Al - 3e = Al^{+3} \qquad (1)$$

However, if we supply high applied voltage or electric current, there are secondary reactions may occur in solution [26, 27]. Example, water is second priority to oxidize forming hydronium cation and oxygen gas. However, in the artificial wastewater, chloride anions is existing in solution, they can be oxidized into Cl_2, promoting to the oxidation of dissolved organic compounds or to the ClOH formation as below reactions [28].

$$2H_2O - 4e = O_2 + 4H^+ \quad (2)$$

$$2Cl^- - 2e = Cl_2 \quad (3)$$

$$Cl_2 + H_2O = ClOH + H^+ + Cl^- \quad (4)$$

At the cathode, water is priority to reduce releasing hydrogen bubbles and hydroxyl anions in solution during electrocoagulation [22].

$$2(H_2O) + 2e^- = H_2 + 2(OH^-) \quad (5)$$

The products from electrocoagulation process depends on initial pH of wastewater. For the Al electrodes, the Pourbaix diagram recommends that, when initial pH<4, soluble species Al^{+3} ions are the main product during electrocoagulation process, contrast, when initial pH in range of 4-10 values, the formation of the insoluble compound $Al(OH)_3$ is predominant in solution. At initial pH>10, the soluble $Al(OH)_4^-$ ions tends to form following Reaction (6) [22, 29]. Therefore, pH is vital important to decide the final product species and their solubility in wastewater during electrocoagulation process.

$$Al + 4OH^- = [Al(OH)_4]^- + 3e \quad (6)$$

Anode dissolution and combination with OH^- groups releases from the cathode may occur via monomeric and polymeric reactions of Al^{3+} and $Al(OH)_2^+$ species [20].

In addition, during electrocoagulation the hydrogen bubbles are generated from cathodes, while only a few oxygen bubbles are generated from the anodes [30]. Therefore, the flotation efficiency is decided by amount of hydrogen bubbles. The size of the hydrogen bubbles can mainly influence their retention time and stability in the solution during electrocoagulation process. There are some studies have proven that the large hydrogen bubbles will promote rising quickly to the surface, reducing the ability of capturing pollutants in solution during flotation process. Whereas, microbubbles of size distributes from 20 – 50 µm can enhance the retention time by several orders of magnitude [31]. Because they keep more longer time in solution, as a result, increasing the probability of capturing pollutants, increasing the COD removal efficiency from artificial wastewater. This experiment used the Sauter (D_{32}) average diameter to decide the hydrogen bubble sizes as showed at Equation 7. The correlation between size of hydrogen bubbles and COD removal efficiency. The D_{32} is considered an appropriate flotation metric due to it is defined as the average diameter of volume to surface-area ratio of all bubbles, where active surface area is important [32].

$$D_{32} = \frac{\sum_{i=0}^{n} d_i^3}{\sum_{i=0}^{n} d_i^2} \tag{7}$$

In which d_i is the hydrogen bubble diameter, and n is the number of hydrogen bubbles obtained from the bubble-size measurement.

2.3. EXPERIMENTAL

2.3.1. Electrocoagulation cell

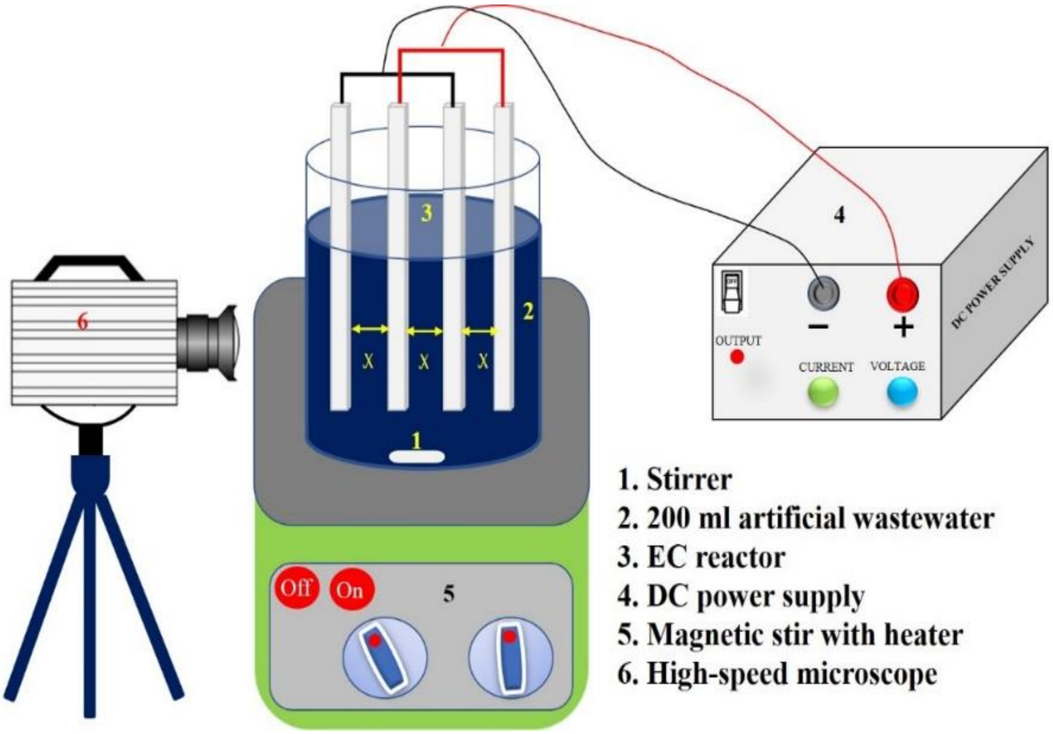

Fig 2.1. Set-up electrocoagulation reactor at the same distance between electrode for all experiment (χ = 1 cm)

Fig 2.1 reveals the electrocoagulation process setup used in this work. The electrocoagulation reactor containing 200 ml of the artificial wastewater. Both anode and cathode electrodes were using aluminum plates. The cathodes and anodes were the same size of 55×20×1 mm^3 as shown in Fig 2.1. The distance between electrodes (x) was fix 1 cm, this value was determined by testing with some distances to find an optimum distance. In this study, a DC power supply (PL-650-0.1, Matsusada Co. Ltd., Japan) was applied under potentiostatic mode with applied voltages from 5–18 V. During electrocoagulation process, the artificial wastewater sample was stirred at 200 rpm at room temperature by using Magnetic stirrer with hot plate, ERC-1000H model to increase contact between pollutants and the metal hydroxide during electrocoagulation process.

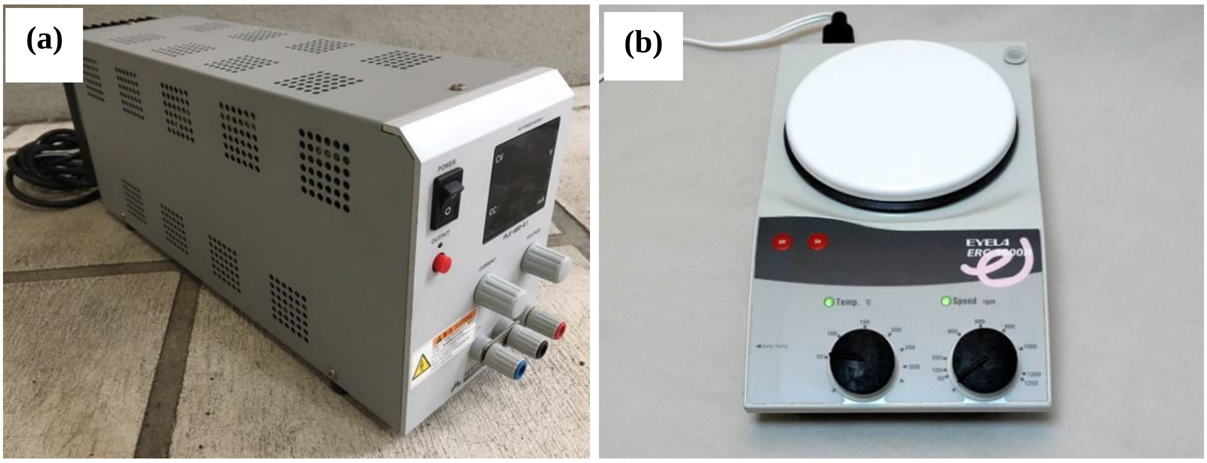

Fig 2.2. DC power supply (a) and Magnetic stirrer with hot plate (b)

2.3.2. Artificial wastewater

Table 2.1. Composition of the artificial wastewater, OECD standard

Composition	Peptone	Meat extract	Urea	NaCl	$CaCl_2$	$MgSO_4$	K_2PO_4
Weight (g)	16	11	3	0.7	0.4	0.2	2.8

The composition of artificial wastewater by using OECD recipe was showed in Table 2.1 [33]. Before each experiment, the nominal composition was diluted with 1 L of deionized water and mixed for 1 h. Artificial wastewater after diluting was stored up to one week in a dark room at 4 °C for using electrocoagulation experiment. HCl and NaOH solution were used to modify the initial pH of artificial wastewater before each experiment.

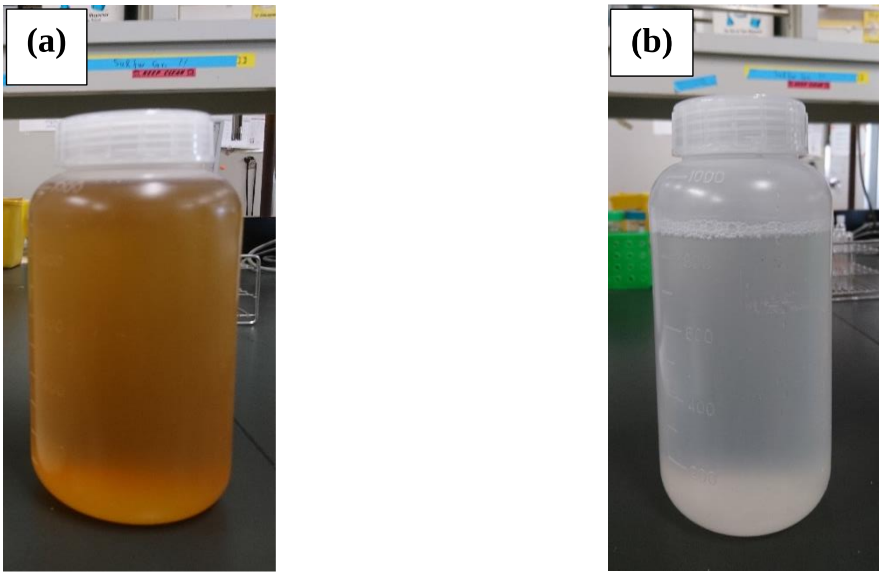

Fig 2.3. Artificial wastewater before (a) and after diluting (b) to experiment

Electrical conductivity and pH parameters were measured immediately before and after the electrocoagulation experiments by a pH meter (Model HM-30R, range from 0.000–14) and a COND meter (Model ES-71), respectively.

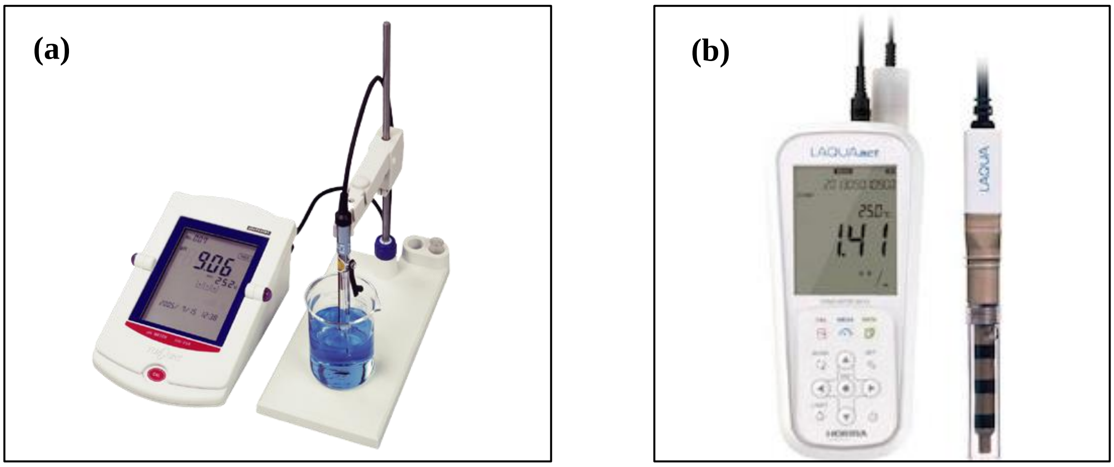

Fig 2.4. pH meter (a) and COND meter (b)

COD before and after experiment was measured following the HACH 8000 method by using The Hach DRB 200 and the Hach DR2800 portable spectrophotometer. Each COD value measurement was conducted in duplicate or triplicate to ensure the repeatability of results.

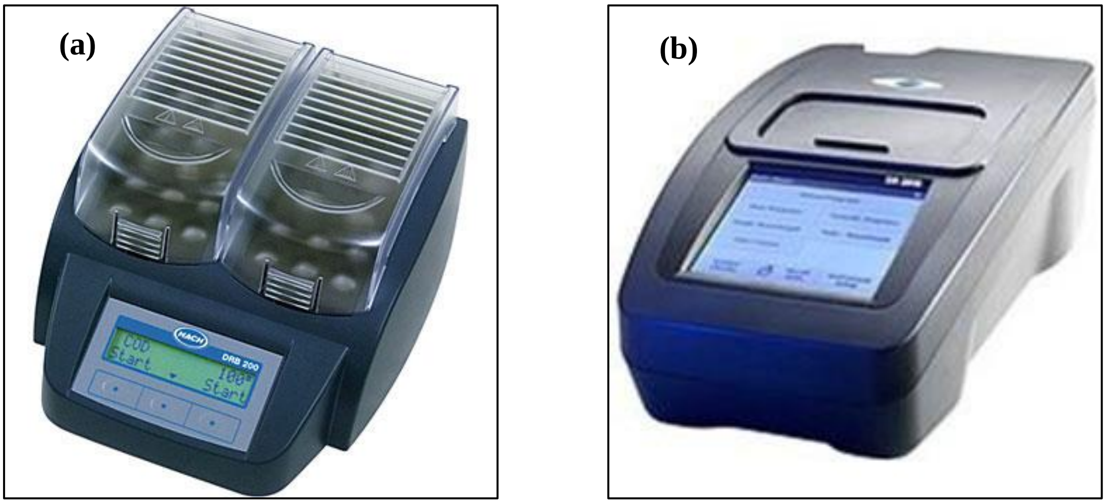

Fig 2.5. COD measure device, (a) DRB 200 and (b) DR 2800

The COD removal efficiency (η) at treatment time *t* is defined as follows:

$$\eta(t) = \frac{COD_0 - COD_t}{COD_0} * 100 \qquad (8)$$

In which COD_0 and COD_t is the COD at the beginning and at treatment time *t* of the experiment, respectively.

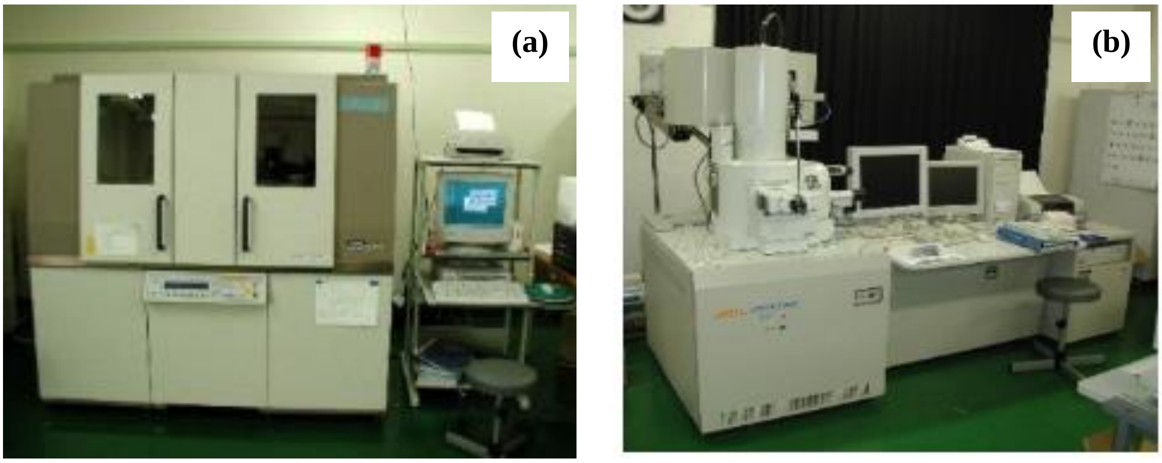

Fig 2.6. XRD (a) and FE-SEM, EDS (b) equipment

The characteristics of precipitation and flotation and the anode morphology were analyzed using FE-SEM (JEOL JSM-6700F), EDS, and XRD (Rigaku RINT-2500, CuK).

2.3.3. Hydrogen bubble size

Fig 2.7. High-speed microscope

The size of hydrogen bubbles released from cathodes, which was recorded using a high-speed microscope (Keyence VW-9000m, Japan). The mode of recording parameters was fixed as following: 6,000-s shutter speed, 2,000 fps frame rate, 640×480 resolution, and ×200 magnification. The ImageJ software was used to calculated the size as well as distribution of the hydrogen bubbles that released from cathodes during electrocoagulation process [34], the results was calculated based on at least 1,000 hydrogen bubbles for each experiment.

2.4. RESULTS AND DISCUSSIONS

2.4.1. Influence of initial pH

Regards to parameters that effect on efficiency electrocoagulation. The pH and applied voltage (or current density) are most important. For initial pH of wastewater, it is a key parameter in the electrocoagulation technology. The pH of the wastewater is known to play an important role to remove pollutants from medium, from that point, enhancing COD removal efficiency. Ther initial pH can influence the coagulant dosage rate and number of generated hydrogen bubble, which in turn effect on the COD removal effiency. In this study, to investigate the effect of initial pH on COD removal efficiency. The pH was changed from 3.8 to 9.4 by using NaoH and HCl.

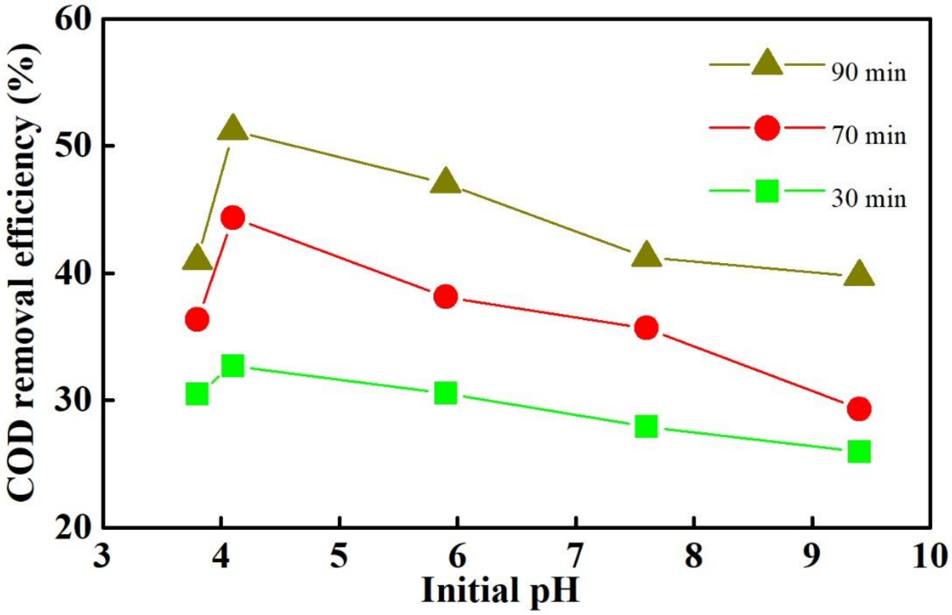

Fig 2.8. Influence of initial pH on the COD removal efficiency for different treatment times under 15 V.

The study about influence of initial pH values on COD removal efficiency from artificial wastewater was showed in Fig 2.8. The results from that figure revealed that the COD removal efficiency from artificial wastewater was up to 51% that was observed at initial pH = 4.1. This value can be explained by the simultaneous varying formation of monomeric and polymeric species that changed to $Al(OH)_3$ formation at the end, as indicated by the complex precipitation in solution during electrocoagulation process. The characteristic of aluminium hydroxide compounds were large surface areas, and in solution they play the role as a coagulant during electrocoagulation process. This product shows advantage of electrocoagulation comparing with the other chemical method. They generate during electrocoagulation, do not need to add any chemical. This is ultimate product that plays role important to remove pollutants from solution. These coagulants are useful for the fast adsorption of soluble organic compounds as well as metal ions in solution, consequently increasing a high COD removal efficiency from artificial wastewater by using aluminium electrodes [35-37]. Nonetheless, the concentration of COD in artificial wastewater after finishing electrocoagulation process that reduced at the initial pH except for 4.1 value. This could be contributed by the amphoteric characteristic of aluminum hydroxide that transformed to Al^{3+} and $Al(OH)_4^-$

ions as the initial pH value was low or high, respectively [22, 29]. Normally, the soluble products are main at high and very low initial pH of artificial wastewater, that was one of reason lead to COD removal efficiency from artificial wastewater to gradually decline.

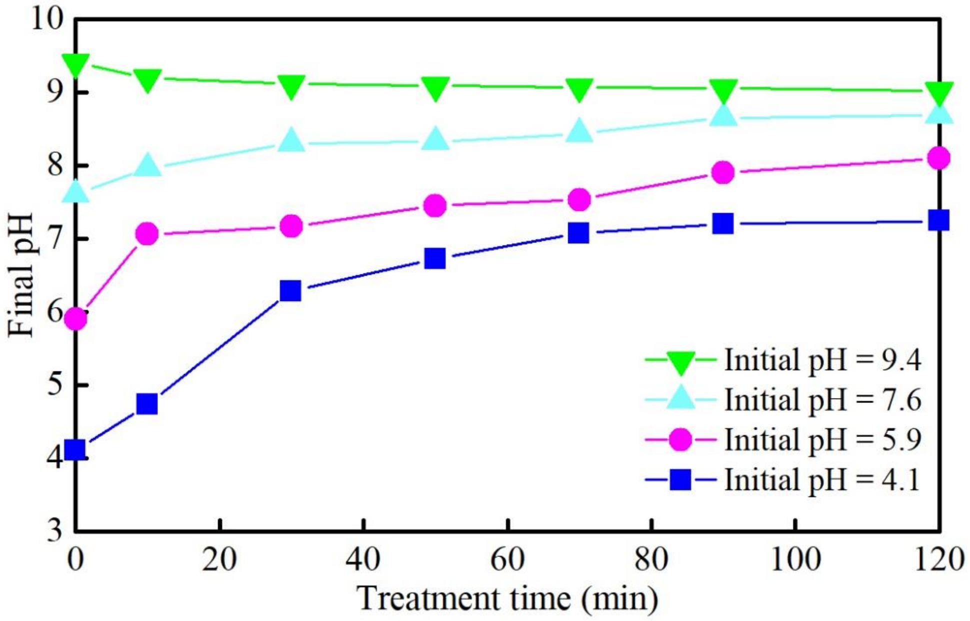

Fig 2.9. Fluctuation of pH with the treatment time at various initial pH at applied voltage of 15 V.

Fig 2.9 reveals the fluctuation of pH during electrocoagulation process based on treatment time with variety initial pH values. In the case of initial pH lower than 9 value, the final pH value enhanced by treatment time that can be explained that: Firstly, the hydrogen released from the cathodes, and secondly partly exchange of Cl^-, $SO_4{}^{2-}$ irons and $PO_4{}^{2-}$ anions with OH^- in $Al(OH)_3$ to discharge free OH^- ions in solution [28]. Whereas, in the case of initial pH higher than 9, the Ca^{2+} and Mg^{2+} cations that exist in medium they will coprecipitate with $Al(OH)_3$, leading to final pH value decrease. Furthermore, at an initial pH higher than 9 value, the $Al(OH)_4^-$ ions was dominant, leading to reduce the final pH of the artificial wastewater after finishing electrocoagulation process [21, 28]. Furthermore, the results from Fig 2.9 reveals that there is no significant final pH fluctuation with treatment time more than 90 min, recommending that the initial pH determines the long-term operating conditions of the electrocoagulation process.

2.4.2. Influence of treatment time

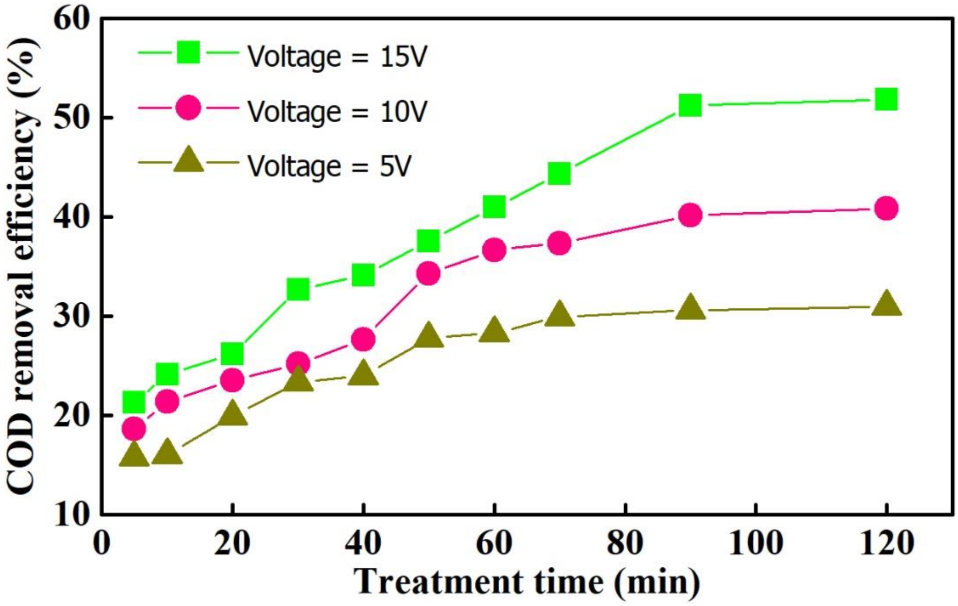

Fig 2.10. Influence of treatment time at initial pH 4.1.

In EC process, each parameter plays different important role. Investigating the optimum condition is necessary. Regarding treatment time, which not only decided the COD removal efficiency but also reduced specific energy consumption. Therefore, for using EC process to clean contamination water, the operation time need to investigate to optimal perform.

The results of influence of treatment time on COD removal efficiency is revealed in Fig 2.10. The results were considered at various allied voltage. Based on the figure, the conclusion could show that the maximum COD removal efficiency from artificial wastewater was gained faster at low applied voltages than at higher applied voltages. Therefore, based on these results it could be concluded that regardless treatment time, low applied voltages were not sufficient to promote more generated $Al(OH)_3$ formations. Moreover, whatever of the applied voltages, the COD removal efficiency from artificial wastewater got up to or stable after 90 min of treatment time for all experiments with different input conditions. This tendency was in total agreement with the fluctuation of initial pH, which is observed in Fig 2.9. The final pH raised fast with the range treatment time of 10 to 90 min due to the number of hydrogen bubbles increased according to Reaction (5). These hydrogen bubbles released from cathodes that are fine, improving the mixing degree of $Al(OH)_3$ and pollutants in medium during electrocoagulation process, and promoted the flotation process of the cell, leading to an increase in the overall COD removal efficiency *[20]*. Furthermore, COD removal efficiency from artificial wastewater depends on the concentration of aluminum and hydroxyl ions generated in the solution by equivalent electrodes. As the treatment time raised, the amount of aluminum dissolved from the anodes in the medium increases, and the hydroxyl ions release from cathodes also increase. As a results, enhancing the amount of $Al(OH)_3$ compounds causes more pollutants to be adsorbed by them, as a result increasing COD removal efficiency from artificial wastewater by using aluminum electrodes *[38]*.

2.4.3. Influence of the distance between electrodes

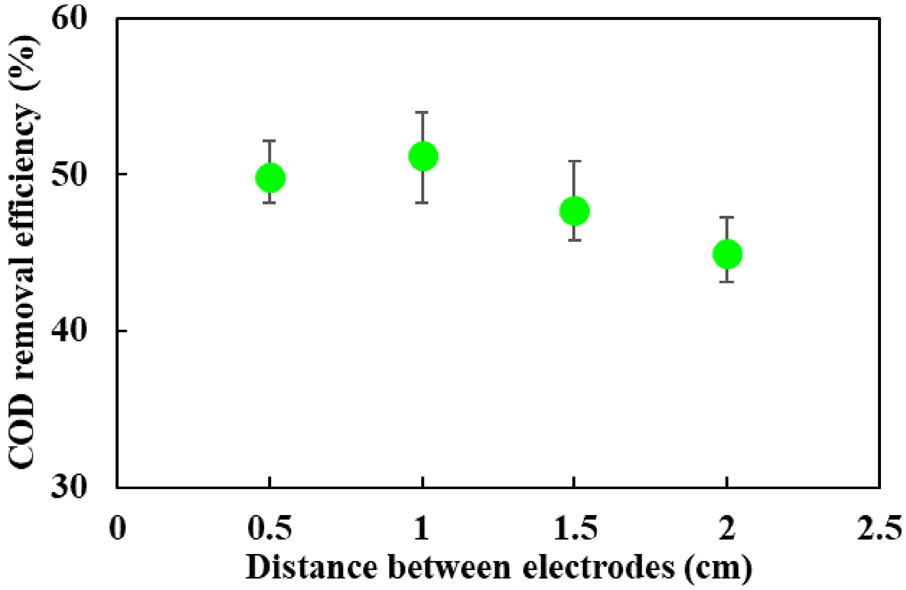

Fig 2.11. Influence of the distance between electrodes, input conditions at 15 V, pH= 4.1, and treatment time = 90 min.

The distance between electrodes plays a vital role to generate temperature in wastewater sample being treated as it strongly impacts the electrical resistance, and consequently the wastewater temperature during electrocoagulation [39]. Furthermore, it is not only strong influences the solubility of the precipitates, but also impacts the ability to produce the hydroxyl radicals, and dissolving of electrodes during electrocoagulation. As a result, the removal efficiency of technology will be determined [40]. Besides, the distance between electrodes effect on the specific energy consumption as well as number of generated coagulant and hydrogen bubbles. The optimum distance electrodes, which will bring to advantage both COD removal efficiency and reducing SEC, as well. In this study, to investigate effect of distance electrodes, the distance was changed from 0.5 to 2 cm. Fig 2.11 presents the influence of the distance between electrodes (x) on COD removal efficiency from artificial wastewater. The input conditions were selected for experiment to find the optimum of distance between electrodes. The results show that the maximum COD removal efficiency from artificial wastewater was observed at x=1 cm. This result can be explained that at short distance between electrodes, leading to higher electrostatic attraction appears in solution during electrocoagulation process. Therefore, the $Al(OH)_3$ formation in solution that played as a coagulant role and removed pollutants from artificial wastewater by sedimentation or flotation by hydrogen bubbles that generated from cathodes, degraded by collisions with each other. Whereas, when the distance of between electrodes increases, the electrostatic effect declined. As a result, the movement of generated ions in solution is slower. Therefore, they have more time to form $Al(OH)_3$ compounds for the aggregation and precipitation of suspended particles and for the adsorption of dissolved pollutants. Consequently, COD removal efficiency from artificial wastewater increased. However, as the distance between electrodes increases above the optimum (x=1 cm) value, the travel times of the ions in solution during electrocoagulation increase extremely, reducing the formation of aluminum hydroxide, that led to reduce the coagulation efficiency during electrocoagulation process. Consequently, the COD removal efficiency from artificial wastewater using aluminum electrodes decreased [41-43].

2.4.4. Influence of applied voltage

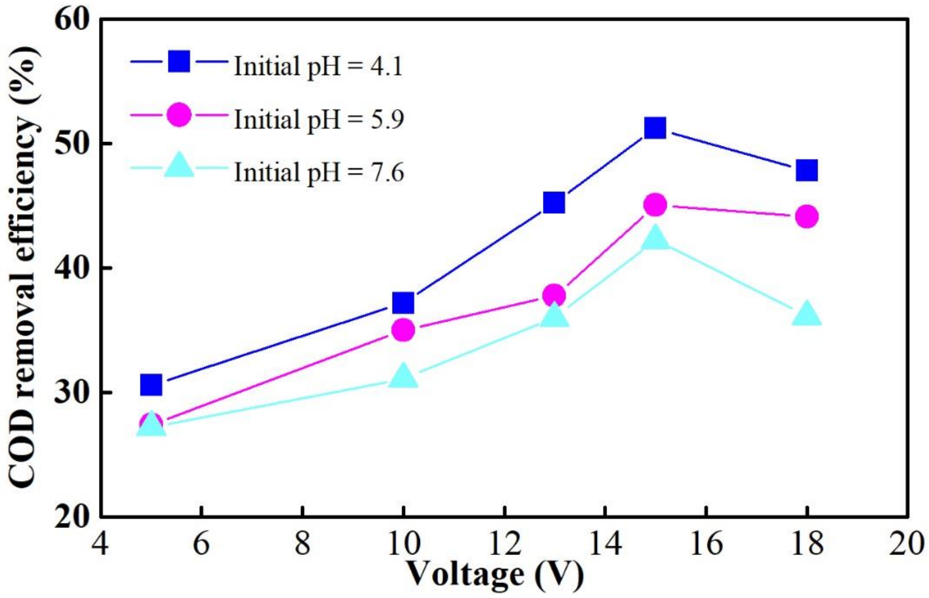

Fig 2.12. Influence of applied voltage, treatment time = 90 min at different pH.

Preliminary laboratory testing of electrocoagulation process that investigated the influence of applied voltage on the COD removal efficiency. It is notable that electrical current/applied voltage not only controls the coagulant dosage rate generated during EC process but also the rate of hydrogen bubble production, size and the floc growth that can effect on the EC process efficiency. Therefore, investigating of applied voltage on COD removal efficiency is necessary. As expected, it reveals that for a certain time, the COD removal efficiency significantly increased by the increase applied voltage for different initial pH of artificial wastewater as showed at Fig 2.12. Furthermore, disregarding of initial pH of artificial wastewater, the COD removal efficiency from this sample increased by the application of voltage on the reactor. The results presented that the COD removal efficiency from artificial wastewater could up to 51 % at applied voltage of 15 V. This result was in excellent agreement with Figure 4, where COD removal efficiency from artificial wastewater becomes stable and approaches its maximum faster at lower applied voltages. It can be explained that if applied voltage was lower than 15 V, the formation of soluble Al^+ ions is dominant in the electrocoagulation cell. Hence, the coagulation effects are less significant. Moreover, in case of low voltage is applied to the electrocoagulation cell that is insufficiently to produce a larger number of Al^{3+} ions as well as OH^- from cathodes, reducing aluminum hydroxide formation. On the other hand, there are no more hydrogen bubbles are generated from the cathode due to insufficient voltage, reducing flotation process. As a result, the COD removal efficiency from artificial wastewater was low.

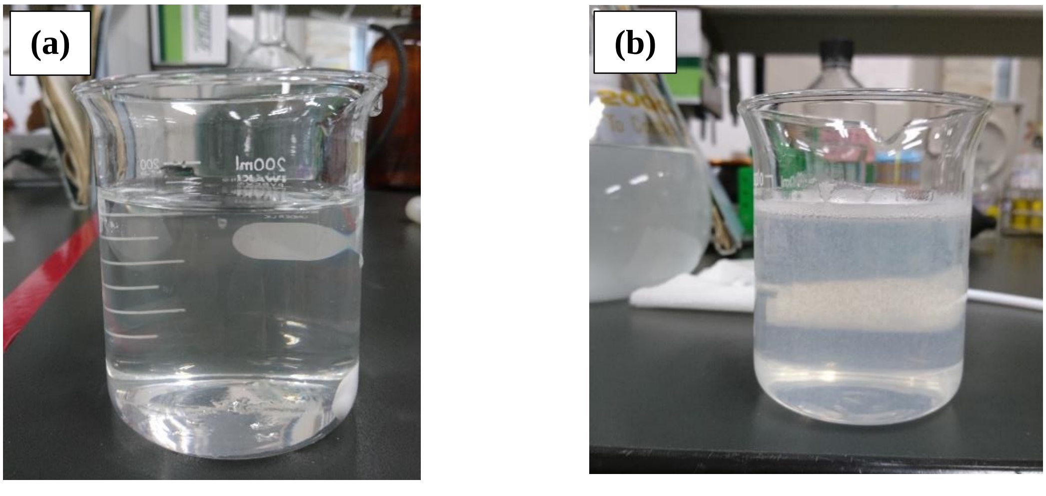

Fig 2.13. Artificial wastewater before (a) and after experiment (b), pH =4.1, V = 15V, t = 90min

In contrast, when applied voltage was more than 15V, the competition between aluminum dissolution and oxygen evolution occurred at the anode electrode, reducing the precipitate formation and leading to a reduce in the COD removal efficiency from municipal wastewater [30, 44].

The Fig 2.13 shows that artificial wastewater before (a) and after (b) electrocoagulation experiment. The results reveal that after electrocoagulation process, there are many with flocs in solution. It is color of aluminum hydroxide that generated from anodes after finishing experiment.

2.4.5. Interaction between the size of hydrogen bubbles and COD removal efficiency

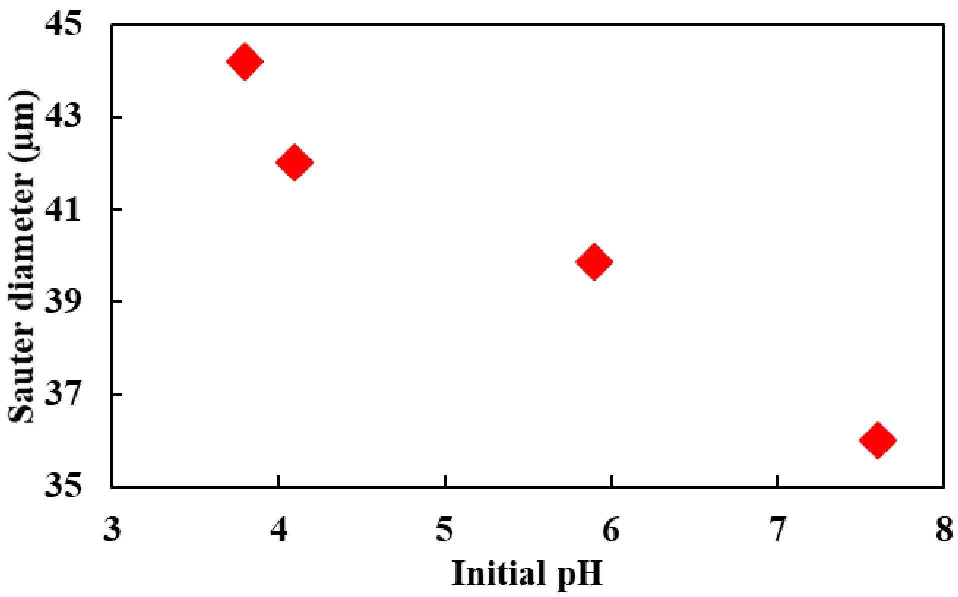

Fig 2.14. Sauter diameter as a function of initial pH, input conditions of applied voltage = 15 V, treatment time = 90 min.

To understand the characteristic of hydrogen bubbles that generated from anodes during electrocoagulation process, the size of them was calculated. Fig 2.14 reveals that the initial pH of artificial wastewater raised from 3.8 to 9.4, the Sauter diameter reduced from 45 to 36 µm, respectively. In general, it has been widely reported that high initial pH of wastewater leads to a reduction in hydrogen bubble size. Therefore, the hydrogen bubble size strong depends on the H^+ concentration in solution during electrocoagulation process. If concentration of H^+ in solution was low, the diameter of the hydrogen bubbles generate from anodes was small, and vice versa [45, 46]. The H^+ concentration in solution reduced significantly due to the alkaline wastewater, resulting in a smaller volume of nucleated hydrogen bubbles, as the Sauter diameter was revealed in Fig 2.14.

Fig 2.15 reveals the correlation between COD removal efficiency from artificial wastewater and the Sauter diameter of hydrogen bubbles in solution during electrocoagulation process. After finishing all experiment, the results show COD removal efficiency from artificial wastewater up to 51 % at hydrogen-bubble sizes at around ~42 µm. Small size of hydrogen bubbles is easily dragged around by the fluid movement, restricting their ascent and promoting foamy formations. In contrast, large bubbles sizes easily breakdown during their go up, reducing the contribution of flotation process to remove COD from artificial wastewater. Thus, the results of this study suggest that hydrogen bubble sizes of ~42 µm could promote flotation process during electrocoagulation, which contributes to pollutant removal from media, resulting in increased COD removal efficiency from artificial wastewater by using aluminum electrodes [47].

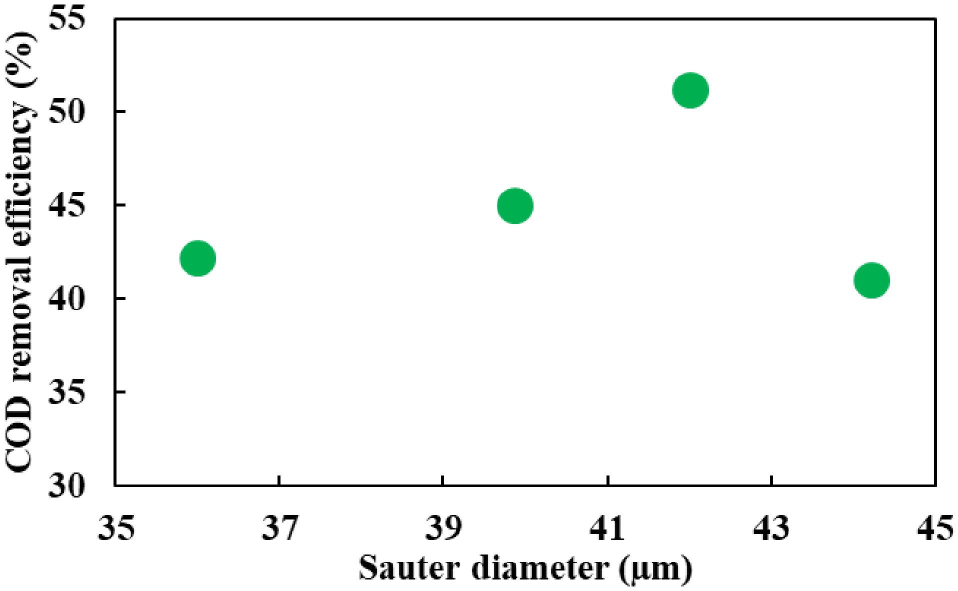

Fig 2.15. The influence of Sauter diameter on COD removal efficiency at variety initial pH, voltage = 15 V, and treatment time = 90 min.

Therefore, the results recommend that to enhance COD removal efficiency from artificial wastewater, it needs to improve flotation efficiency process should include: control of influent and effluent pH of solution during the electrocoagulation process, and narrow and controlled hydrogen bubble size, instant, through the use of an external bubble generator.

2.4.6. Analysis by using SEM, XRD, and EDS

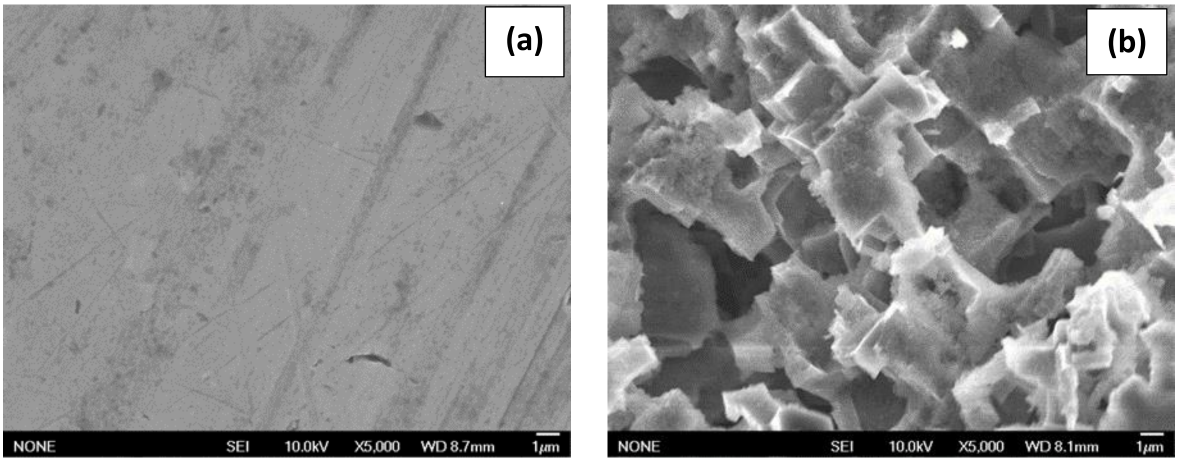

Fig 2.16. FE-SEM images of anode electrode (a) before and (b) after the electrocoagulation process.

In this work, the surface microstructure of the anode was observed through FE-SEM. Fig 2.16 reveals the surface of the anode before(Fig 2.16a) and after (Fig 2.16b) the electrocoagulation process. The results reveal that the morphology surface of the anode was rough and indentations shape were generated. This phenomenon was explained that the anode dissolution during electrocoagulation process. The formation of indentations can be understood by the consumption of anode material at the active sites because of the production of oxygen at the surface of anodes [48].

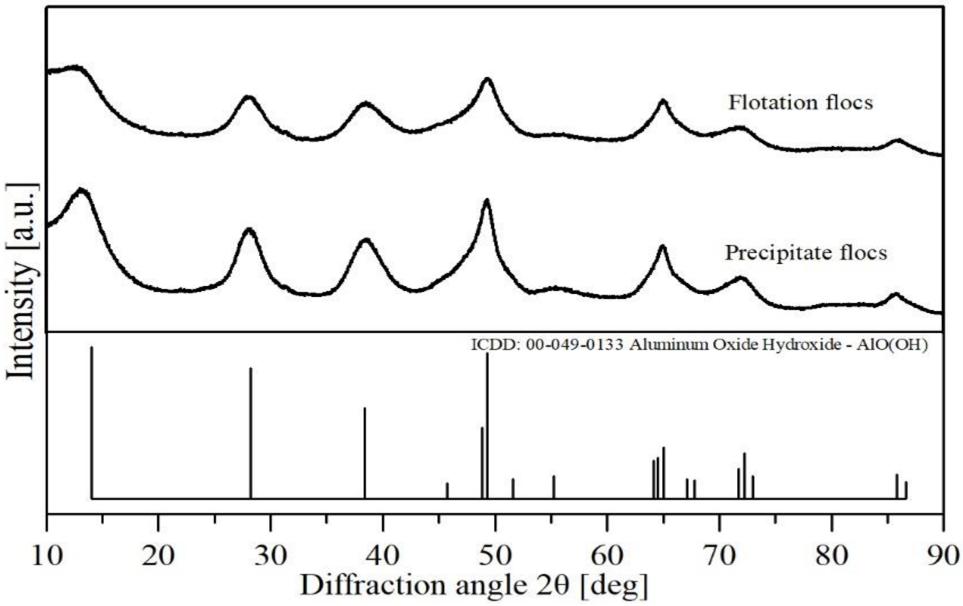

Fig 2.17. X-ray diffraction patterns of flotation and precipitation

The X-ray diffraction patterns of flotation and precipitation after electrocoagulation process was revealed in Fig 2.17. For flotation, the signal intensities from the X-ray diffraction was slightly lower than that of precipitation. The intensity of flotation decreased compared with precipitation, that can be attributed to better soluble organic compound adsorption during flotation process than precipitation process [49]. Furthermore, X-ray diffractions were found to suitable the values of aluminum oxide hydroxide in both powders that were collected from flotation and precipitation (ICDD 00-049-0133). For the other elements diffraction signal, which could not see due to the low content in crystallites, such that the signal was covered by that of hydroxides [47].

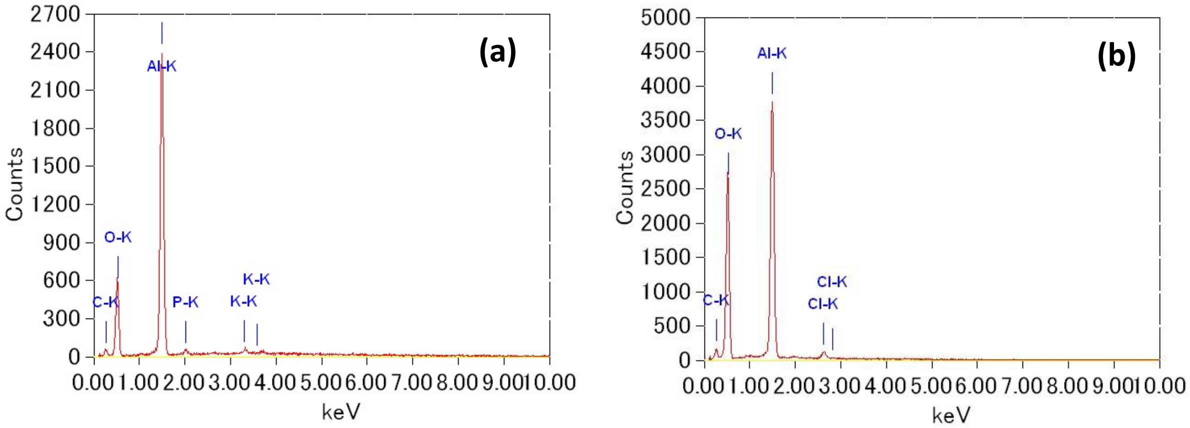

Fig 2.18. Type of elements were adsorbed after electrocoagulation process: for (a) flotation and (b) precipitation.

The type of elements in powder that was collected from precipitation and flotation after finishing electrocoagulation process as showed in Fig 2.18, such as Al, O, P, K, and Cl. The result from figures confirmed that the elements of C, P, and K were entrapped within the $Al(OH)_3$ complex during electrocoagulation process and were removed by flotation process (Fig 2.18a). On the other hand, Cl element was adsorbed by the coagulant and it was removed by precipitation as showed in Fig 2.18b. The results from Fig 2.17 and Fig 2.18 could be said that the ability of flotation can adsorb more pollutants than precipitation [47]. Therefore, a bubble generator and pH control in initial as well as during electrocoagulation process could enhance the flotation function, thus increasing COD removal efficiency from artificial wastewater using aluminum electrodes.

2.5. CONCLUSIONS OF CHAPTER

Electrocoagulation was used to reduce the chemical oxygen demand (COD) from a standard artificial wastewater. Highest COD removal efficiency (51 %) was gained by using Al electrodes, and adjusting the influent pH = 4.1. The results reveal that the initial pH seems to manage the effluent pH during electrocoagulation process, and therefore, it determined the final COD removal efficiency of artificial wastewater treatment. Thus, at initial pH=4.1 the main electrocoagulation products corresponded to the insoluble $Al(OH)_3$, whereas at higher influent pH, a gradual formation of soluble Al^{3+} based species was promoted and therefore, the final COD removal efficiency tends to reach a lower yield. Furthermore, a minimum applied voltage at 15 V could be applied to promote an enough formation rate of insoluble species from the anode dissolution and cathode hydrogen bubbling. In addition, the results also show that the size of hydrogen bubble releases from cathodes that contributed to enhance COD removal efficiency from artificial wastewater. Hydrogen bubble size around 42 µm may be suitable to promote the flotation process. Further experiments, for instance, using external bubble generators and controlling influent and effluent pH, are going to be performed for determining the impact of floatation process on the wastewater purification process under electrocoagulation. Finally, the results showed that the flotation could be better than precipitate in removing pollutants from artificial wastewater.

CHAPTER 3. USING AN NANOSECOND PULSE TO ENHANCE COD REMOVAL EFFICIENCY FROM MUNICIPAL WASTEWATER.

3.1. ABSTRACT

This work is carried out to compare the efficiency of nanosecond pulse (NSP) and direct current when they are used as a main power supplies for electrocoagulation to remove COD from municipal wastewater. All experiment used municipal wastewater from the Sewage Center in Nagaoka, Japan. Four commercial grade aluminum plates connected in monopolar-parallel shape, which were used as the main electrodes during the electrocoagulation process. The results show that as using a DC power supply, the COD removal efficiency from municipal wastewater up to 68 %, and this value was 80 % as Nanosecond pulse instead of DC power supply. The use of an NSP power supply allows for operation at higher voltage, promoting higher number of coagulant as well as amount of hydrogen bubbles, enhancing in a high COD removal efficiency. Furthermore, at the similar COD removal efficiency was around 68 %, the use of an NSP power supply can reduce the specific energy consumption (SEC) around 15% of compared to a DC power supply. Additionally, to increase COD removal efficiency from 60 – 68 %, the specific energy consumption of NSP power supply was two to three times less than that in use of a DC power supply. On the other hand, the results recommend that as using NSP power supply as a main power, the optimum conditions of frequency (*f*) and pulse width (*pw*) were 10 kHz and 1µs pulse to get a low specific energy consumption, respectively. An NSP was applied to operate electrocoagulation could enhance COD removal efficiency but low specific energy consumption. That is advantage pint to promote using electrocoagulation with NSP power supply for industry wastewater.

3.2. INTRODUCTION

Nowadays, the municipal wastewater is big problem in many countries in the world, typically in the developing countries. The management of municipal wastewater and economy development is difficult topic at those countries. In the fact, there are many wastewaters such as household and industries concentrate in sewage center where have to clean before discharge to reduce the negative impacts of urban development on the environment.

However, in developing or poor countries, they have a lot of things to do such as infrastructure building, education, factory, etc. than investigation to build sewage center because the benefits are not directly received, and they are not linked to immediate economic benefits. On the other hand, the cost of the maintenance and operation of a wastewater treatment plant is still quite expensive [50]. As described above chapter, the COD parameter is the amount of oxygen used in the chemical oxidation of inorganic and organic matter in water in general and wastewater in particular. It is a traditional parameter and it is used as an indicator to determine of water quality [18, 51].

One more time to say that electrocoagulation is having confidence technology to clean wastewater due to its high efficiency and compact size. Moreover, outstanding of electrocoagulation process exposes that it integrated the benefits of 3 process: flotation, coagulation and electrochemistry [29]. Moreover, the electrocoagulation can be applied with renewable energy that easily to use in rural or isolation area. The use of renewable energy sources to operate electrocoagulation process, promoting an eco-friendly route for wastewater treatment that reduces the total carbon footprint [52]. Contributing to reduce greenhouse gas.

Currently, the pulsed technology is popular to apply in some areas. It is considered as tool to replace traditional process in some fields. It is applied in molecular biology for electroporation, materials synthesis, and food industry for bacterial inactivation, and the results were acceptable. Furthermore, the pulse technology also used to remove organic compounds from wastewater. The last studies have proved that it is a sustainable non-chemical method with no adverse effects [53-56]. Additionally, last researches in the use of nanosecond pulse used as main power supply for operation of electrocoagulation show that this power supply is more efficient than that using direct current due to its slower anode polarization, lower anode overvoltage, and passivity. On the other hand, the pulse technology can reduce the operation time. Therefore, it requires less energy than DC power supply [57-59].

Currently, the electrocoagulation have been considering a reliable technology to remove COD from different types of wastewater such as vegetable oil refinery [60], textiles [61], landfill leachate [62] and petroleum refinery [63], industries such as dairy [64], chemical mechanical polishing [65], laundry [66], and tobacco [67] as well as that from domestic usage [68], and hospital operations [69]. Moreover, the pathogenic microorganisms were removed from wastewater and river water by using electrocoagulation process [70-72]. Furthermore, the last studies show the efficiency to remove pollutants from municipal wastewater using electrocoagulation [73-75]. However, regarding power supply to operate electrocoagulation process. All last studies applied DC power supply as a main power. To extent of my knowledge, there is few or have no researches that used to remove COD from municipal wastewater using nanosecond pulse power supply [76]. Therefore, in this work I investigated the nanosecond pulse efficiency as used for electrocoagulation to remove COD from municipal wastewater. The compression between nanosecond pulse and direct current was also conducted.

In this experiment, the Al electrodes were selected to remove COD from municipal wastewater. When voltage is applied, the main reactions appear in solution at anode as follows:

$$Al - 3e = Al^{+3}. \qquad (1)$$

At the same time, at the cathode the water reduction occurs to release hydroxyl ions (OH^-) and hydrogen bubbles:

$$2(H_2O) + 2e^- = H_2 + 2(OH^-). \qquad (2)$$

The Al^{3+} cations release from anodes that will combine with OH^- from cathodes, finally forming insoluble coagulant of $Al(OH)_3$, removing from solution by precipitation and flotation process after it adsorb pollutants [29]. Moreover, hydrogen bubbles float on most of the flocs in solution. As a result, allowing the formed aggregates to be removed from the wastewater by decantation or flotation [77].

3.3. MATERIALS AND METHODS

3.3.1. Experiment wastewater

In this work, municipal wastewater samples were collected from a municipal sewage treatment center in Nagaoka, Japan. The characteristics of this wastewater were showed in Table 3.1.

Table 3.1. Characterization of municipal wastewater.

Parameters	Units	Value
pH	-	7.1
COD	mg/L	177
Electrical conductivity	mS/m	61.2
n-hexane extract	mg/L	33
Cu	mg/L	0.03
Zn	mg/L	0.08
Dissolved Fe	mg/L	0.28
Dissolved Mn	mg/L	0.07
Total N	mg/L	45.7
Ammonia compounds	mg/L	13.6
Total Fe	mg/L	0.65
Total Mn	mg/L	0.09
Cl-	mg/L	60.3
TN (mg/L)	mg/L	28.6
TP (mg/L)	mg/L	3.5
NO_3^- (mg-N/L)	mg-N/L	0.1
NH_4^+ (mg-N/L)	mg-N/L	12.9

In this work, the pH was measured by pH meter (Model HM-30R, 0.000–14 range), and electrical conductivity were determined by using a conductivity meter (Model ES-71) before and before and as soon as after the electrocoagulation process. The COD was measured following the HACH 8000 method. The other parameters were supplied from Nagaoka sewage center.

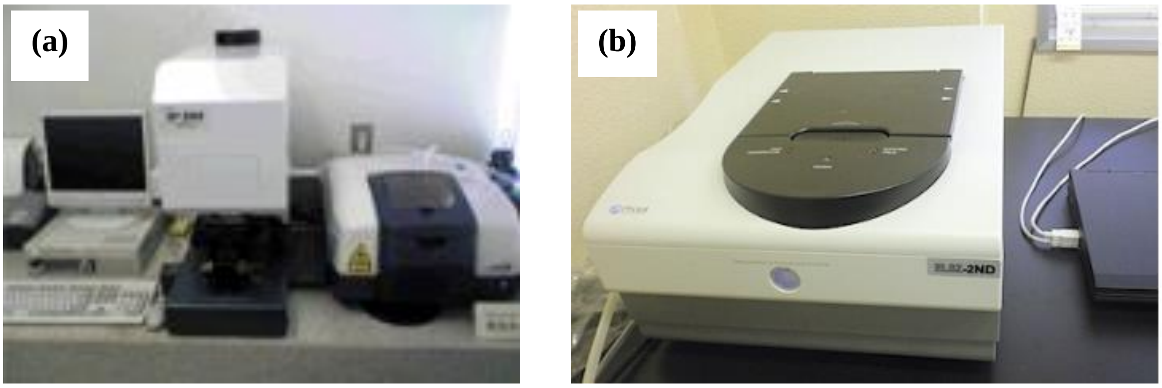

Fig 3.1. FT-IR 4200 (a) and Zeta Potential & Particle Size (b) equipment

Beside equipment that were described in Chapter 2, FT / IR-4200 JASCO Corporation and Zeta Potential & Particle Size – model ELSZ-2nd (Otsuka Electronics) were used to analyze precipitate characteristic.

The COD removal efficiency (η) from municipal wastewater at treatment time *t* was determined as follow:

$$\eta(t) = \frac{COD_0 - COD_t}{COD_0} * 100 \quad (3)$$

In which COD_0 was COD at beginning, and COD_t was COD at treatment time *t*.

For SEC in use of NSP power supply that could be calculated as follows [76]:

$$SEC_{NSP} = \frac{\int_{t_1}^{t_2} u(t)i(t)dt \times f \times \tau}{3.6 \times 10^6 \times v} \quad (4)$$

In which SEC_{NSP} is specific energy consumption of NSP power supply (kWh/m^3); u(t) is the applied voltage (V); i (t) is current intensity (A); t_1 and t_2 represent the time range for a single pulse (s); *f* is the pulse repetition frequency (Hz); τ is the treatment time (s), and v is the municipal wastewater volume (m^3).

For DC power supply, the SEC could be calculated as follows [76]:

$$SEC_{DC} = \frac{UIT}{1000\, v} \quad (5)$$

In which SEC_{Dc} is specific energy consumption of a DC power supply (kWh/m^3); U is the applied voltage (V); I is the current intensity (A); and T is the treatment time (h).

The equations (3), (4) and (5) are used to calculate COD removal efficiency and specific energy consumption for next chapters.

3.3.2. Designed of experiment cell

The set-up of electrocoagulation experiment as showed in Fig 3.2. The beaker contained 200 ml of municipal wastewater sample. The Al material was selected to make 4 electrodes and connected with monopolar parallel. The dimension of electrodes was the same of 1 × 20 × 55 mm^3, and they were arranged the same distance between electrodes (x = 1 cm), as shown in Fig 3.2.

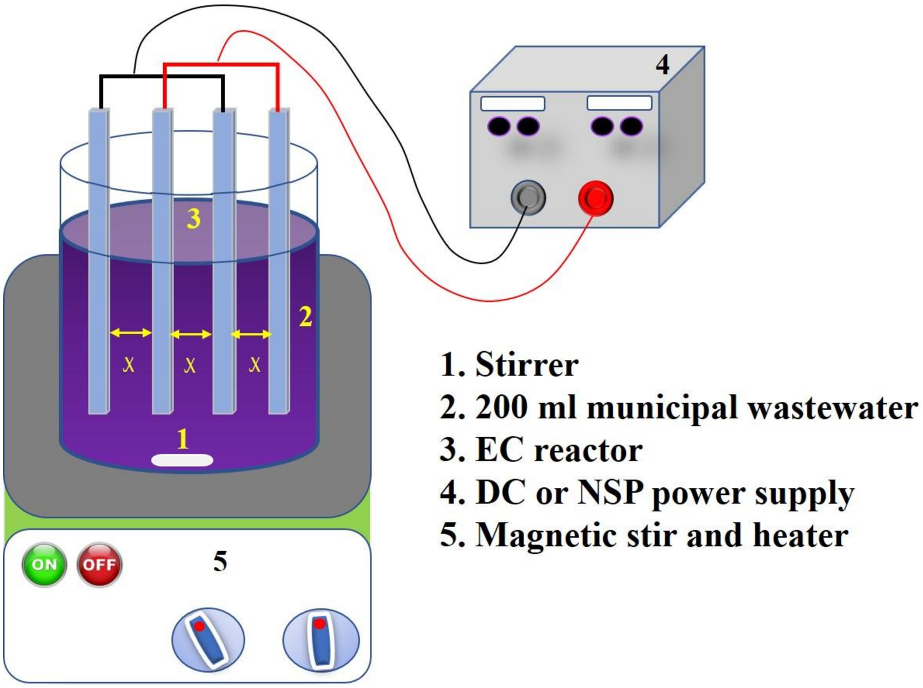

Fig 3.2. The EC setup in laboratory at the same of distance between electrodes x = 1 cm for all experiment.

In this work, the PL-650-0.1 (DC power supply) and HK-10N (NSP power supply) from Matsusada Precision Inc. (Japan) were used in the potentiostatic mode. The suitable voltage ranges were selected to avoid breakdown voltage. For a DC power supply, the range of voltage from 1 V to 5 V, and 1 V to 50 V in use of NSP power supply. Regarding an NSP power supply, the parameters effect on the COD removal efficiency were investigated, such as frequency and pulse width (*pw*) were set to ranges of 4 kHz –12 kHz and 0.4 µs –1.2 µs, respectively. The optimum input conditions were determined as investigated *pw* and *f*, *pw*=10 KHz and *f* = 1 µs were used for all experiment.

All electrocoagulation experiment, the municipal wastewater samples were stirred at 200 rpm at room temperature, ensuring mix between the pollutants and coagulant (aluminum hydroxide) that generated from electrocoagulation cell.

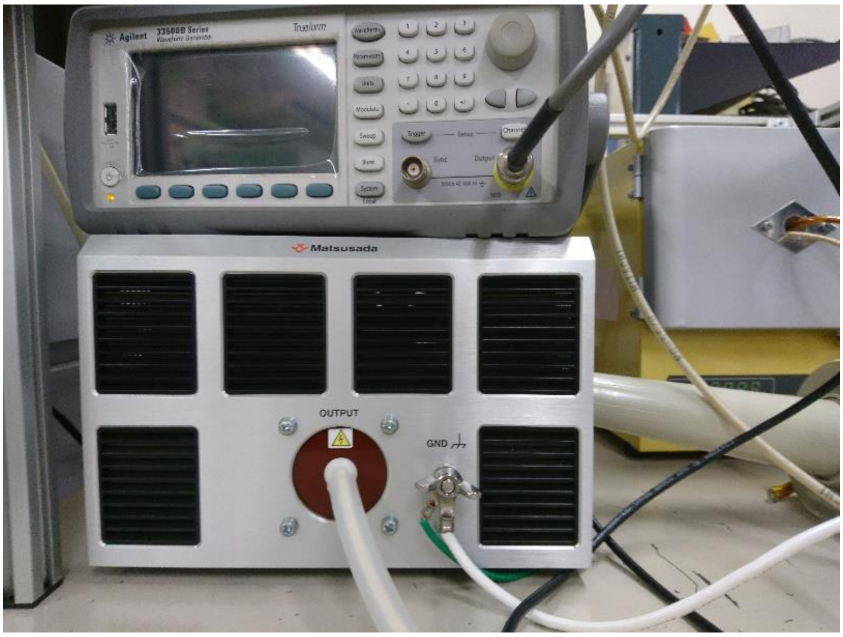

Fig 3.3. High voltage power supply HK-10N

3.4. RESULTS AND DISCUSSION

3.4.1. Influence of pH

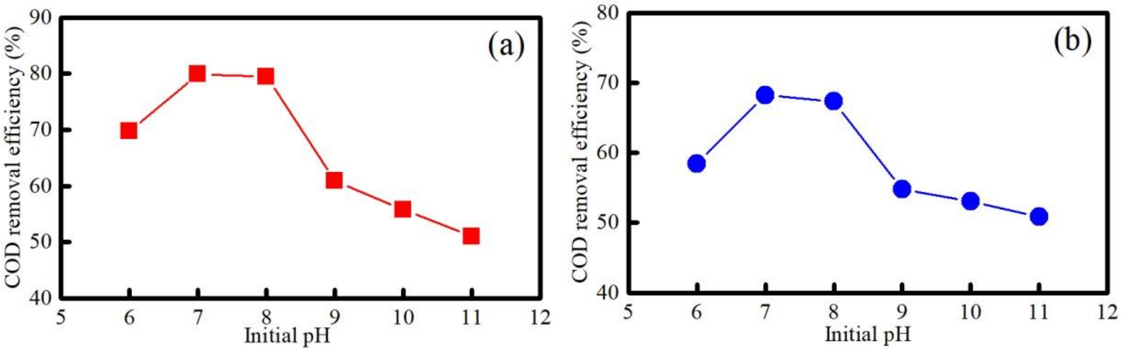

Fig 3.4. Influence of pH on the COD removal efficiency in use of (a) NSP = 50 V and (b) DC = 5 V, and treatment time = 90 min.

pH is one of most important parameters that effects on the type of products generated during electrocoagulation. Optimum pH value will decide a lager of coagulant dose that promote removing COD from municipal wastewater. For recognizing the effect of pH on COD removal efficiency from municipal wastewater, the initial pH of the wastewater samples was changed from 6.0-11.0 values by using HCl or NaOH. Fig 3.4 reveals that as using of a DC power supply and an NSP power supply, which led to the results in different maximum COD removal efficiencies. Regarding a DC power supply, the maximum was 68%. Whereas, in case of an NSP power supply, the maximum CO removal efficiency from municipal wastewater was 80%. These results gained between range of pH 7 and 8. This could be caused to the simultaneous variation of the formation of monomeric and polymeric species that are transformed to $Al(OH)_3$ at the end. Aluminum hydroxide is coagulant and insoluble. It is useful for the rapid adsorption of soluble organic compounds and capturing of colloidal particles in solution [78], finally removing them from solution by precipitation or flotation process. As a result, enhancing the COD removal efficiency from municipal wastewater by using aluminum electrodes. Whatever in use of DC or an NSP power supplies, the COD removal efficiency from municipal wastewater reduced at initial pH that did not belong the range of pH 7–8 value. This could be attributed to the amphoteric characteristics of aluminum hydroxide that will be transferred to Al^{3+} at low initial pH or $Al(OH)_4^-$ ions at high initial pH value [78, 79], the soluble products generate during electrocoagulation is factor to reduce the COD removal efficiency.

However, there is advantage point in this work that the initial pH value of natural municipal wastewater changes from 7 to 8. Thus, all electrocoagulation experiments were used to directly experiment with no additional HCl or NaOH to change of initial pH value.

3.4.2. Influence of applied voltage

Among the various parameter that effect on the COD removal efficiency from municipal wastewater. The voltage plays important role that strongly influences the efficiency of method. During electrocoagulation process, the applied voltage effects on the rate of electrochemical reactions that decides the quantity of coagulant generated and number of hydrogen bubbles as well as their size. Furthermore, the applied voltage determines the reactions that occur on the electrode surface.

After all experiments with different input conditions, the results show that whatever in use of a DC or an NSP power supplies, the COD removal efficiency increased monotonically by an increase applied voltage as showed in Fig 3.5. This can be understood by relationship between the number of ions released in solution and applied voltages. The detail of the amount of the Al^{3+} released from the anode electrodes and OH^- ions generated from cathode increased. Consequently, the dose of aluminum hydroxide floc formation in solution during electrocoagulation is promoted under

Equation (6). The last researches show that the aluminum hydroxide compounds show large surface areas and they play as coagulants role in solution, making easily fast adsorption of soluble organic compounds and metal ions from municipal wastewater, and get rid of them from solution. That promoted enhancing the COD removal efficiency from municipal wastewater by using electrocoagulation process with aluminum electrodes [80, 81].

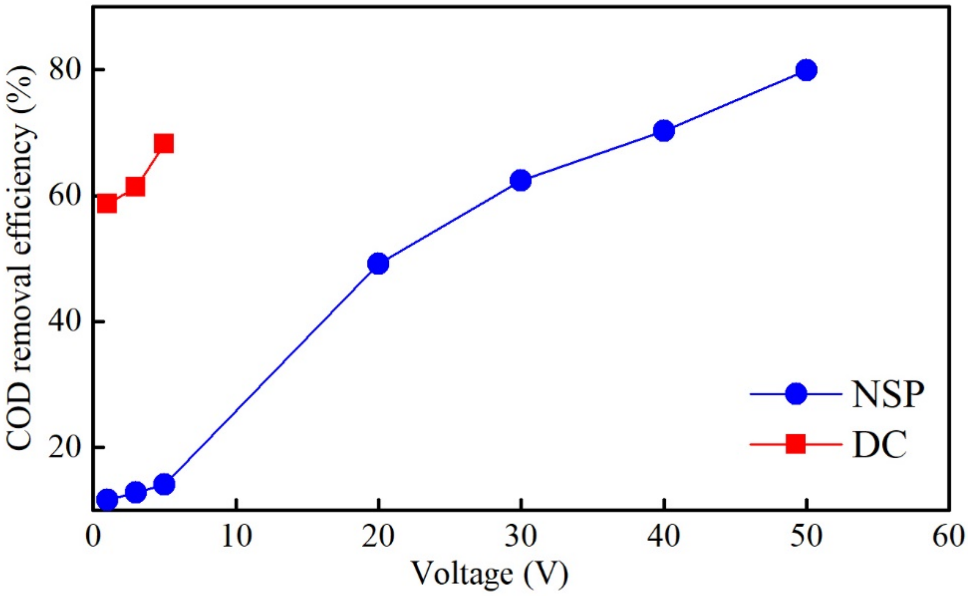

Fig 3.5. Influence of voltage on the COD removal efficiency in use of DC and NSP power supplies, treatment time = 90 min.

Furthermore, there was relation between applied voltage and the number of hydrogen bubbles that released from cathodes during electrocoagulation process. In the fact the hydrogen bubble formation rate released from the cathode electrode during electrocoagulation increase with an increase the applied voltage. The hydrogen bubbles generate from electrocoagulation process will increase the ability mixing between coagulant and pollutant, then the hydrogen bubbles will adsorb flocs during operation time, finally they contribute to the removal of pollutants by flotation process. Here is one of advantage of electrocoagulation, that can use the advantage of coagulation and flotation process in one cell [76].

$$Al^{3+} + 3H_2O = \ Al(OH)_3 + 3H^+ \qquad (6)$$

The results show that the COD removal efficiency from municipal wastewater using aluminum electrodes up to 68% as using a DC, and 80% were obtained in use of an NSP power supply. The different the maximum in COD removal efficiency that can prove the advantage of an NSP power supply comparison with a DC power supply. The NSP can promote the efficiency of EC process. On the other hand, because the operating conditions for maximum COD removal efficiency from municipal wastewater was differed between these power supplies, 5 V in use of DC and as using an NSP at 50 V. Therefore, a similar COD removal efficiency of $COD_{NSP} \approx COD_{DC} \approx 68\%$ was used to more directly compare the specific energy consumption and COD removal efficiencies from municipal wastewater using aluminum electrodes at 5 V for a DC power supply and 40 V for an NSP power supply, as showed in Fig 3.5.

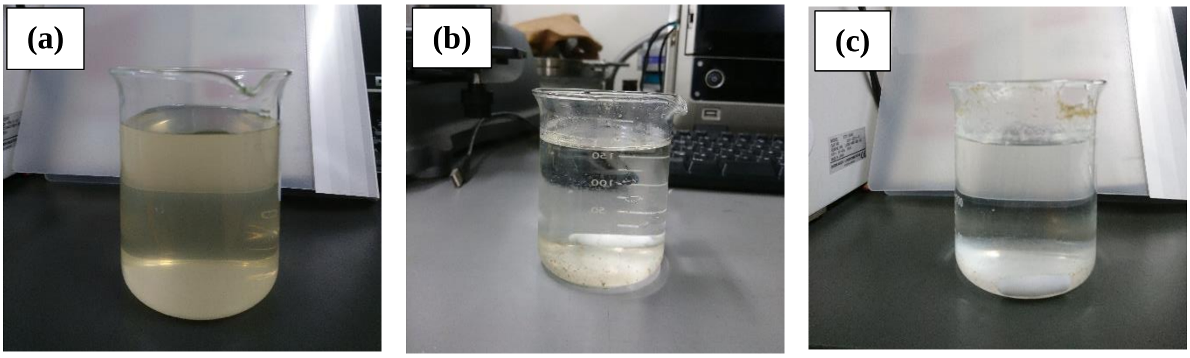

Fig 3.6. The wastewater sample before (a) and after EC process, (b) using NSP-50V and (c) DC-5V, treatment time 90min

Fig 3.6 show that the municipal wastewater before and after EC process as using NSP (b) and DC (c). The results of experiment reveal that the wastewater treated is more transparent than before that one. On the other hand, regardless power supplies there are many white flocs inside the wastewater after experiment, which proves that aluminum hydroxide was generated during electrocoagulation process.

Increasing of COD with applied voltage that can be explained by zeta potential. The degree of the zeta potential in solution that can point the potential stability of the colloidal system in medium during electrocoagulation process. If all the particles in suspension have a large negative or positive zeta potential. This condition makes them tend to repel each other. As a result, there will be no potential for the particles to come together. However, if the particles have low zeta potential values then there will be no force to prevent the particles coming together and flocculating. Therefore, the particles easily adherence pollutants in medium at low zeta potential. As a result, the pollutants are removed from water is increasing. The magnitude of the zeta potential is predictive of the colloidal stability of the solution, as shown Table 3.2 [82]

Table 3.2. The stable of particle based on zeta potential

Zeta potential	Unit	Stability behavior
0 to ±5	mV	Flocculation or coagulation
±10 to ±30	mV	Incipient instability
±30 to ±40	mV	Moderate stability
±40 to ±60	mV	Good stability
More than 60	mV	Excellent stability

For zeta potential is less than positive of +25 mV or greater than negative of −25 mV that will eventually agglomerate because of interparticle interactions, including van der Waals and hydrophobic interactions, and hydrogen bonding [82]. Therefore, regarding to raw municipal wastewater, the zeta potential is -21 mV. This is good condition for electrocoagulation process.

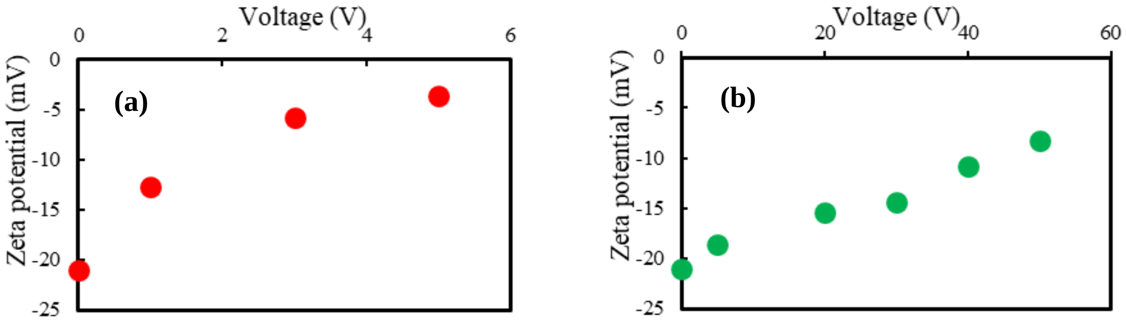

Fig 3.7. Effect of applied voltage on Zeta potential, using DC (a) and NSP (b)

Fig 3.7 shows that zeta potential as function of voltage regardless NSP or DC. Zeta potential tends to 0 mV value as applied voltage increases from 1 – 5 V of DC and 5 – 50 V of NSP. After finishing the experiment, the zeta potential using a DC reached to -3.53 mV at 5V. While the zeta potential of NSP was -8.29 mV. These values were lower than 10 mV. It is worth noticing that the particles have a tendency to agglomeration each other. This is an advantage for removing pollutants from wastewater.

As a consequence, the COD removal efficiency increases. Furthermore, this also implies that the flocs will increase with time. In this study, the growing of floc was investigated.

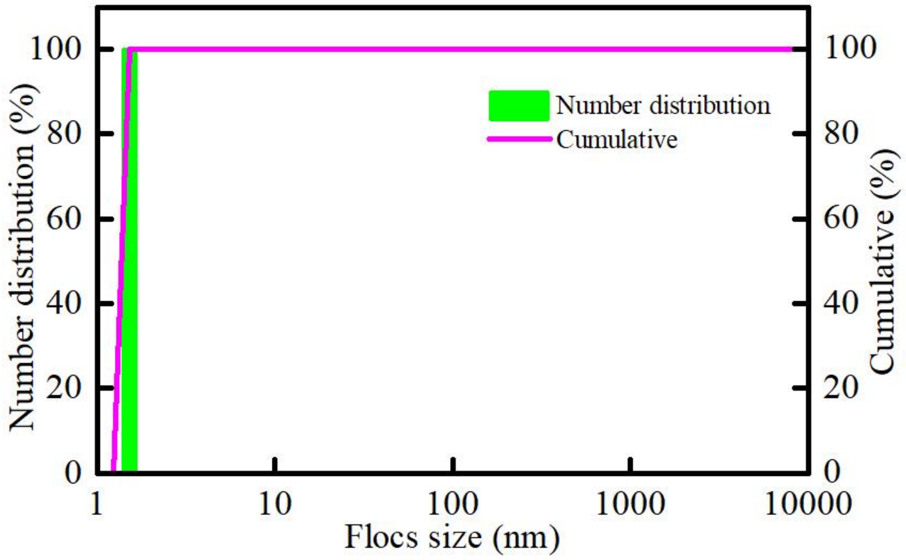

Fig 3.8. Then flocs size distribution of raw wastewater

Fig 3.8 show that the almost size of flocs in municipal wastewater is 1.52 nm. This size increased by applied voltage after EC experiment both DC and NSP. Regarding DC, the size of the flocs increased to 43.3 nm (99.8 %) at 1V (Fig 3.9). As the applied voltage was 3V, the flocs size fast increased. Where, 69.2 % of flocs that had 81.1 nm of size, 20.2 % (99.9 nm), 5.8 % (123.3 nm), and less than 3 % of flocs size from 6579.3 – 8111.3 nm as shown Fig 3.10a. Additionally, the Fig 3.10b reveals that percentage of the big size of floc made up higher as 5V applied voltage, such as 57.6 % of 151.9 nm of flocs size, 18.9 % with flocs size around 187.4 nm, and more than 10 % of flocs size that fluctuated from 6579.3 – 8111.3 nm.

Regarding NSP power supply, although the zeta potential is higher than DC after the experiment. However, in the case of NSP, the size of the flocs is bigger than DC after EC process. This demonstrated that the ability coagulation using NSP is higher than in the use of DC. As a result, there are more pollutants that will be removed from the medium as using NSP as a comparison with DC.

As the applied voltage was 5V, the zeta potential is -18.65 mV after the EC experiment (Fig 3.11a). This value is not a significant difference with the zeta potential of raw municipal wastewater (-21mV). This is causing the flocs that grew slowly.

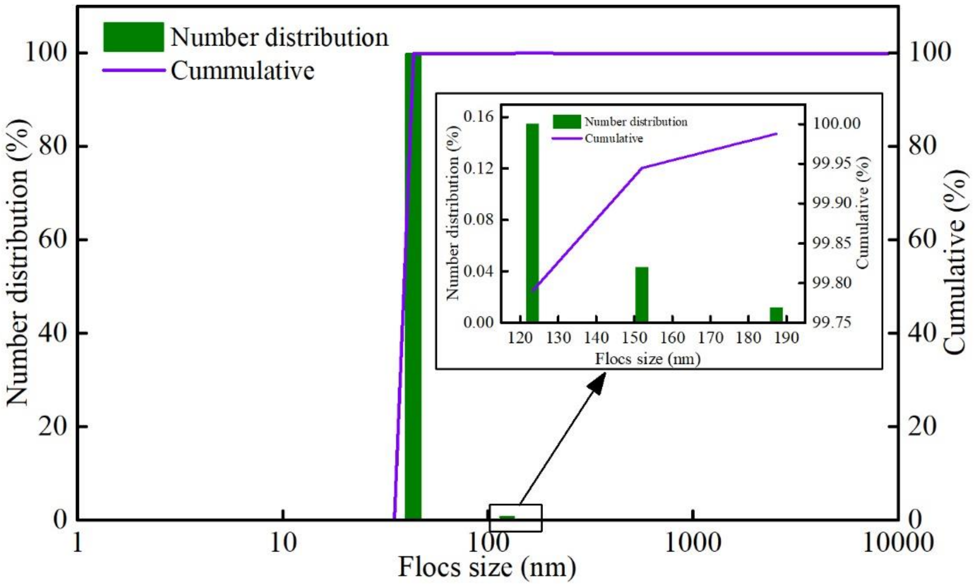

Fig 3.9. Flocs size distribution by using 1V of DC

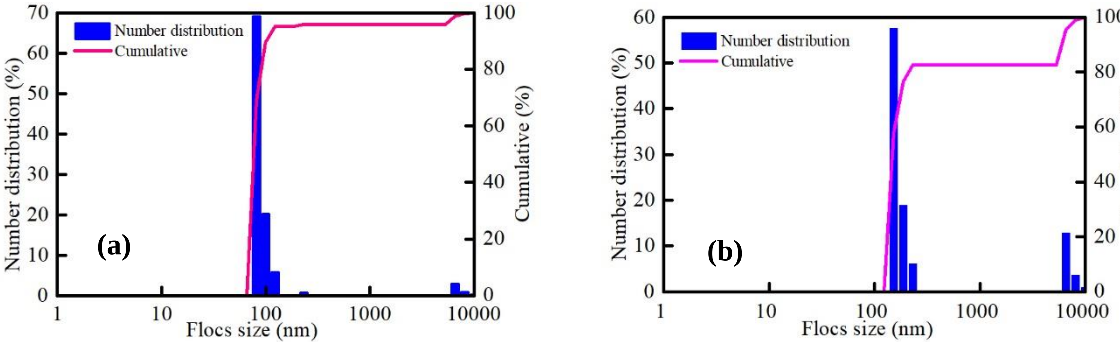

Fig 3.10. Flocs size distribution by using DC, 3V (a) and 5V (b)

Fig 3.11a shows that almost flocs size is distribution around 1.8 nm and 2.3 nm that equivalent 39.8 % and 24.7 %, respectively. As applied voltage increases that lead to the flocs size increases. At applied voltage 20V, the distribution of flocs size is quite large. Around 31.4% with floc size is about 231 nm, and 29.3 % is the percentage of flocs with a size of 284.8 nm. The third one position for the distribution of flocs size is 19.8 % (53.3 nm size) as shown Fig 3.11b.

The Fig 3.11c shows that the flocs size continues to grow up as applied voltage is 40 V. There are 41.8 % that flocs size distribution around 284.8 nm and the second popular is 27.1 % with size of 231 nm. This size sharply increases to 6579.3 nm (make up 85.3 %) at applied voltage of 50 V. The other size is distributed range of 8111.3 – 10000 nm with the percentage from 12.7 – 2.0 % (Fig 3.11d).

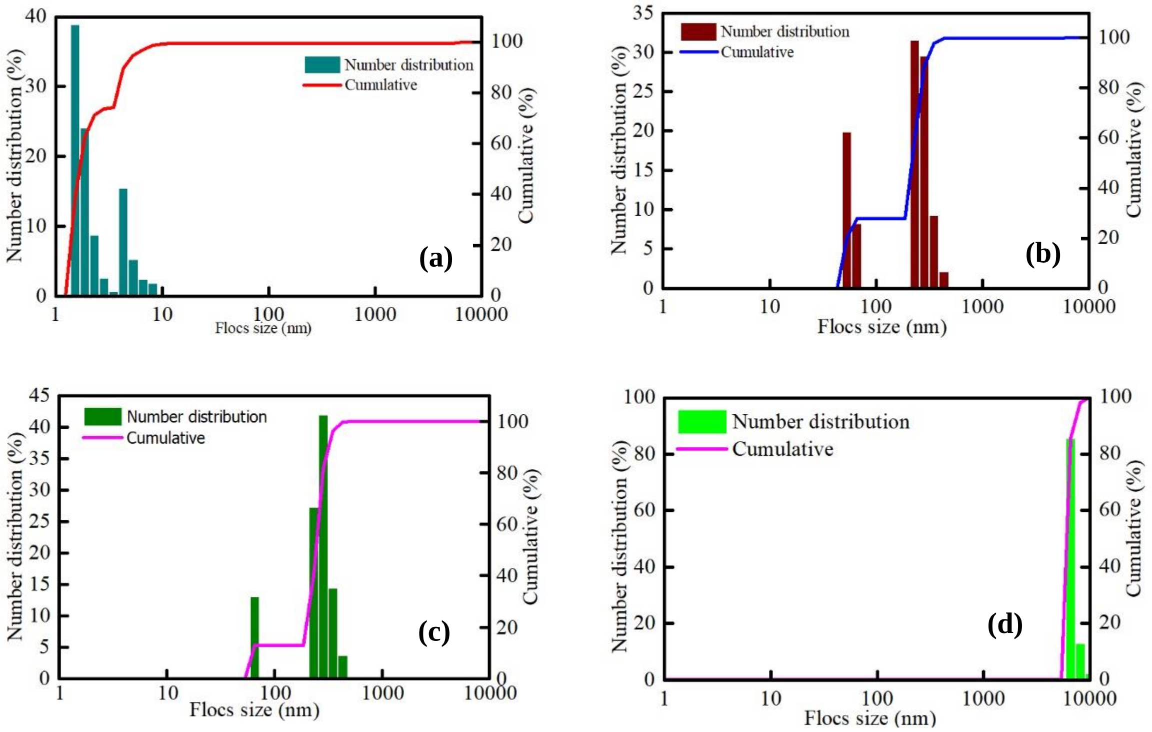

Fig 3.11. Flocs size distribution by using NSP, 5V (a), 20V (b), 40V (c) and 50V (d)

3.4.3. Interaction between applied voltage and SEC

Nowadays, the efficiency of technology is measured by treatment capacity and energy consuming. Therefore, reducing the energy consumption during operation time that show that the technology is feasible and can compete with the other technology. So, the calculation of specific energy consumption is key parameter to evaluate the technology. The applied voltage and specific energy consumption are close relation. Increasing applied voltage leads to increase the specific energy consumption.

Fig 3.12 reveals the relationship between specific energy consumption and applied voltage at treatment time of 90 min. Regardless a DC and an NSP power supplies, when applied voltage raised from 1 to 5 V in use of a DC and 1 to 50 V for an NSP power supply that lead to increase the specific energy consumption from 0.2 to 3.2 kWh/m^3 and from 0.01 to 5.2 kWh/m^3, respectively.

The Fig 3.12 also shows that the specific energy consumption as using a DC power supply increased strongly when comparison with the specific energy consumption as using an NSP power supply, which can be understood that as a DC power supply was applied, the constant transfer of the input voltage to the electrodes. Whereas, electrocoagulation process is active only when a pulse is available, it is mean of time on with an NSP power supply. These results had significant for selection type of power supplies because the specific energy consumption as using an NSP power supply was always below that of the specific energy consumption in use of a DC power supply in the all applied voltage range [76].

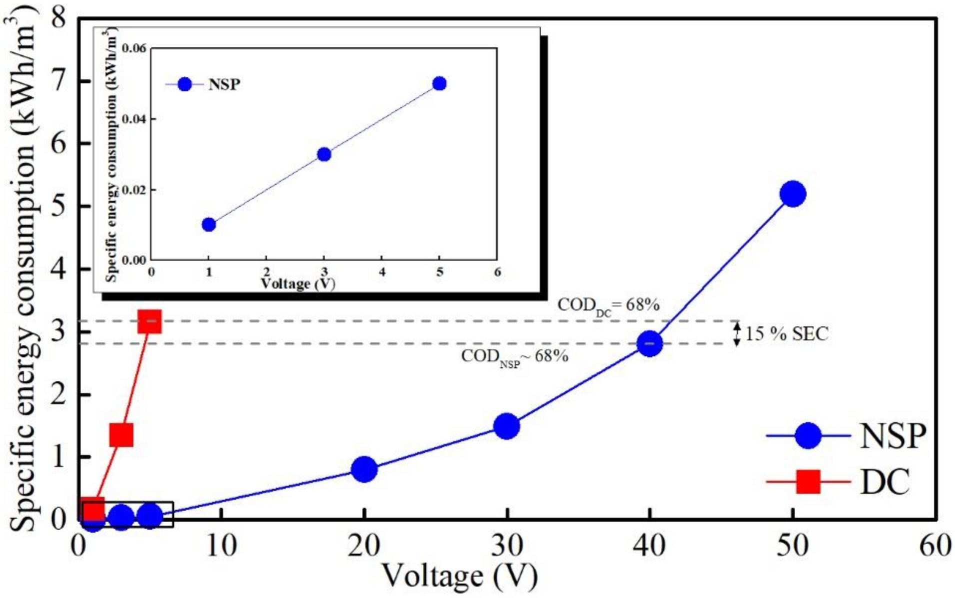

Fig 3.12. The relationship between SEC and applied voltage for using DC and NSP, treatment time = 90 min

On the other hand, for the low range of applied voltage < 5 V, the COD removal efficiency from municipal wastewater was only 10 % in use of NSP power supply. Meanwhile, at the same above range of applied voltage, the COD removal efficiency from municipal wastewater is 68 % in use of DC power supply. Therefore, at the low range of applied voltage, the COD removal efficiency from municipal wastewater in use of NSP power supply is significantly lower than DC power supply, as showed in Fig 3.5. Therefore, from these results it is very important to conclude that an NSP power supply operation at low voltage is not recommended without an increased effective treatment time [76].

Furthermore, regarding specific energy consumption in use of a DC or an NSP power supplies that is showed in Fig 3.12 that the specific energy consumption in use of an NSP power supply demanded a significant lower, increasing from 0.01 to 0.05 kWh/m^3 when increasing applied voltage from 1 V to 5 V. Whereas, the specific energy consumption in use of a DC power supply was several orders of magnitude higher, raising from 0.2 to 3.2 kWh/m^3. These results are in excellent agreement with those showed in Fig 3.5. These results could be understood by relation between the specific energy consumption and potential electrolysis. When electrocoagulation process required high specific energy consumption, increasing potential electrolysis. As a result, increasing Al^{3+} ions that was released from anodes. While, the increasing potential electrolysis led to increase the OH^- ions that released from cathodes. Therefore, promoting to form aluminum hydroxide in solution. This formation promoted the ability coagulation of the soluble organic compounds as well as metal ions in solution, consequently COD removal efficiency increased [42, 83]. Based on that reason, the COD removal efficiency increased only 12–14% for NSP compared with 59–68 % for DC, as showed in Fig 3.5.

Moreover, from the results could bring out the significant conclusion that at the similar COD removal efficiency from municipal wastewater with aluminum electrodes, the specific energy consumption demanded for an NSP power supply is at least 15% less than that in use of DC power supply, at around 2.8 kWh/m^3 and 3.2 kWh/m^3, respectively, as showed in the Fig 3.12. Therefore, using an NSP power supply to operate electrocoagulation process could save operation cost as compared a DC power supply. Furthermore, the figure also suggests that the use of an NSP power supply is advantageous in terms of increasing the removal COD from municipal wastewater using aluminum electrodes.

3.4.4. Influence of treatment time on SEC and COD removal efficiency

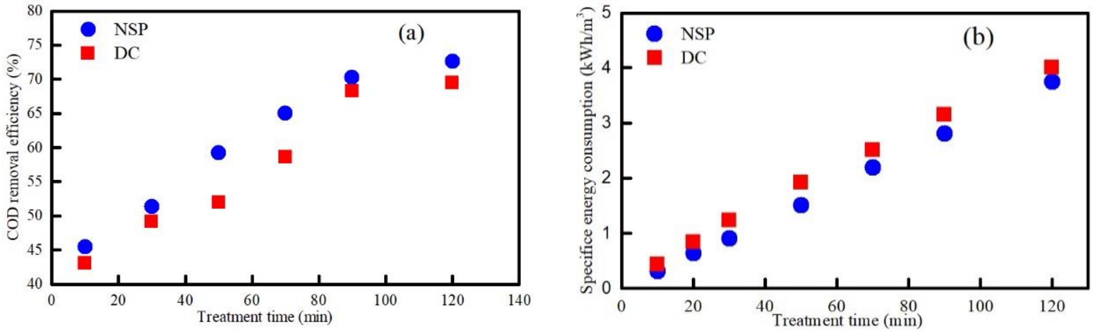

Fig 3.13. Influence of treatment time on (a) COD removal efficiency and (b) SEC, DC = 5 V, and NSP = 40 V.

Treatment time is an important parameter that effects on both COD removal efficiency and specific energy consumption. Increasing treatment time leads to increase the quantity of Al ion released from anode that determines the quantity of coagulant during electrocoagulation. Moreover, increasing treatment time leads to increase number of hydrogen bubbles from cathodes that promotes the flotation process. On the other hand, increasing of specific energy consumption is consequence of increasing treatment time. Therefore, evaluating the treatment time to find the optimum experiment condition.

The results from Fig 3.13 reveals that the variation of COD removal efficiency upon treatment time. The COD removal efficiency from municipal wastewater increased by increasing treatment time (electrolysis time) regardless a DC power supply or NSP power supply, which were used to operate electrocoagulation system. The results also reveal that the COD removal efficiency from municipal wastewater increased until 90 min of treatment time, then almost constant. The COD removal efficiency increase due to Al^{3+} and OH^- ions are continuously formed during electrocoagulation as increasing treatment time. As the aluminum hydroxide formation in solution increases, more pollutants are adsorbed on the aluminum hydroxide surface. Then, finally they will be removed from the solution [38, 80].

Moreover, when the treatment time increased that led to increase the number of hydrogen bubbles in solution that released from cathodes during electrocoagulation process, promoting the contact degree of aluminum hydroxide and pollutants, which encourage flotation process. As a result, COD removal efficiency from municipal wastewater with aluminum electrode increased [20].

On the other hand, increasing COD from municipal wastewater is not significant when treatment time was over 90 min, just only < 2%. This can be understood by two reasons: firstly, the sufficient amount of flocs available to remove the pollutants [84, 85] and secondly the cathodic reduction and new electro-coagulant flocs formation decreased [86].

Fig 3.13b points that the specific energy consumption increased straight with the treatment time. Moreover, this figure also reveals that the an NSP power supply require in specific energy consumption was lower than that for a DC power supply, as expected from Equations (4) and (5). Therefore, from the results that could bring the conclusion that in use of NSP power supply led to higher COD removal efficiency from municipal wastewater as well as demanded lower specific energy consumption than in use of DC power supply whatever treatment time.

3.4.5. Interaction between COD removal efficiency and SEC

For studies in electrocoagulation, there is few or no studies that discuses relation between specific energy consumption and COD removal efficiency. Typically, as using an NSP power supply as main electrodes. Investigating this relation that can consider the ability of method that whether be scale up in real industry.

Fig 3.14 reveals the relation between COD removal efficiency from municipal wastewater with aluminum electrodes and specific energy consumption. The specific energy consumption as using a DC power supply revealed typical elastic-like behavior with the COD removal efficiency, suggesting that a marginal increase in the efficiency significantly increased the specific energy consumption.

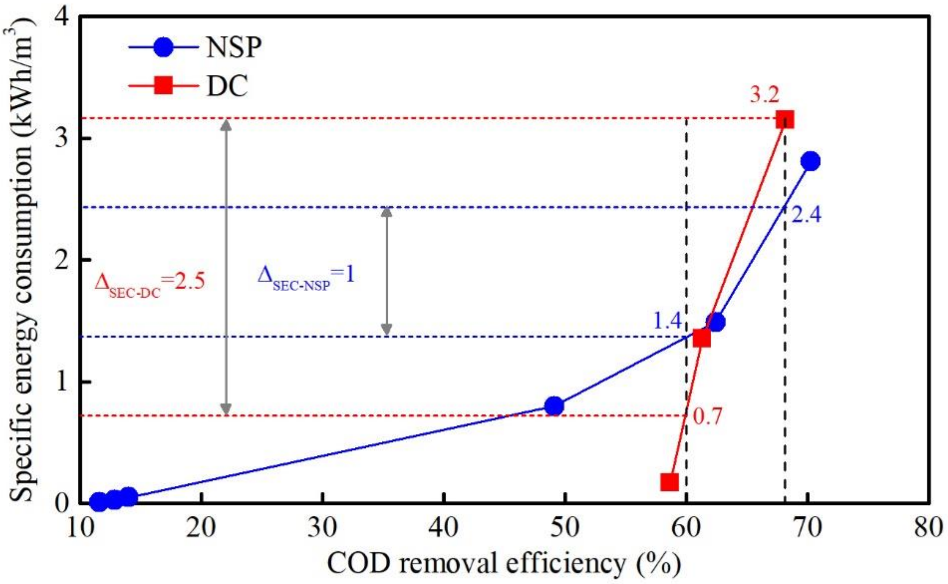

Fig 3.14. Interaction between the and COD removal efficiency and SEC in use of a DC and an NSP.

Whereas, in case of NSP power supply, the specific power consumption revealed a more elastic-like behavior with the COD removal efficiency, implying that the enhanced efficiency demands less energy compared than that needed with the DC power supply. So, based on this relation, the conclusion can be shown that using an NSP power supply will save energy than using a DC power supply [76]. This is one of advantage of an NSP power supply to remove COD from municipal wastewater using aluminum electrodes was comparing with a DC power supply.

Example, to increase the COD removal efficiency from municipal wastewater from 60 % to 68 %, specific energy consumption in case of NSP power supply required $\Delta_{SEC\text{-}NSP}$ = 1 kWh/m^3, whereas in case of DC power supply demanded $\Delta_{SEC\text{-}DC}$ = 2.5 kWh/m^3. The COD removal efficiency less than 60% is not relevant due to the treatment efficiency had to enhance for commercial wastewater treatment systems.

3.4.6. Effect of frequency and pulse width on the NSP efficiency

Frequency and pulse width are very important parameters as using an NSP power supply. Since, the frequency and pulse width values will decide the electrolysis time. Which will effect on COD removal efficiency from municipal wastewater.

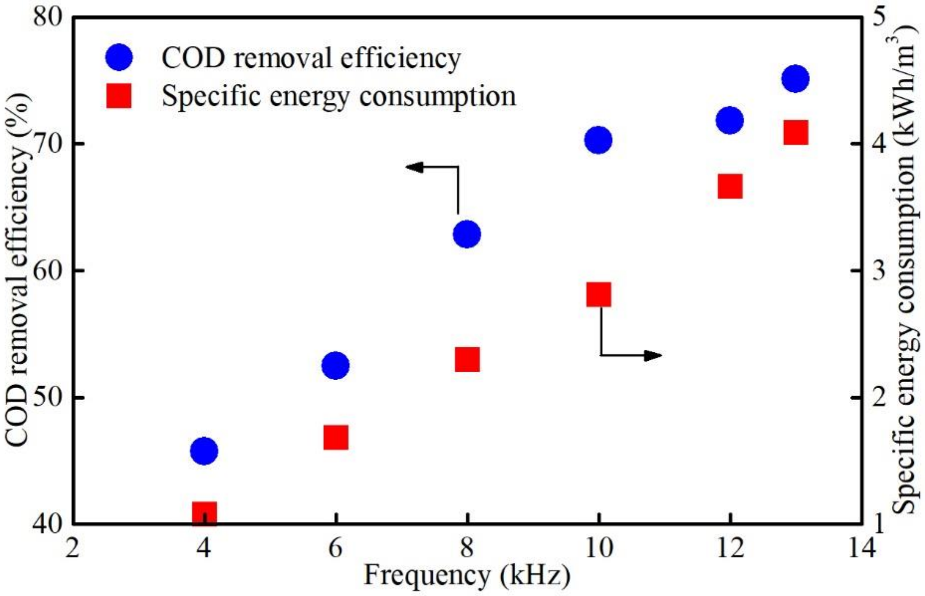

Fig 3.15. Influence of frequency on the COD removal efficiency and SEC, NSP = 40 V, treatment time = 90 min.

The relation between COD removal efficiency from municipal wastewater and specific energy consumption was showed on the Fig 3.15. The results show that the COD removal efficiency and specific energy consumption were linear tendency with frequency. It could be indicated that non-linear effects caused by anodic passivation were not seen that against to the reported in last period research [80]. The absence of non-linear tendency in the graph is not well known but it may be connected to the short effective treatment time produced as using NSP power supply [76]. The suitable of operation frequency was selected according to the specific energy consumption and COD removal efficiency targets. Instance, in put condition of *f* = 10 kHz produced an enough trade-off to get a high COD removal efficiency from municipal wastewater at a low specific energy consumption. Therefore *f* = 10 kHz was selected as optimum condition for all experiment.

The interaction between pulsed width and COD removal efficiency from municipal wastewater as well as specific energy consumption was showed in the Fig 3.16. The COD removal efficiency from municipal wastewater with aluminum electrodes increased from 44 % to 78 % when the pulse width raised from 0.4 to 1.3 μs. In addition, as the pulse width above range, the specific energy consumption increased from 1.7 kWh/m^3 to 3.8 kWh/m^3.

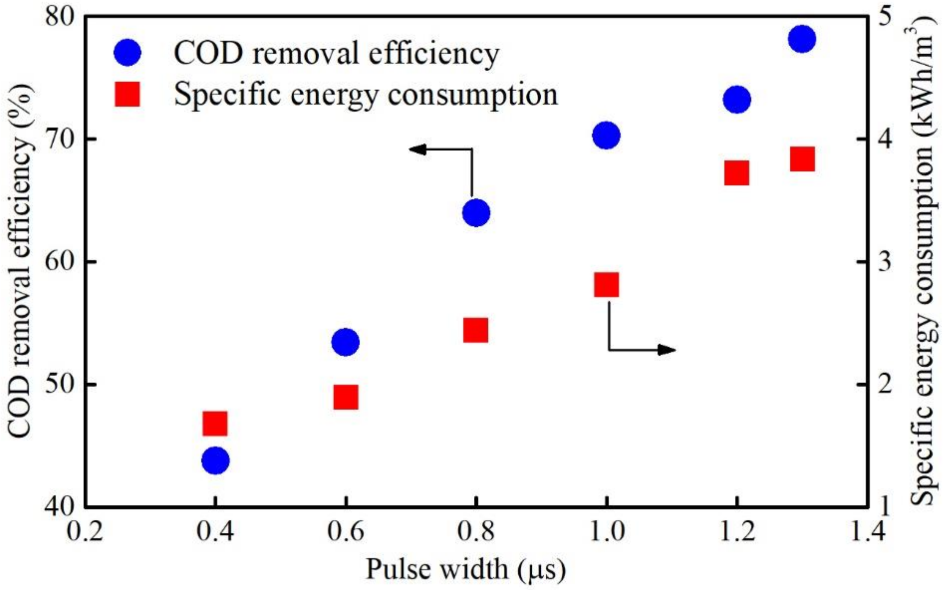

Fig 3.16. Influence of pulse width on the COD removal efficiency and SEC, NSP = 40 V NSP, treatment time = 90 min.

This tendency is similar to that revealed in Fig 3.16, where increased pulse width led to increase the electrolysis time. The electrolysis increased led to the amount of Al^{3+} released in solution from the anodes increased, which promoted the formation of aluminum hydroxide in medium, captured the pollutants from there, as a result, enhancing COD removal efficiency after finishing electrocoagulation process [76]. Moreover, as the electrolysis increased that led to generate more hydrogen bubbles, which released from the cathodes. This tendency is useful to enhance the flotation process efficiency, resulting in enhancing COD removal efficiency from solution [20, 84]. Furthermore, to find optimum condition, the pulse width was investigated to increase from 1 to 1.2 µs. The results show that the COD removal efficiency was not significant increased, only <3%, meanwhile the specific energy consumption demanded around 1 kWh/m^3. From above results, which could be brought the conclusion that pulse width of 1 µs is a good trade-off between high COD removal efficiency from municipal wastewater using aluminum electrodes and low specific energy, as a result, reducing the operation cost. Therefore, from the results *f* = 10 kHz and a *pw* =1 µs were used as an optimum condition to remove COD from municipal wastewater.

3.4.7. Characterization of anode using FE-SEM

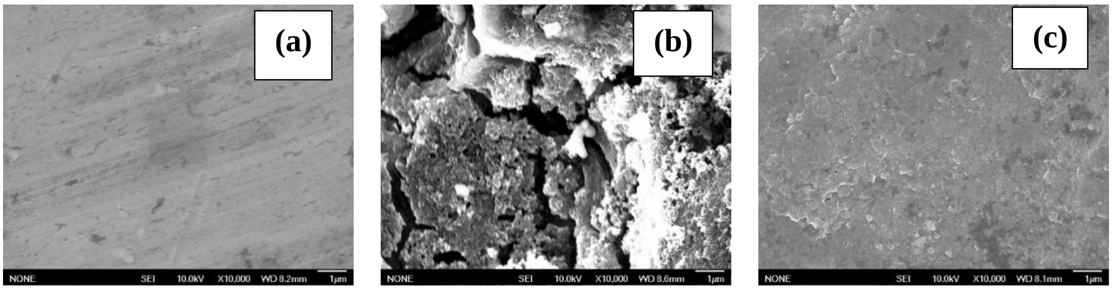

Fig 3.17. The morphology of anode (a) before and after EC process in use of (b) DC and (c) NSP.

The level of dissolving of anode during electrocoagulation will decide the life time of system. Therefore, to investigate the effect of the electrocoagulation process on the electrode surfaces using a DC power supply and an NSP power supply, the morphology of the anode surfaces before and after the electrocoagulation process was observed by scanning electron microscopy (FE-SEM) to compare and evaluated. The surface of aluminum electrodes before electrocoagulation process is showed in the Fig 3.17a. Meanwhile, the morphology of anode electrodes after electrocoagulation process is revealed in the (b) in case of DC power supply, and (c) in use of NSP power supply. In use of a DC power supply, the morphology of anode was rough and there were many indentations, as showed in the Fig 3.17b. This phenomenon can be understood by consumption of the anode electrodes at active sites during electrocoagulation process. At that position, the anode dissolution generates aluminum hydroxide [87]. Whereas, in case of using NSP power supply to operate electrocoagulation process, the morphology of anode shows the few disordered pores and a smooth microstructure as showed in the Fig 3.17c. This state could be conclude that the aluminum anode electrodes dissolve uniformly during the electrocoagulation process [76].

3.4.8. Characterization of by-products from EC cells

In this study, scanning electron microscope (SEM) was used to analyse the precipitate generated after EC experiment to describe the morphology of surface.

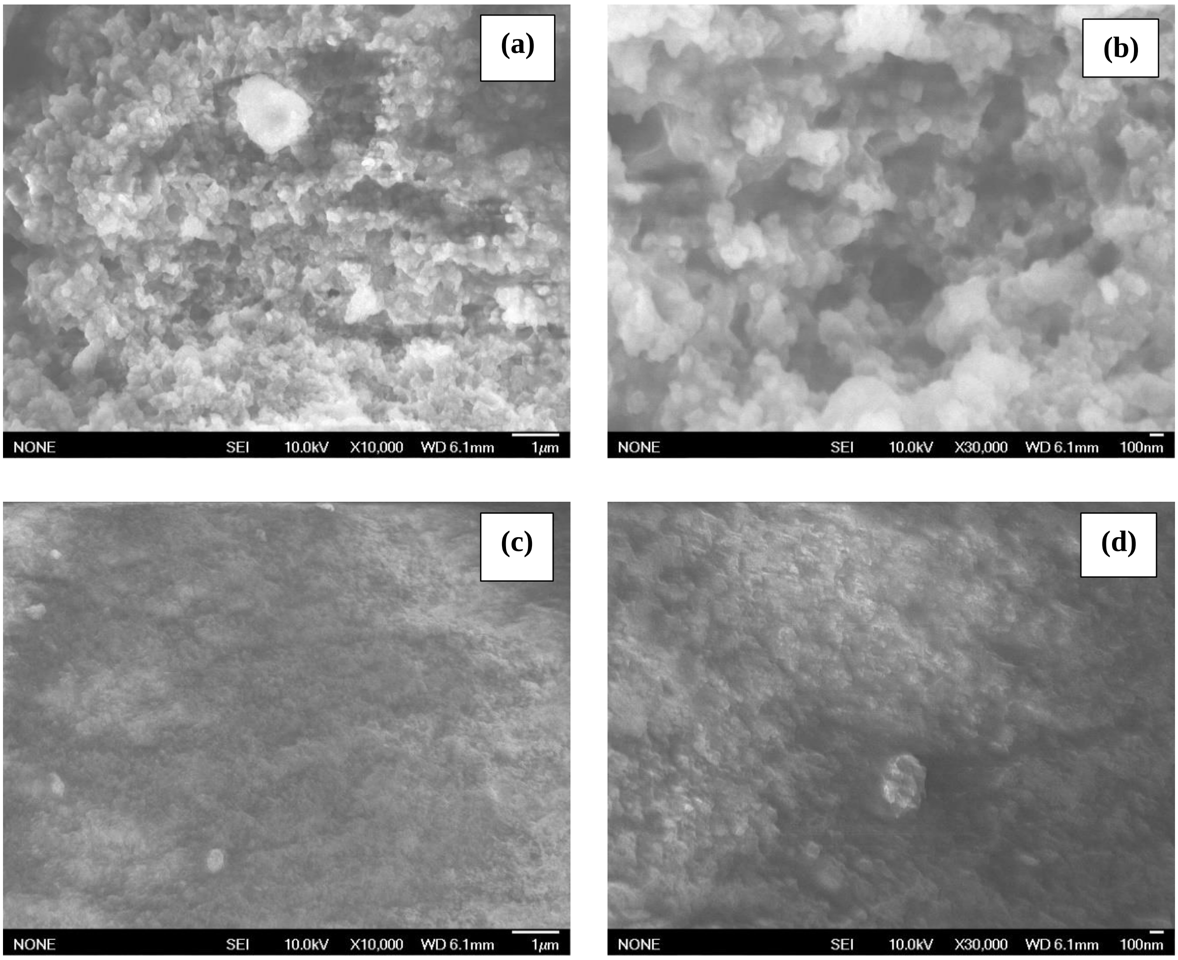

Fig 3.18. SEM images of EC sludge, using NSP (a and b) and DC (c and d)

To understand ability adsorption of coagulant generated during electrocoagulation, the FE-SEM is best method. From the result of FE-SEM images, the advantage assessment for a DC and an NSP power supply will be recognized. The FE-SEM image of the electrocoagulation sludge is regular shape in case of a DC power supply (Fig 3.18). In contrast, the morphology of precipitate generated as using an NSP power supply is composed of agglomerated smaller particle size and hence higher surface area of aluminium hydroxide colloids favours dense floc formation when compared to aluminium hydroxide flocs obtained in case of a DC power supply [76]. Furthermore, this results totally agree with Fig 3.9, Fig 3.10 and Fig 3.11. Due to the generated sludge include small particles size. Therefore, they are easily to be flocculation. As a result, the flocs size in case of an NSP power supply will be larger than that one in case of DC. This result was described elsewhere [88].

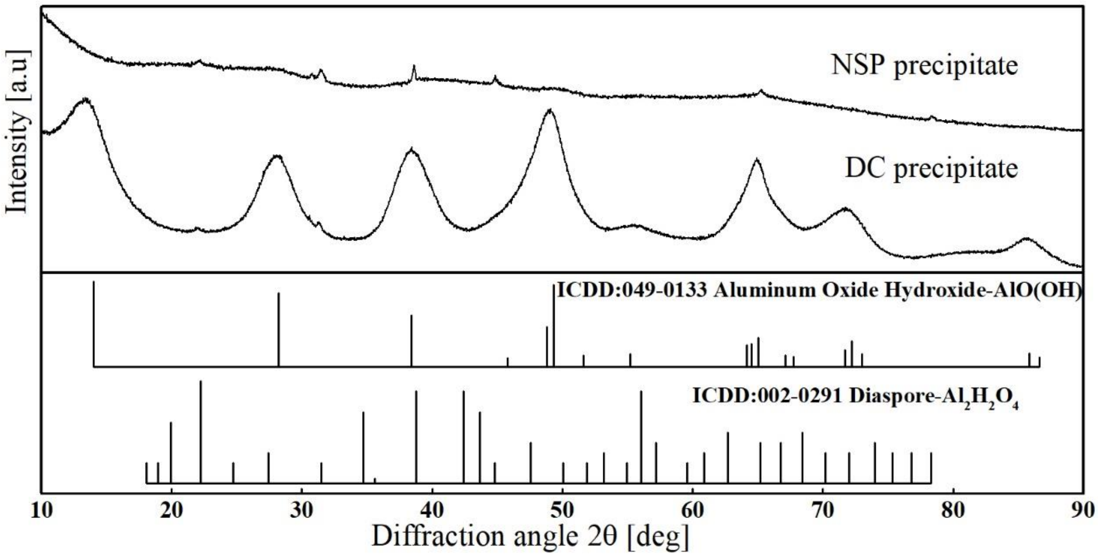

Fig 3.19. Diffraction patterns of precipitate of sample treated by EC using DC and NSP

The X-ray diffraction patterns of generated sludges was reported by a diffractometer operating with a Cu Kα radiation source. The XRD analysis result is shown in Fig 3.19. The 2θ scans were carried out from 10^0 to 90^0. It can be observed that the XRD pattern for DC power supply sludge exposed strong output signals with distinct peaks. Furthermore, the peaks of signal show very broad and shallow. This characteristic of peaks such broad humps is described as amorphous or poorly crystalline in nature [76]. Because crystallization of Al hydroxides/oxyhydroxides is a very slow process, it is reported that Al hydroxides and aluminium oxyhydroxides are either amorphous or very poorly crystalline [89]. Whereas, as using NSP the XRD pattern suggested that Aluminium hydroxide is more amorphous as comparing with Aluminium hydroxide generated in the case of DC. The decreasing of signal in case of NSP compared to DC that may be caused better adsorption of organic material during precipitating. This result is an agreement with the above results. This is one of reason for why using NSP can remove higher COD from municipal wastewater as the comparison with DC power supply [49].

EDS was used to analyse the elements that were adsorbed on the aluminium hydroxide. As seen in Fig 3.20, the percentage of the mass of elements in the following order: O>Al>C>Si>P>Na and O>Al>C>Si>P>Ca>Cl>S>Na in case of DC and NSP, respectively. Using a DC, high contents of oxygen (59.71 %), Aluminium (30.51 %), Carbon (7.37 %), Silicon (1.54 %), Phosphorous (0.8 %) and Sodium (0.07 %).

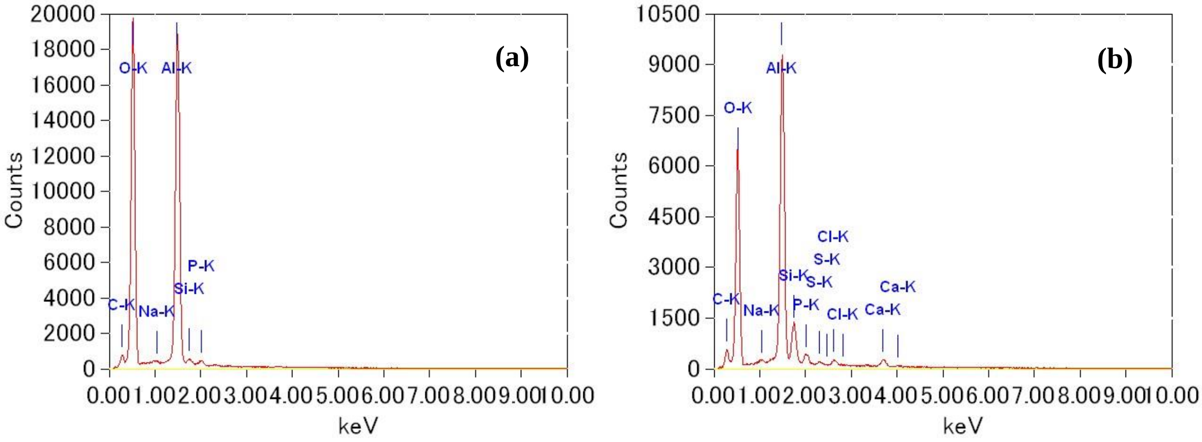

Fig 3.20. The EDS patterns of precipitate sample, using DC (a) and NSP (b)

Meanwhile, in use of NSP power supply the highest contents also belong to Oxygen (48.91 %), and next descending orders are aluminium (28.25 %), Carbon (12.02 %), Silicon (5.68 %), Phosphorous (1.74 %), Calcium (1.65 %), Chlorine (0.9 %), Sulphur (0.49 %) and Sodium (0.35 %). In both DC and NSP power supplies, the highest content is oxygen. It may be understood that part of oxygen content comes from the atmosphere during sample preparing. Aluminium is second high contents in the sample due to the use of aluminium as electrodes. The aluminium content is normal higher than the other element as aluminium using as electrodes. This is agreement with another author. In aluminium electrode used, the high charged poly-nuclear hydroxyl aluminium complexes, such as $Al_2(OH)_2^{4+}$, $Al_7(OH)_{17}^{4+}$, $Al_{13}(OH)_{34}^{5+}$, $Al_3(OH)_4^{5+}$, $Al(OH)_6^{3-}$, $Al(OH)_7^{4-}$ and AlO_2^{-}, were produced [90]. The peaks of the other elements were recognized in the precipitate samples because of from municipal wastewater. As seen Fig 3.20, it is worth noticing that aluminium hydroxide generated in use of NSP power supply is better adsorption pollutants than that one using DC power supply [76].

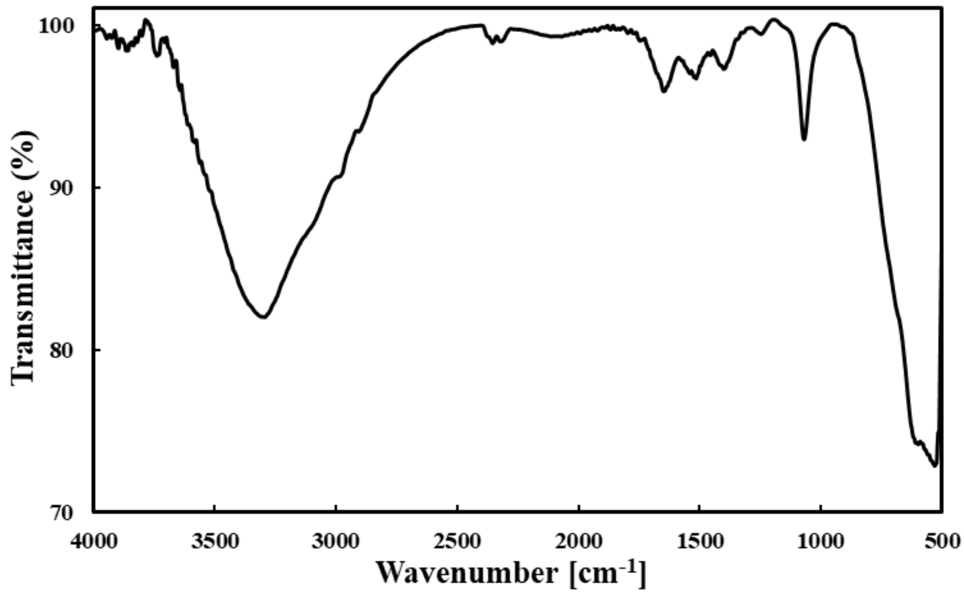

Fig 3.21. FT-IR spectra of the precipitation EC process by-products using a DC

The FT IR spectra of precipitate generated by using electrocoagulation process with DC and NSP power supply are showed in Fig 3.21 and Fig 3.22, respectively. Both of DC and NSP, the broadband appears between 3000 cm^{-1} to 4000 cm^{-1} that may be attributed to N-H and O-H stretching vibration. This is because of the (O–H) stretching vibration in the Aluminum hydroxide structures [91-93].

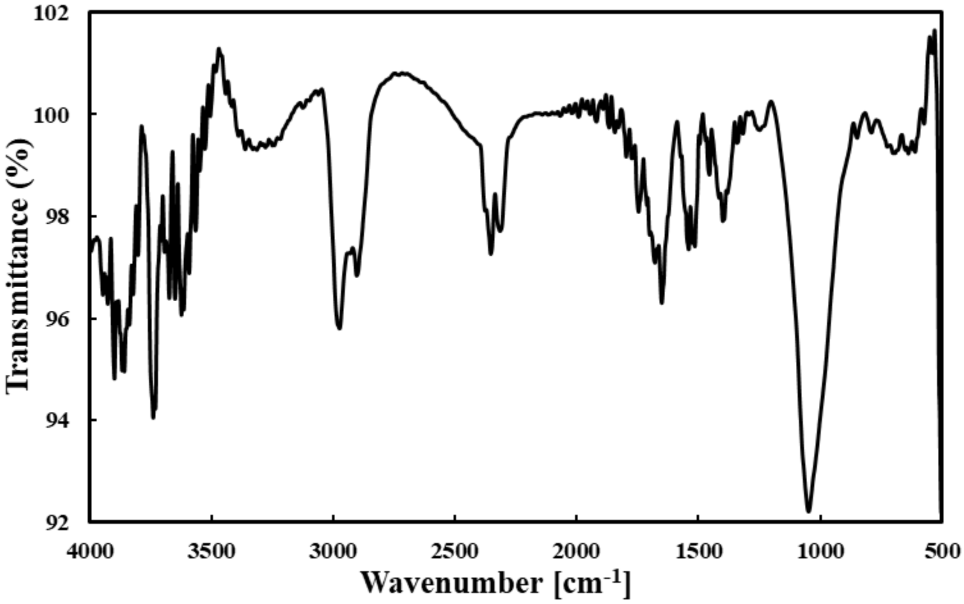

Fig 3.22. FT-IR spectra of the precipitate EC by-products using NSP

The adsorption bands at around 2352.73 cm^{-1} to 2973.7 cm^{-1} corresponding to bond stretching C-H (-CH_3 and CH_2). The 1046.19 cm^{-1} to 1067 cm^{-1} peak indicate the bent vibration of C-O. For both DC and NSP the low peaks (461.94 cm^{-1} to 798.88 cm^{-1}) appear that implies that there is the presence of silica SiO_2. This result is agreement with Fig 3.20 that shows Si and O in the generated precipitate for both DC and NSP power supplies [92].

3.5. CONCLUSIONS OF CHAPTER

The results from this study that showed the comparison the efficiency of direct current and nanosecond pulse as using for electrocoagulation to remove COD from municipal wastewater with aluminum electrodes. This study shows that to get a similar COD removal efficiency from municipal wastewater, the specific energy consumption as using NSP can reduce at least 15 % compared with DC power supply. Moreover, to enhance COD removal efficiency from municipal wastewater over 60 %, the SEC in case of nanosecond pulse can reduce two or three times in respected to DC power supply. Therefore, using an NSP can reduce the specific energy consumption and enhancing the COD removal efficiency from municipal wastewater. These results will promote using electrocoagulation with nanosecond pulse in industrial. It contributes to reduce the carbon footprint of wastewater treatment process.

CHAPTER 4. APPLICATION NANOSECOND PULSE FOR ELECTROCOAGULATION TO REMOVE COD FROM TEXTILE WASTEWATER AT LOW SPECIFIC ENERGY CONSUMPTION

4.1. ABSTRACT

This paper proposes in use of nanosecond pulsed power supply in the electrocoagulation system to remove COD from textile wastewater. Four aluminum plates arranged in a monopolar-parallel configuration are utilized as electrodes in a 200 ml electrocoagulation reactor. Chemical oxygen demand and specific energy consumption are utilized to characterize the performance of NSP power supply. A DC power supply is considered as a benchmark. Field-emission scanning electron microscopy, X-ray diffraction, and energy-dispersive spectroscopy are utilized to characterize flocs. The results reveal that a maximum COD removal efficiency is 77% that can be achieved as using of an NSP power supply, while a value of only 60% can be achieved by applying a DC power supply. In addition, an NSP power supply consumes at least 24% less specific energy than a DC power supply at a similar COD removal efficiency from textile wastewater. As using an NSP power supply for textile wastewater treatment allows for high COD removal efficiency with a significantly lower specific energy consumption compared to traditional DC power supply. It is believed that the low specific energy consumption exhibited by NSP power supply could be useful for promoting the application of electrocoagulation for cleaning of textile wastewater treatment and could contribute to the reduction of the carbon footprint of this process.

4.2. INTRODUCTION

The discharge of effluents by the textile industry is a major cause of water pollution. The main pollutants from the textile industry are released from wet-processing operations, such as scouring (sodium hydroxide, pectin, oils, surfactants), bleaching (organic stabilizer, hydrogen peroxide), mercerizing, and dyeing (metals, colors, salt) [94]. The textile wastewater is big problem in developing countries now. There are many textile factories change from develop countries to developing countries. Wastewater discharge from the textile factories has high levels of chemical oxygen demand, pH, organic load, and synthetic color with low biodegradability [95, 96]. Therefore, textile wastewaters must be treated prior to their discharge to reduce their harmful effects on the natural environment as well as healthy human being.

As discussed above chapters, the electrocoagulation is a technology that is more advantage then chemical conventional method such as efficiency, adaptability or flexibility, safety, lower costs, and easily manageable. Electrocoagulation process implies the formation of coagulants in situ by applying electricity current due to the dissolution of the iron or aluminum electrodes. During the electrocoagulation process, the anodes release metal ions, and hydroxide ions as hydrogen bubbles generate from cathodes, formation coagulant to adsorb flocs in solution. As a results, they are removed from solution by precipitation or flotation process [4]. Electrocoagulation has been evaluated for wastewater treatment for many years. However, in the first period the high price of electrical energy is a fundamental obstacle limiting its application in industry [22, 29]. Recently, electrocoagulation is considered as an alternative electrochemical treatment method which has gained increasing attention because of its simple operation, high removal efficiency, little sludge produced and need less chemicals. Furthermore, there are more renewable energies that again promotes the attractive electrocoagulation for wastewater treatment in recent year. Because it can reduce specific energy consumption as using electrocoagulation. Reducing energy consumption is crucial for enhancing the economic feasibility of electrocoagulation. Recently, the utilization of pulse-sourced electrocoagulation has been proposed to reduce energy consumption and avoid undesirable passivation of electrocoagulation electrodes [97].

DC and AC systems have also been considered as power sources for EC [98]. Coagulants are generated in situ by the dissolution of metal ions from consumable anodes and simultaneous formation of hydroxide ions at cathodes [99]. This paper proposes the utilization of a nanosecond pulse power supply to enhance textile wastewater treatment based on electrocoagulation process. NSP power supply facilitates electrocoagulation can operate at high voltages without any breakdown of the medium between electrodes, thereby promoting the formation of metal hydroxide flocs as well as increasing the amount of hydrogen bubbles, which enhances the efficiency of pollutant removal by coagulation and flotation process.

Regarding electrode materials, Zn, steel, carbon graphite, Al, and Fe. However, Al and Fe plates have been utilized as electrodes for EC based on their abundance and low cost. During dissolution, they produce hydroxides, oxyhydroxides, and polymeric hydroxides [100], resulting in high-valence Fe or Al hydroxides with low toxicity that facilitate pollutant removal and increase the treatment efficiency of EC [22].

The main electrochemical reaction that occurs when Al is utilized as an electrode can be summarized as follows:

Anode: $Al - 3e = Al^{+3}$ (1)

Cathode: $2(H_2O) + 2e^- = H_2 + 2(OH^-)$ (2)

In the solution: $Al^{3+} + 3H_2O = Al(OH)_3 + 3H^+$ (3)

Al^{3+} and OH^- are generated at the electrodes according to reactions (1) and (2). They form various monomeric and polymeric species that eventually transform into insoluble $Al(OH)_3$ flocs, which adsorb pollutants from wastewater solutions and eventually remove them via precipitation and flotation [29].

To date, there have been few studies that have investigated industrial textile wastewater [96]. While the textile wastewater is very dangerous and big problem in some developing countries due to many textile factories in the world have concentrated in there. The results of these studies have shown that electrocoagulation process is efficiency to remove COD from textile wastewater [83, 99, 101-103]. Most of these studies utilized DC power supply as a main power source and focused on the investigation of the effects of some parameters such as pH, treatment time, and current density on COD reduction efficiency. There are no or very rarely using NSP to remove the COD from textile wastewater. In this work, which proposes in use of NSP power supply to enhance COD removal efficiency at low SEC. To the best of our knowledge, no studies have compared the effects of an NSP and a DC power supplies on COD removal efficiency and specific energy consumption. Therefore, this study focuses on such comparisons. This work also compares the characteristics of the precipitation generated from electrocoagulation processes in use of a DC and an NSP power supplies utilizing XRD, EDS, and FE-SEM. Such precipitations have not been investigated previously researches.

4.3. MATERIALS AND METHODS

4.3.1. Textile wastewater

Table 4.1. Characteristics of textile wastewater.

Parameters	Units	Value
pH	-	9.8
COD	mg/L	350
Electrical conductivity	mS/m	150
Color	-	5104
BOD	mg/L	96
TN	mg-N/L	24

Textile wastewater samples were collected from Minatoya Co., Ltd in Nagaoka, Japan. Table 4.1 contains the composition of the textile wastewater.

4.3.2. Analytical methods

In case of pH and electrical conductivity, they were measured before and after each electrocoagulation experiment in use of a pH meter (Model HM-30R, range of 0.000–14) and COND meter (Model ES-71), respectively. COD and total nitrogen (TN) were measured using the HACH 8000 method. Biochemical oxygen demand was measured according to the APHA (2005) Standard Methods for the Examination of Water and Wastewater. Color was measured utilizing a color meter (TZ7700, Nippon Denshoku). Each experiment was performed at least three times to ensure the results.

The chemical and physical properties of precipitates were analyzed utilizing EDS, FE-SEM (JEOL JSM-6700F), and XRD (Rigaku RINT-2500, CuKa).

4.3.3. Experimental setup

Fig 4.1 shows a schematic diagram of electrocoagulation process experimental setup, which includes a 200 ml electrocoagulation reactor for textile wastewater and four aluminum electrodes. The electrodes are arranged in a monopolar-parallel configuration and separated by 1 cm, as shown in Fig 4.1. All electrodes include 2 anodes and 2 cathodes have the same dimensions (1 × 20 × 55 mm).

The electrodes are connected to a PL-650-0.1 (DC) or a HK-10N (NSP) power supply to run electrocoagulation process under potentiostatic conditions. The voltage ranges are defined as follows to avoid any breakdown of the medium between electrodes: V_{DC} from 1 V to 5 V for the DC power supply and V_{NSP} from 1 V to 45 V for the NSP power supply [35]. On the other hand, regarding an NSP power supply, the pulse width (pw) = 1 µs, f = 10 kHz) were used for all experiments.

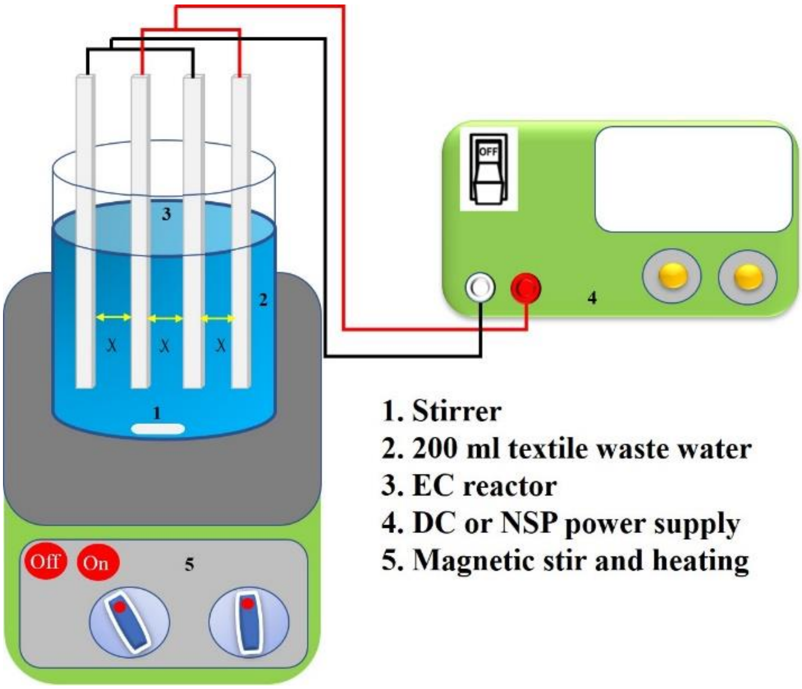

Fig 4.1. EC setup in laboratory (same separation in all cases: χ = 1 cm).

During electrocoagulation process, the textile wastewater was stirred at 200 rpm at room temperature to enhance contact between the pollutants and coagulant that generated from reactions during electrocoagulation experiment.

4.4. RESULTS AND DISCUSSION

4.4.1. Influence of voltage on COD removal efficiency

The applied voltage effects on electrocoagulation performance process and controls the rate of coagulant dosage during the electrocoagulation process. Moreover, this parameter also effects on the amount of hydrogen bubbles released from cathodes that promoting the flotation process. The effect of various applied voltage on the COD removal efficiency is investigated, the results were shown in Fig 2. It is obviously that the COD removal efficiency increases monotonically by variously applied voltage as using a DC as well as an NSP power supplies. This phenomenon is caused of increasing in the applied voltage, the ability anode dissolution rate increases. Moreover, there are more OH^- ion from cathodes that is dosed into the solution. As a result, this leads to an increase in the quantity of $Al(OH)_3$ formation as show in an Equation (3). These aluminum hydroxide compounds have large interfacial areas and are active as coagulants in solution during electrocoagulation process. It is mean they promote the rapid adsorption of pollutants such as organic compounds, heavy metal ions and anions, consequently increasing COD removal efficiency from textile wastewater by using aluminum electrodes [80, 81].

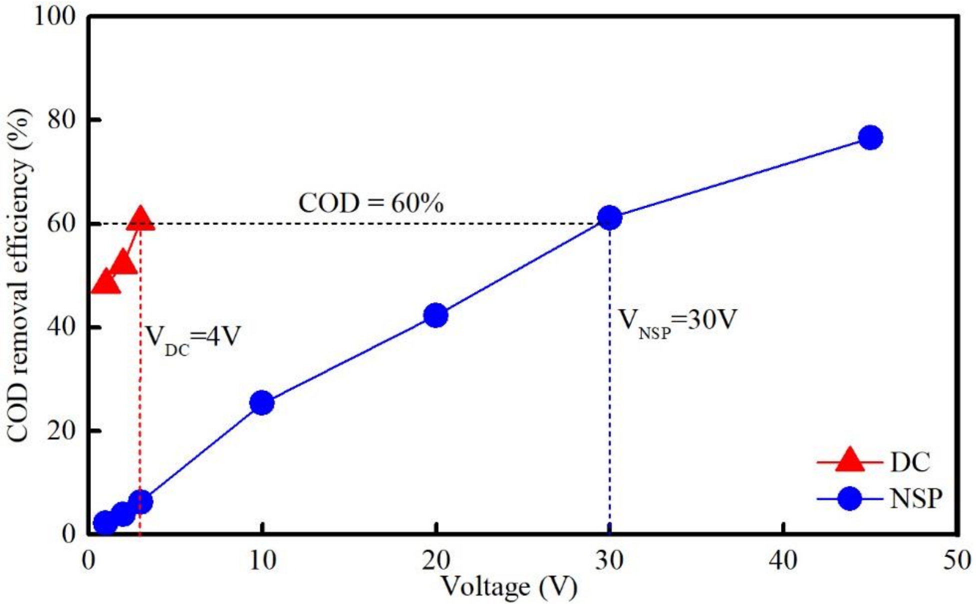

Fig 4.2. Effects of voltage on COD removal efficiency in case of a DC and an NSP power supply, treatment time = 60 min.

Furthermore, the number of hydrogen bubbles released from cathodes that will increase by increasing various applied voltage, which contributes to the removal of pollutants through via flotation process. It can be recognized that this phenomenon is one of the advantages in EC process that electrocoagulation, which can integrate the advantage of coagulation and flotation to remove COD from textile wastewater in a singer cell.

On the other hand, the Fig 4.2 also depicts that a DC and an NSP power supplies operate at different voltage ranges. Here is outstanding trait of nanosecond pulse as comparing with a DC power supply. In case of a DC power supply, the voltage can apply up to 4 V to avoid the breakdown voltage. Whereas, for an NSP power supply that can applied maximum of 45 V without breakdown voltage. In addition, because of the different allied voltage operation that lead to the maximum COD removal efficiency from textile wastewater are 60% and 77% as using of a DC and an NSP power supplies, respectively.

Notably, As applied 4 V for a DC and 30 V in use of an NSP power supply results in a similar COD removal efficiency ($\eta \approx 60\%$) from textile wastewater by using aluminum electrodes. Therefore, these configurations were utilized to simplify the comparisons and discussion presented below.

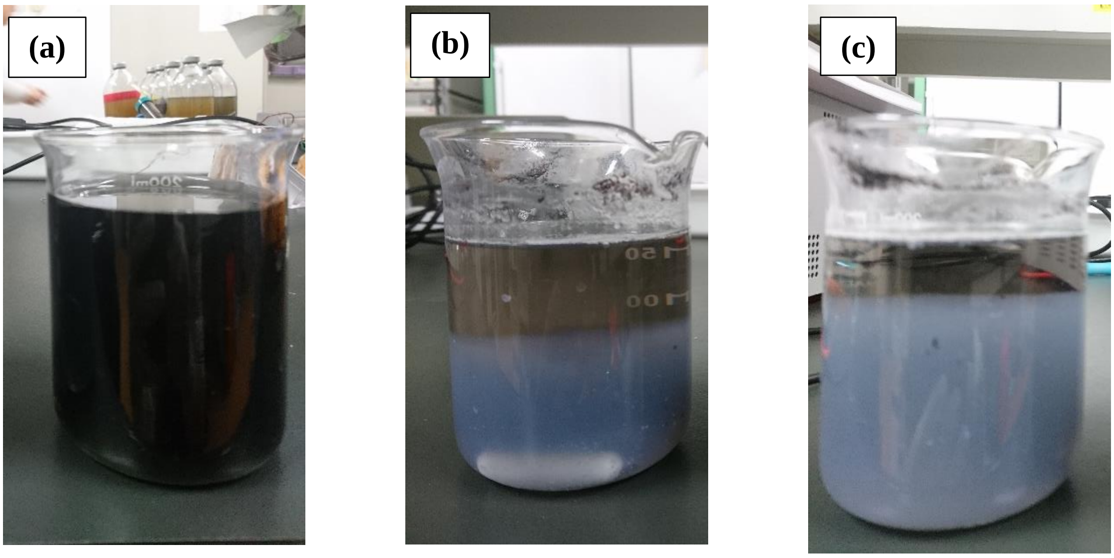

Fig 4.3. The textile wastewater before (a) and after EC process, (b) using NSP-45V and (c) DC-4V, treatment time 60min

Fig 4.3 shows that the textile wastewater before and after experiment as using NSP and DC. The changing from very to transparent color that is evidence to prove the efficiency of electrocoagulation process. Aluminum hydroxides are produced as a result of EC and acts as coagulant/flocculant for the suspended solids to convert them into flocs of enough density to be sediment under gravity. The flocs gradually settle as soon as finishing EC process. They can separate from treated wastewater by filter or centrifugation.

4.4.2. Dependence between SEC and voltage

The relationship between SEC and applied voltage is showed in the Fig 4.4. Specific energy consumption increases as the applied voltage increases regardless a DC or an NSP power supplies. However, the results reveal that as using a DC power supply, the specific energy consumption tends to increase faster than an NSP power supply. It can be understood that case of a DC power supply, the input voltage is constantly transferred to the electrodes during electrocoagulation process. As a result, coagulation and flotation process operates whole treatment time. Whereas, in use of a NSP power supply, the coagulation process as well as flotation process are only active when a pulse is available, it is mean that time is on. Therefore, obviously results that $SEC_{NSP} < SEC_{DC}$, regardless of the applied voltage range.

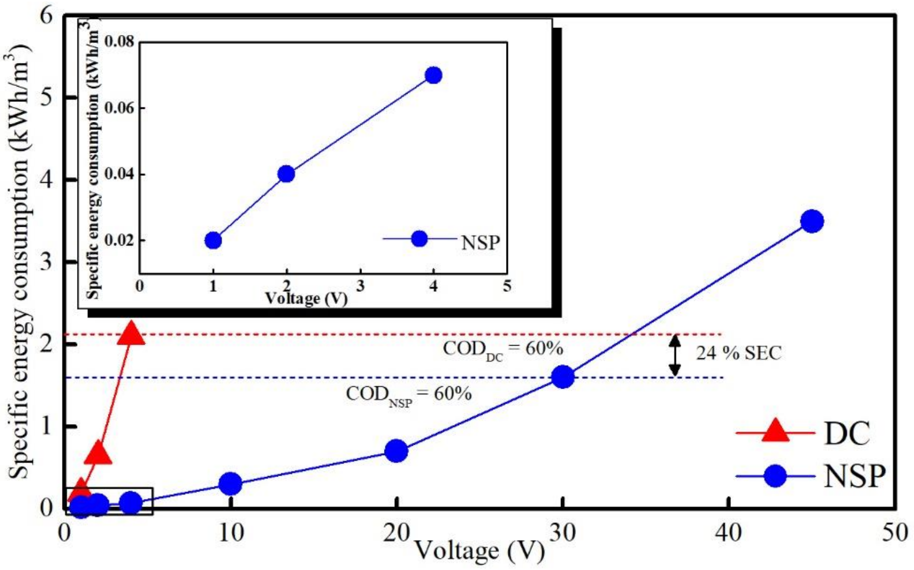

Fig 4.4. Relationship between SEC and applied voltage, using a DC and an NSP power supply, treatment time = 60 min.

Fig 4.4 also reveals that in use of an NSP power supply that led to the results in a very low specific energy consumption at low voltages (<4 V). The specific energy consumption as using a DC power supply is several orders of magnitude greater. This result is in strong agreement with the results that is shown in Fig 4.2 and can be attributed to the direct proportionality between specific energy consumption and potential electrolysis. This mention that a high specific energy consumption value leads to the generation of more aluminum and hydroxide ions, thereby promoting the formation of aluminum hydroxides, which are necessary for coagulating pollutants. As a result, the COD removal efficiency increases. Therefore, in use of an NSP power supply the COD removal efficiency is significantly lower (η < 7 %) than that when a DC power supply (η = 60%) was applied at the same voltage (< 4 V), as shown in Fig 4.2. Therefore, above results permit to conclude that an NSP power supply is not recommended for operation at low voltages due to its COD removal efficiency is significantly lower than of using a DC power supply.

Fig 4.4 also shows that the specific energy consumption at similar COD removal efficiency ($\eta \approx 60\%$) are 2.1 and 1.6 kWh/m^3 for a DC and an NSP power supplies, respectively. It is vital point to say that using of NSP power supply incurs around 24% less specific energy consumption compared to a DC power supply as showed at dashed lines to achieve the similar COD removal efficiency.

4.4.3. Influence of treatment time on COD removal efficiency and SEC

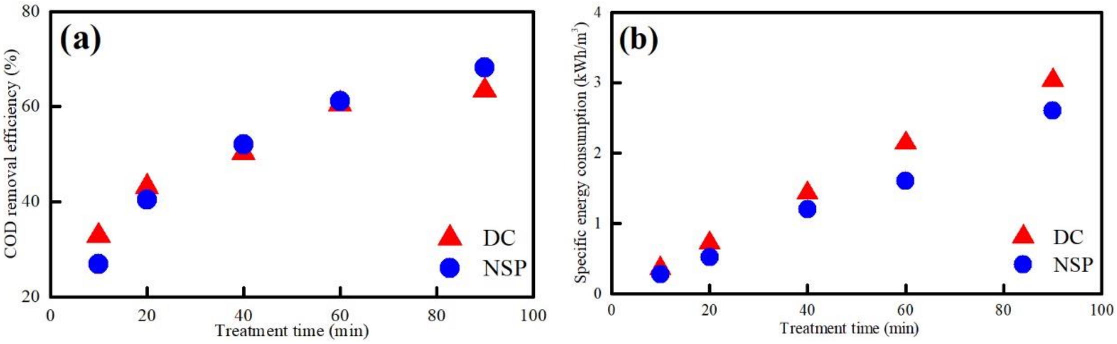

Fig 4.5. Influence of treatment time on (a) COD removal efficiency, and (b) SEC at 4 V and 30 V in case of a DC and NSP power supplies, respectively.

Fig 4.5 depicts the COD removal efficiency and specific energy consumption as functions of treatment time. Fig 4.5a shows that regardless a DC and an NSP power supplies, COD removal efficiency from textile wastewater by using aluminum electrodes increases by treatment time until reaching stable of around 60% and 61% for a DC and an NSP power supply, respectively. These results can be due to the formation of Al^{3+} and OH^{-} ions, which is proportional to treatment time. It is mean that those ions increase with treatment time (electrocoagulation operation time). Therefore, the formation of hydroxide precipitates $Al(OH)_3$ increases over time and pollutants tend to adsorb onto the $Al(OH)_3$ surfaces, resulting in their removal from the medium. As a result, the COD removal efficiency increases [38, 80]. Moreover, in the fact the number of hydrogen bubbles releases from cathodes electrode increases by treatment time, which promotes the degree of contact between $Al(OH)_3$ and pollutants, thereby promoting flotation process. Consequently, the COD removal efficiency increases [20]. Fig 4.5a also shows that in the first period of electrocoagulation process, the COD removal efficiency as using of an NSP power supply is lower than that in us of a DC power supply. This is due to the electrolysis time as using an NSP power supply is shorter than that as using a DC power supply. However, when treatment time increases, the COD removal efficiency as using an NSP power supply increases faster than that in use of a DC power supply. This is because the application of an NSP power supply results in better current efficiency than the use of a DC power supply because it avoids waste outputs in the form of heat or the electrolysis of water.

Moreover, COD removal efficiency is almost stable after 60 min of electrocoagulation operation with a change of less than 5% for a treatment time of up to 90 min. It can be understood by at least two factors. Firstly, it could be caused by the fact that a sufficient number of flocs are available for removing pollutants [85]. Secondly, it could be caused by the decreased level of cathodic reduction and formation of new electrocoagulant flocs [86].

Fig 4.5b shows a direct linear correlation between specific energy consumption and treatment time (electrocoagulation operation time). However, it is worth noting that an NSP power supply incurs less specific energy consumption than a DC power supply over the entire treatment time range. It is very important to indicate that an NSP power supply provides higher COD removal efficiency from textile wastewater by using aluminum electrodes and lower specific energy consumption compared to a DC power supply.

4.4.4. Dependence between SEC and COD removal efficiency

Fig 4.6 reveals specific energy consumption as a function of COD removal efficiency. The changing in COD removal efficiency is insignificant as using of a DC power supply. Whereas, for an NSP power supply, the COD removal efficiency changes significantly with specific energy consumption. At a COD removal efficiency of η = 56 %, both DC and NSP power supplies incur the same specific energy consumption of 1.4 kWh/m^3. From this perspective, the specific energy consumption demanded to enhance COD removal efficiency from 56% to 60% is greater as using of DC power supply than in use of NSP power supply ($\Delta_{SEC\text{-}DC}$ = 0.7 kWh/m^3 and $\Delta_{SEC\text{-}NSP}$ = 0.2 kWh/m^3, respectively). Therefore, it is very good point to conclude that the utilization of a DC power supply will require at least three times more specific energy consumption compared to the utilization of an NSP power supply. Moreover, NSP power supply facilitates higher COD removal efficiency (η = 77 %) at a higher specific energy consumption (3.5 kWh/m^3).

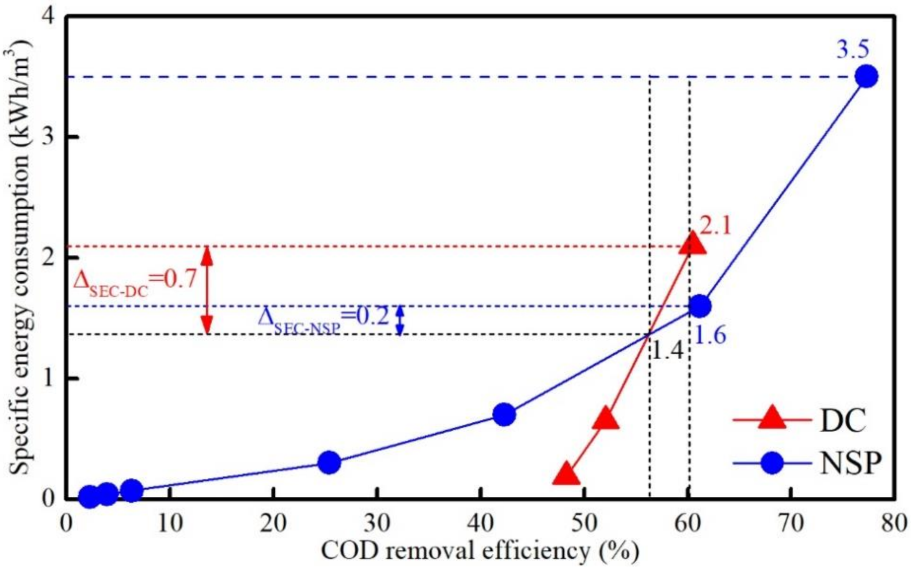

Fig 4.6. Correlation between SEC and COD removal efficiency using a DC and an NSP power supplies, treatment time = 60 min, and applied voltage ranging from 1 to 45 V.

Fig 4.6 also reveals that a DC power supply is preferable at low specific energy consumption due to there is no significant improvement in COD removal efficiency ($\Delta\eta$ $\approx$ 6 %) from textile wastewater as specific energy consumption increases.

4.4.5. Characterization of by-products from EC cells

In this part, the characteristic of precipitation that generated as using a DC and an NSP power supplies will be measured, included FE-SEM, XRG, EDS, and FT-IR. From that point, the ability adsorption of aluminum hydroxide in case of a DC and an NSP will be compared.

Fig 4.7 shows FE-SEM images of the surfaces of precipitates after utilizing a) DC and b) NSP power supplies. The FE-SEM images show that the DC power supply precipitate exhibits a regular shape (Fig 4.7a). Whereas, the NSP power supply precipitate includes many small particles (Fig 4.7b). As a results, a greater surface area of aluminum hydroxide can be achieved by the dense precipitates generated by

NSP power supply compared to the uniform precipitates generated by DC power supply [49].

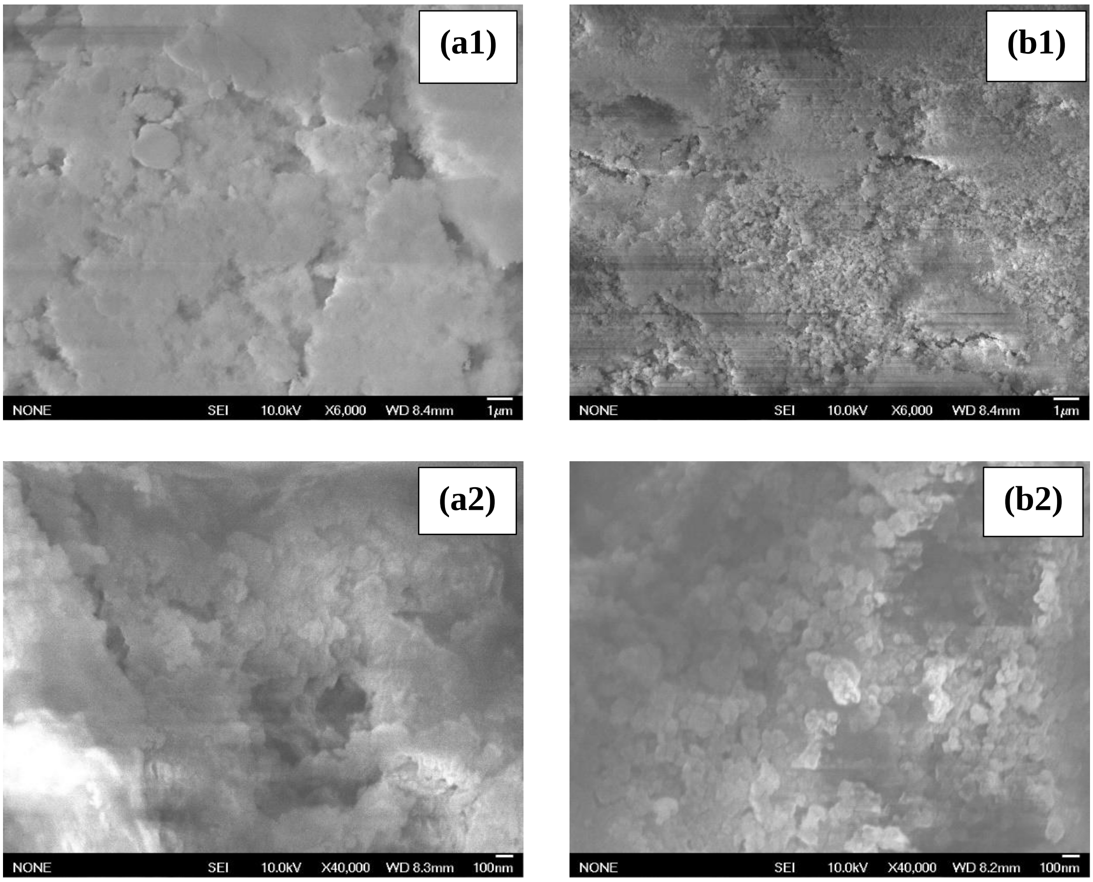

Fig 4.7. The morphology of precipitation formation in case of a DC at 4 V (a1, a2) and an NSP at 30 V (b1, b2), treatment time = 60 min.

Fig 4.8 shows that the XRD peak intensities of the aluminum hydroxide precipitates from an NSP power supply are significantly lower than those from a DC power supply. The lower XRD peak intensity as using of NSP power supply can be attributed to superior organic adsorption compared to a DC power supply [49]. In addition, Fig 4.8 shows that the diffraction peaks are broad in use DC power supply and shallow with low intensity as using NSP power supply. These traits indicate that the coagulants are amorphous or very poorly crystalline at best, which has been reported previously for Al hydroxide/oxyhydroxide precipitates [104]. The diffraction signals of the other elements are absent based on their low content in crystallites, which results in their signals being covered by those of the hydroxides.

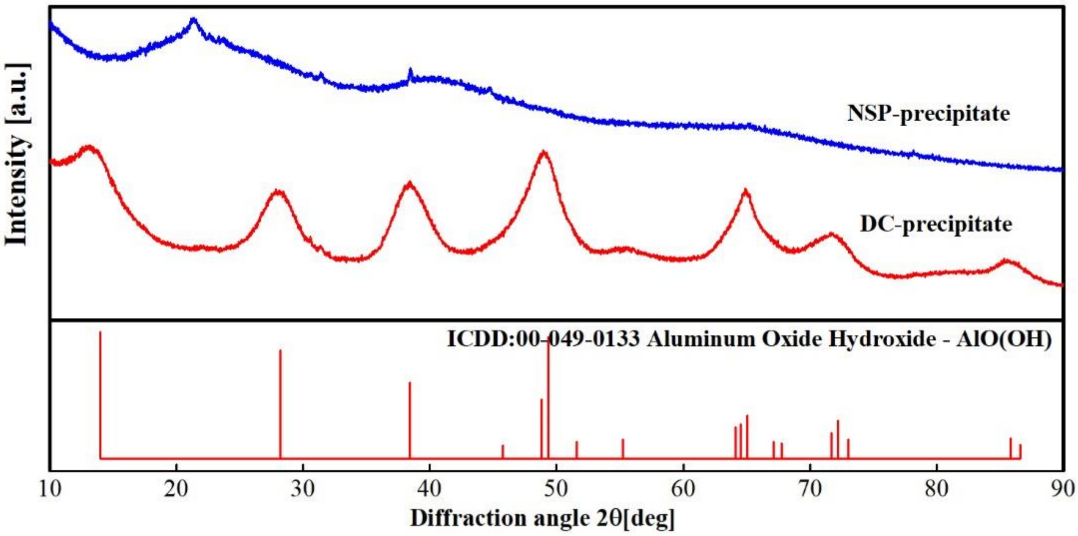

Fig 4.8. XRD spectra of precipitation formation in case of a DC = 4 V and an NSP = 30 V, treatment time = 60 min.

These FE-SEM and XRD pattern results are in close agreement with the results in Fig 4.6. The specific energy consumption as using an NSP power supply is lower than that in use of a DC power supply, which could be because the amount of precipitate generated as using an NSP power supply is less than that as using a DC power supply. However, the precipitate generated when using an NSP power supply exhibits better pollutant adsorption characteristics than that generated by a DC power supply was applied. As a result, COD removal efficiency is not significantly different between an NSP 30 V (1.6 kWh/m^3) and a DC 4 V (2.1 kWh/m^3) power supply at any given time.

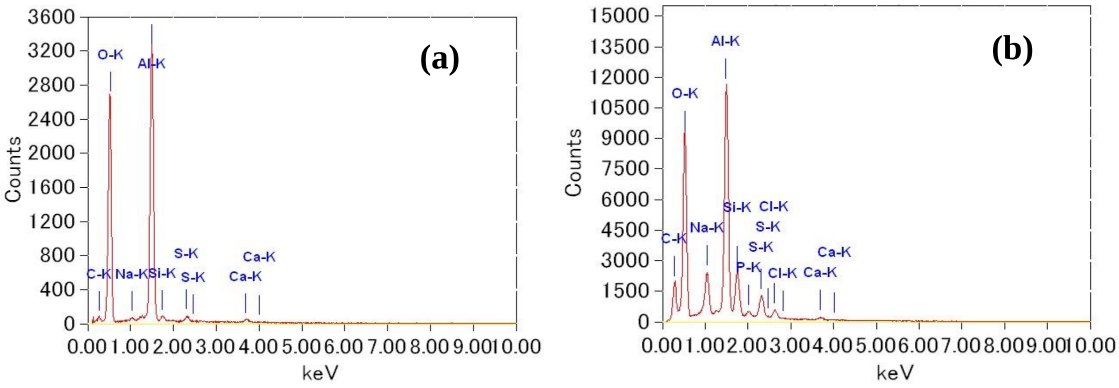

Fig 4.9. EDS analysis of precipitation from (a) DC = 4 V and (b) NSP = 45 V, treatment time = 60 min.

To understand the reasons for the large difference between the maximum COD removal efficiencies of DC and NSP, precipitate samples captured at DC 4 V and NSP 45 V were analyzed utilizing EDS.

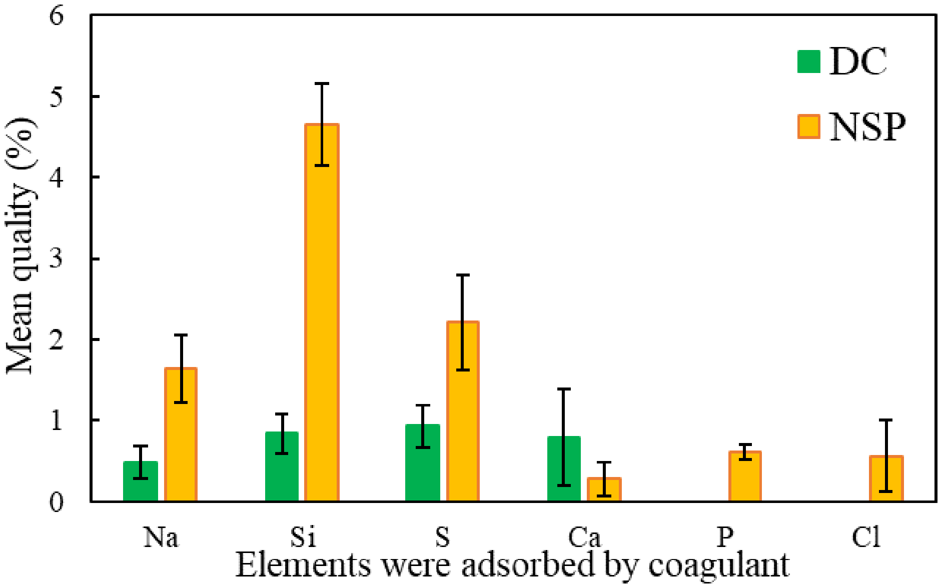

Fig 4.10. Mean quantity of elements with 95% confidence intervals in the precipitates formed utilizing a DC = 4 V and an NSP = 45 V, treatment time = 60 min.

Fig 4.9 shows the EDS spectra of the precipitate when using a) DC and b) NSP power supply following the electrocoagulation process experiment. One can see that Na, Si, S, and Ca are trapped by the aluminum hydroxide complex and removed via precipitation, regardless of the power supply utilized. Furthermore, in addition to the elements above, Cl and P are present in the NSP power supply precipitate (Fig 4.9b). To determine if NSP power supply can adsorb more pollutants than DC power supply, 50 samples were randomly selected from the precipitates of a DC and an NSP power supplies and analyzed utilizing by EDS method. Fig 4.10 shows mean values with 95% confidence intervals for all elements detected in the precipitates. One can see that the NSP power supply adsorbed more elements than the DC power supply.

In addition, for elements adsorbed by both systems (such as Na, Si, and S), the elemental percentage content in the an NSP power supply precipitate is greater than that in a DC power supply precipitate. It is worth noting that the flocs of aluminum hydroxide in the NSP power supply adsorbed more pollutants than those in a DC power supply.

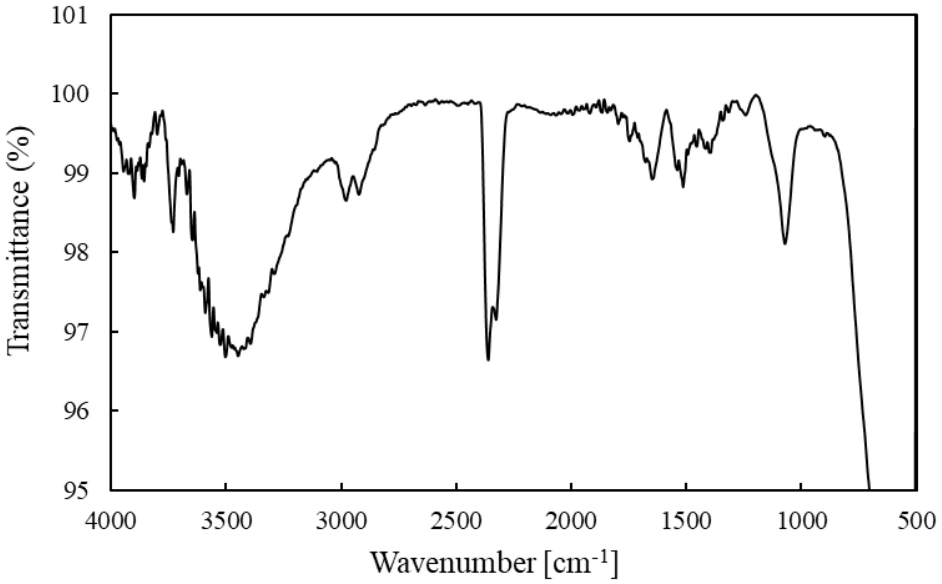

Fig 4.11. FT-IR spectra of the precipitate EC by-products using DC

In this chapter, the FT-IR spectra of precipitation in use of a DC power supply and an NSP power supply also is showed. Regarding FT-IR, this is popular methods to determine the chemical component and making a clearly the compounds structures. Furthermore, the results from FT-IR that is considered as one of the most important analytical techniques available. The best advantage of FT-IR is short time to measure. On the other hand, the FT-IR can be used with many sample statements such as: pastes, liquid, powders, solutions, films, gases, fibers, and surface [105].

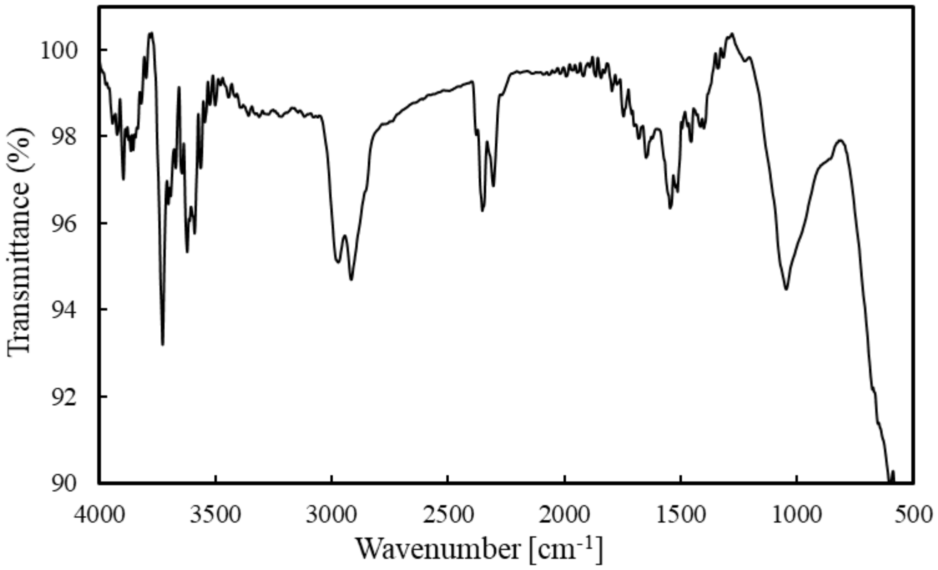

Fig 4.12. FT-IR spectra of the precipitate EC by-products using NSP

From Fig 4.11 and Fig 4.12 illustrates the variation of the FT-IR spectrum of generated sludge show the peaks at wavenumber from 400 – 4000 cm^{-1}. This range is chosen because the absorption radiation of most organic compounds and inorganic ions is within this region. The FT-IR spectra show wavenumber range of 3000 – 4000 cm^{-1} such as 3898.4, 3729.66, 3503.06 cm^{-1} for using DC and 3926.36, 3899.36, 3866.58, 3729.66, 3705.55, 3646.73, 3624.55, 3592.73, 3566.7, 3527.17 and 3504.02 cm^{-1} in use of NSP, which represent O-H for aluminum hydroxide/oxyhydroxides phases or N-H functional groups [91-93, 104]. The peaks at 2977.55, 2370.44 cm^{-1} in use of DC and 2974.66, 2917.77, 2353.69, 2306.45 cm^{-1} of NSP are assigned to the C-H stretching region. The strong intensity bands in the range of 1647.88, 1512.88 of DC and 1746.23, 1648.84, 1545.67, 1455.03 in use of NSP which could be assigned to the C-C bonds group [92, 106]. The final peaks that shows small wavenumber as 1070.3 and 1045.23 cm-1 in use of DC and NSP, respectively, which is attributed to the C=O or C-N stretching [92, 107].

4.5. CONCLUSION OF CHAPTER

In this part, the electrocoagulation with aluminum electrodes was used to remove COD from textile wastewater. On the other hand, the COD removal efficiency from textile wastewater in case of a DC and an NSP power supplies were compared. Results show that in case of an NSP power supply could reduce at least 24% specific energy consumption compared with a DC power supply. In addition, to enhance COD removal efficiency by 4%, for instance from 56 – 60 %, in use of an NSP power supply demands less than three times the specific energy consumption compared with a DC power supply. Moreover, SEM, XRD and EDS analysis revealed that use of an NSP power supply could be preferable for removing pollutants than using a DC power supply. Therefore, it is believed that an NSP power supply could have a net impact on reducing the operation cost of wastewater treatment facilities, hence promoting the use of electrocoagulation processing; ideally in couple with renewable energy, to contribute to reduction of carbon emission footprint during the wastewater processing

CHAPTER 5. COMPARISON BETWEEN NSP AND DC FOR REMOVING COD FROM MUNICIPAL WASTEWATER USING FE ELECTRODES

5.1. ABSTRACT

In this work, to remove COD from municipal wastewater, the electrocoagulation process is used with iron electrodes. The nanosecond pulse also applied and compared with direct current power supply. The sample for experiment was used the same above chapter, which was collected from the sewage centre in Nagaoka City, Japan. In this experiment, 4 iron electrodes were prepared to connected each other by a monopolar parallel configuration. The results showed that COD removal efficiency from municipal wastewater with Fe electrodes could up to 72 % in case of a DC power supply, and 82 % as using NSP power supply. The similar as using Al electrode to remove COD from municipal wastewater, in case of NSP power supply apply for electrocoagulation with Fe electrodes that could use at high voltage to enhance COD removal efficiency at a low specific energy consumption as compared with DC power supply, and there had no breakdown voltage. In use of NSP power supply could reduce around 40 % of specific energy consumption, compared with DC power supply at 72 % of COD removal efficiency from municipal wastewater with Fe electrodes. Therefore, in use of Fe electrodes, an NSP power supply was still more advantage than DC power supply due to reduce specific energy consumption at higher COD removal efficiency. Moreover, the analysis of precipitation in case of NSP and DC power supplies by using FE-SEM, XRD, and EDS. That showed that the flocs generated during electrocoagulation process in case of NSP was better performance than that ones in case of DC power supply. Therefore, an NSP power supply could be useful to promote the spread of electrocoagulation process as a commercial wastewater treatment technology.

5.2. INTRODUCTION

As explained at above chapter, The COD is popular parameter that is used to evaluate quality of water. The compassion to make increasing COD in water, included biodegradable organic, nonbiodegradable and inorganic oxidizable compounds [18, 74].

Nowadays, the economy area almost covers by other ones. In many countries, they focus to develop the economy, sometime they forget to protect natural environment. Typically, in the city where there is high density of population as well as other infrastructure. Therefore, currently the municipal wastewater the big problems in developing countries as well as poor countries. The municipal wastewater can be come from variety discharge sources, such as industrial buildings, groundwater and surface water, residences, institutions, commercial, etc. [108]. The municipal wastewater will be toxic to the natural environment if directly discharging to natural without cleaning. This action led to eutrophication phenomenon that is one of the most dangerous problem in natural [109]. However, to operate as well as maintain of sewage centre is quite expensive for developing countries as well as poor countries [50]. Therefore, the low-cost technology is priority at those countries. The electrocoagulation is potential technology, which can be match that requirement. Currently, electrocoagulation process can be used at isolate area due to renewable energy can be applied. This point makes electrocoagulation is highly desirable to promote an eco-friendly route for wastewater treatment technology [110].

For power supply, direct current and alternating current power supplies are used as the main power supply for electrocoagulation process [16]. As results showed in last chapter, the NSP power supply is more advantage than DC power supply to remove COD from municipal and textile wastewater using aluminium electrodes. Therefore, in this work, an NSP power supply will be applied to compare with DC power supply in removing COD from municipal wastewater with Fe electrodes. On the other hand, in this study characteristic of precipitation that generated in case of NSP power supply and DC power supply were analysed, using the FE-SEM, XRD, and EDS that no consideration has investigated up to now.

In this work, the material of electrode used is Fe. The main reaction that appears at the anode during electrocoagulation process [111, 112] is as follows:

$$\mathrm{Fe} - 2e^- = Fe^{2+} \qquad (1)$$

At the same time, at the cathode water reduction reaction occurs to release hydroxyl ions (OH^-) and hydrogen bubbles.

$$H_2O + e^- = \frac{1}{2}H_2 + OH^- \qquad (2)$$

For Fe electrodes, the ultimate products are significant dependent on the reaction rate of Fe^{2+} oxidation to Fe^{3+}, pH value of solution and oxygen saturation conditions in nonelectrochemical processes. With the solution is alkaline conditions, Fe^{2+} will immediately oxidize to change to Fe^{3+} (pH = 7.6-14) [113]. In this work, the initial pH of municipal wastewater changes around of 7. However, the final pH values of municipal wastewater were 10.5 and 8.1 after 90 min of treatment time of electrocoagulation process with DC power supply and an NSP power supply, respectively. As a result, the Fe^{2+} ion could be oxidized easily to Fe^{3+} due to oxygen is present in solution as follows reactions (3) and (4) [111]:

$$Fe^{2+} + OH^{-} = Fe(OH)_2 \qquad (3)$$

$$2Fe(OH)_2 + \frac{1}{2}O_2 + H_2O = Fe(OH)_3 (4)$$

5.3. MATERIALS AND METHODS

5.3.1. Experiment wastewater samples

The experiment wastewater samples were collected from the sewage treatment centre of Nagaoka City, Japan. Some municipal wastewater quality parameters were analysed by myself and the other they were supplied from above organisation, as showed in the Table 3.1.

As the same process as above chapter, pH meter (Model HM-30R, range from 0.000-14) and COND meter (Model ES-71) were also used to determine pH value and electrical conductivity of municipal wastewater before and after experiment, respectively. The other methods such as the Hach Method 8000 was applied to determined COD and TN in municipal wastewater. While, the Hach Method 8190 used to measure concentration of TP in sample. On the other hand, to measure DO in solution, the Hach Method 8166 was used. All experiment as well as measurement carried out at least 3 times. Furthermore, the XRD (Rigaku RINT-2500, CuKα), EDS and FE-SEM (JEOL JSM-6700F) were used to analysed characteristic of precipitation after finish electrocoagulation process.

All equations to calculate the COD removal efficiency, SEC in case of NSP power supply as well as in use of DC power supply were used as Chapter 3.

5.3.2. Laboratory scale experiment setup

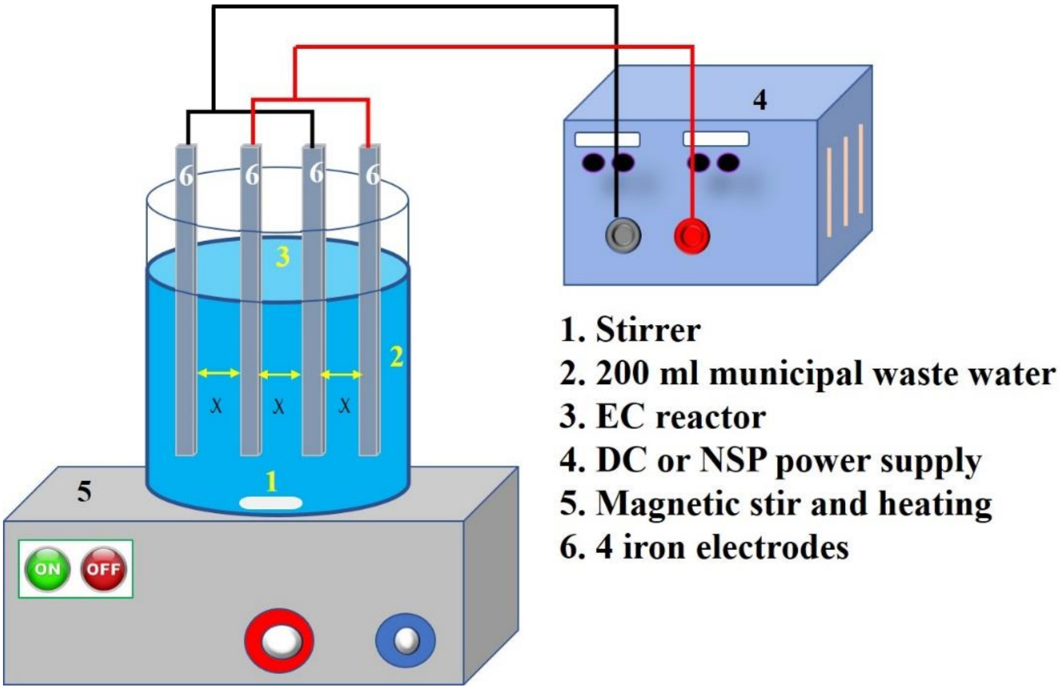

Fig 5.1. Setup EC cell at laboratory for all experiment

The electrocoagulation cell in laboratory was set up as showed in the Fig 5.1. The volume of municipal wastewater sample was 200 ml. The Fe plate was made 4 electrodes in the same size 1x20x55 mm^3 for experiment. The distance between electrodes was fixed 1 cm for all experiment.

Direct current (PL-650-0.1) and Nanosecond pulse (HK-10N) were applied as the main power supply under potentiostatic mode. The range of voltages was used different between DC power supply and NSP power supply, from 1- 5 V and 1- 50 V for NSP to avoid breakdown voltage, respectively. For NSP power supply, the frequency (f) = 10 KHz and pulse width (pw) = 1 µs were used as the optimum conditions.

Regarding experiment, the municipal wastewater sample was stirred 200 rpm at room temperature.

5.4. RESULTS AND DISCUSSIONS

5.4.1. Influence of the applied voltage

In this study, the effect of various voltages on the COD removal efficiency from municipal wastewater was studied by applying the EC process using different DC and NSP power supply.

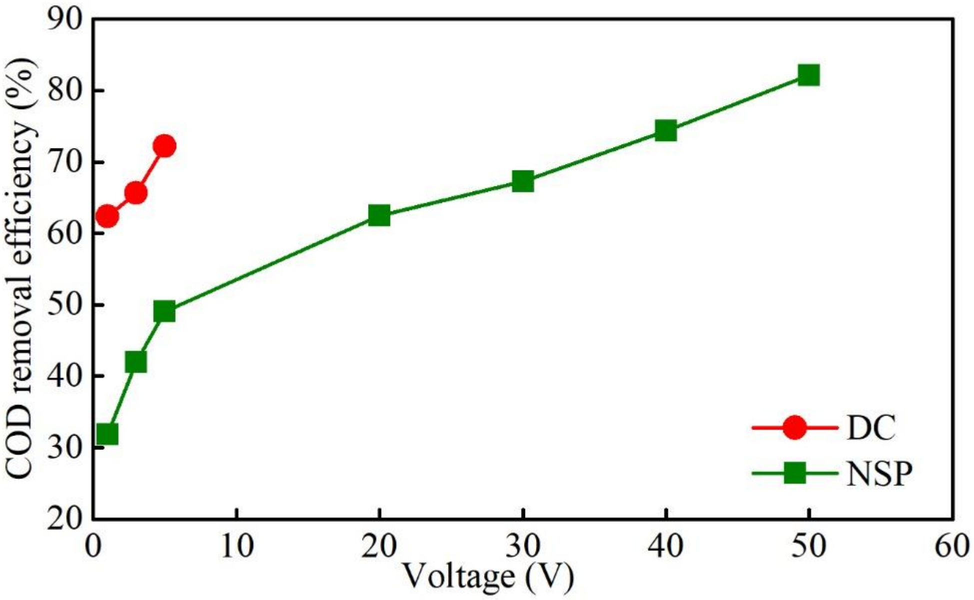

Fig 5.2. Influence of the voltage on the COD removal efficiency, treatment time = 90 min, applied voltage for DC from 1 – 5V and NSP from 1 – 50V

Regarding DC power supply, the applied voltages were selected at 1 V, 3 V and 5 V. Whereas, in case of NSP power supply, the applied voltages were set up at 1 V, 3 V, 5 V, 20 V, 30 V, 40 V, and 50 V. The results after all experiments in use of DC power supply and NSP power supply were revealed in the Fig 5.2. The results achieved from experiment in this work agreed with above chapters results, disregarding of DC or an NSP was used, when applied voltage increased, as a result the COD removal efficiency increased. This phenomenon can be proved by the relation between applied voltages and dose of coagulant generated and the amount of hydrogen bubbles that released from cathodes during electrocoagulation process. In the detail, when applied voltages increased, which led to increase the number of iron ions from anodes and number of hydroxide ions from cathodes, as a result increasing iron hydroxide that actives as a coagulant in solution [114]. Moreover, the number of hydrogen bubbles that released from cathodes also increased by applied voltage increased. That a reason to increase flotation process efficiency. As a result, promoting to enhance COD removal efficiency from municipal wastewater after finishing electrocoagulation process [80].

To be more understand this phenomenon, following the Faraday’s law, there is relation between the quantity of ferrous or ferric ions in solution during electrocoagulation process with the applied voltages. Obviously, based on that equation when applied voltage increased that led to the number of ferrous or ferric ions increased in solution. Consequently, the coagulants such as ferrous or ferric hydroxide increased, it is vital important to enhance the COD removal efficiency. Simultaneously, hydrogen bubbles also increased, promoting flotation process efficiency. The flotation and precipitation can remove from medium by centrifugation or filter [41, 80].

On the other hand, in the low range of voltage from 1 V to 5 V, the COD removal efficiency from municipal wastewater fast increased regardless a DC power supply or an NSP power supply, as shown in the Fig 5.2. The results are interesting to conclude that at the low range of applied voltage as above, the COD removal efficiency from municipal wastewater in use of DC power supply was much more significant lager than in case of an NSP power supply [114]. For instant, in range of 1 v to 5 V, the COD removal efficiency from municipal wastewater in case of DC power supply from 62 – 72 %, whereas in use of NSP power supply, the COD removal efficiency from municipal wastewater from 32 – 49 %.

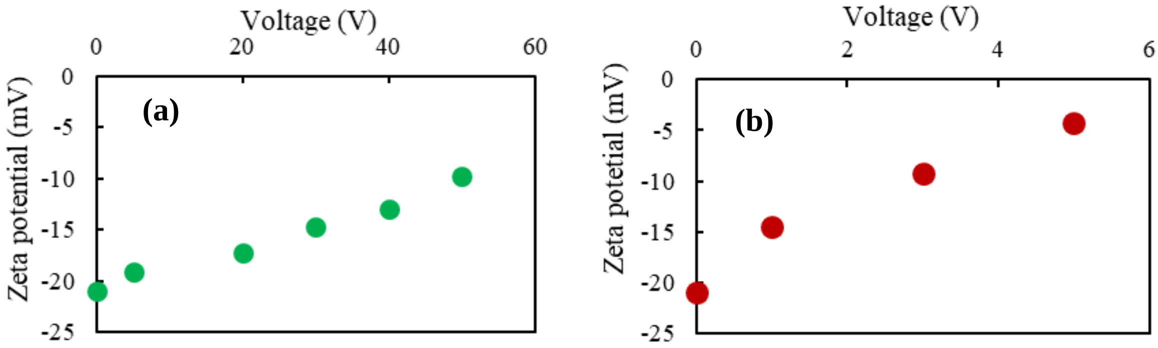

Fig 5.3. Variation of zeta potential with voltage, suing NSP (a) and DC (b)

In addition, to operate electrocoagulation process for removing COD from municipal wastewater, the range of applied voltage operation was different between DC power supply and NSP power supply, as shown in the Fig 5.2. For a DC power supply, the applied voltage could up to 5 V to avoid breakdown voltage. However, regarding an NSP power supply, the applied voltage could increase up to 50 V. These results play important role that decide the maximum COD removal efficiency when using DC or the NSP, i.e., 72 % and 82 %, respectively.

Furthermore, at the similar COD removal efficiency from municipal wastewater of 72 %, the applied voltages in case of DC was 5 V and in use of an NSP power supply was 40 V. Therefore, 5 V in case of DC power supply and 40 V in case of an NSP power supply were used to simplify the comparison and discussion between DC and the NSP.

To deeply understand the cause of COD removal efficiency increased by applied voltage increased. The zeta potential is measured in both power supplies. The zeta potential is used to determine the colloidal dispersions stable as well as the ability of electrostatic repulsion between adjacent, similarly charged particles in the solution for using electrocoagulation process.

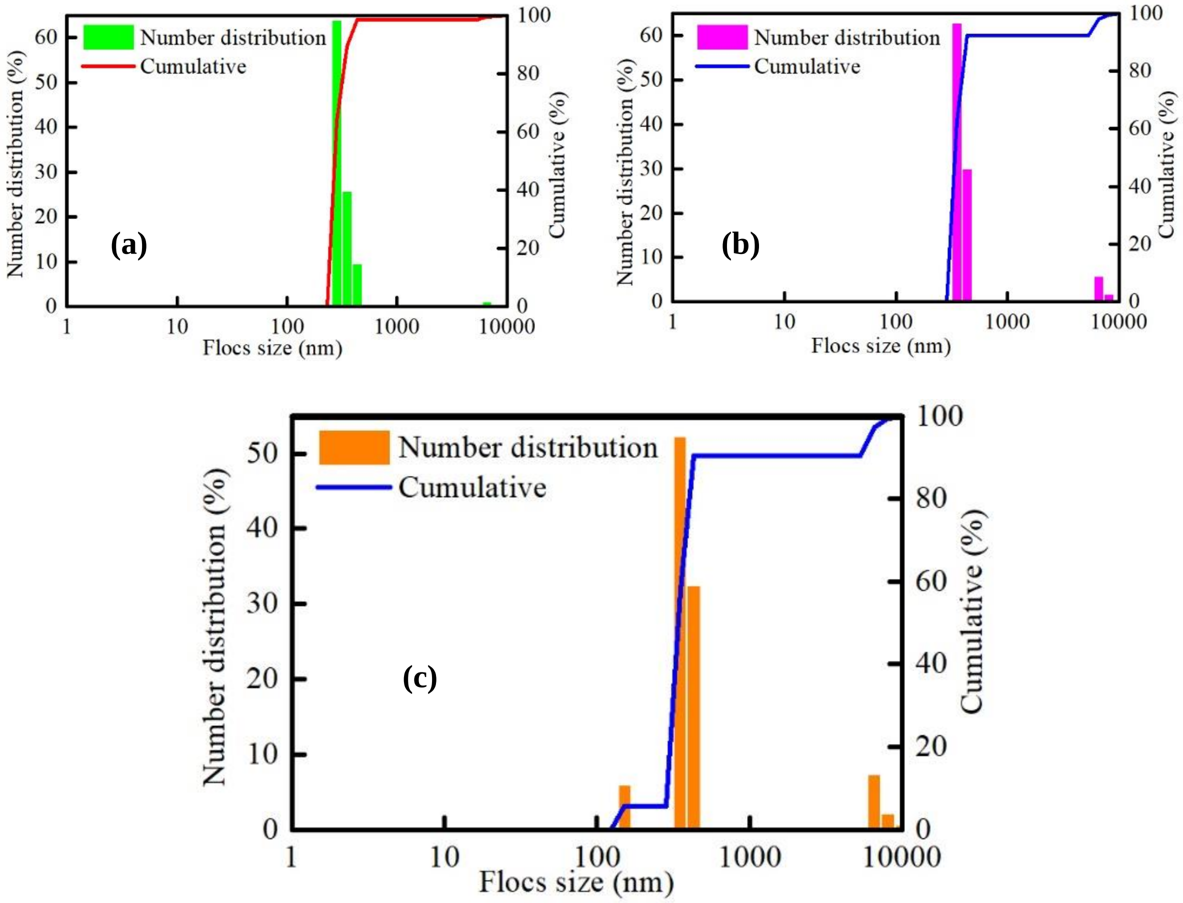

Fig 5.4. Flocs size distribution by using DC, (a) 1V, (b) 3V and (c) 5V

The Fig 5.3 shows that zeta potential tend to zero in response to an increase in applied voltage. The zeta potential fluctuated from -19.73 to -9.79 mV as applied voltage from 5 – 50 V, using NSP. Meanwhile, when the DC is used, the zeta potential fluctuated from -14.42 to -4.31 mV with applied voltage increased from 1 – 5V. So, regardless power supplied, the zeta potential values tended to zero. It could be demonstrated that when applied voltage increased the colloidal was easy to aggregate each other, the flocculation phenomenon was promoted. Consequently, more pollutants were adsorbed that led to COD removal efficiency increased after finishing electrocoagulation experiment.

Changing zeta potential values effects on colloidal aggregation. The zeta potential is nearly zero that is easy flocculation and enhancing the efficiency of electrocoagulation for removing COD from municipal wastewater. Based on the results that were showed in Fig 5.3, the size of the flocs will increase by the applied voltage.

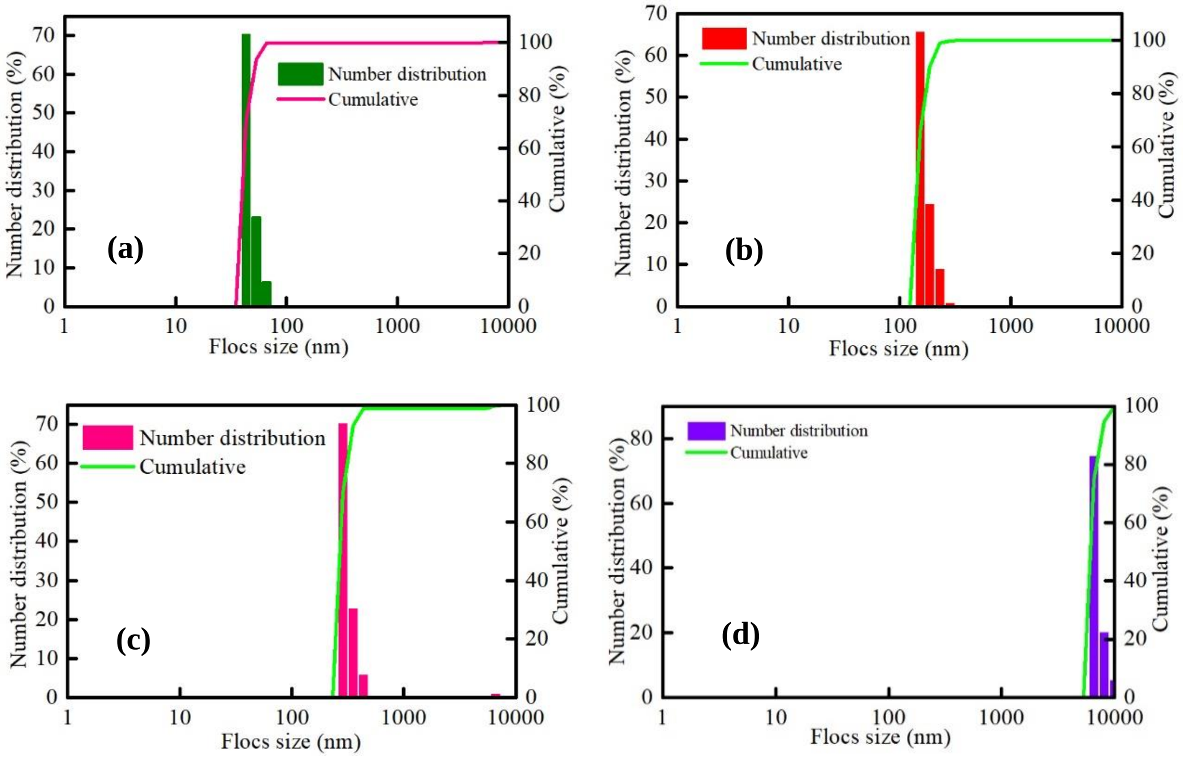

Fig 5.5. Flocs size distribution by using NSP, (a) 5V, (b) 20V, (c) 40V, and (d) 50V

Fig 5.4 reveals the flocs size increased by applied voltage from 1 to 5 V. When 1V was applied, more than 90 % of flocs size fluctuated within 250 - 450 nm. There was only about 1% of the flocs size that was bigger than 6500 nm. Whereas, when applied voltage increased to 3 V, the percentage of flocs size within 250 - 450 nm that was similar to 1V. However, the size of the big flocs (>6500 nm) that reached 6 %. The percentage of this big size continued to increase to about 11% as 5V was used. Moreover, the size of the flocs from 400 – 450 nm that occupied around 85 % in total.

For using NSP, the size of flocs significantly increased when the applied voltage increased from 5V, 20V, 40V, and 50V. At 5V, the size of the flocs was mainly within 43 – 66 nm that made up more than 99 %. The results comparison between Fig 3.11 and

Fig 5.5 show that electrocoagulation with Fe electrodes is easily to floc than using Al electrodes. As a results, the COD remove efficiency as using Fe was higher than Al electrodes at 5V (seeing Fig 3.5 and Fig 5.2). The size of the flocs continued increasing with applied voltage. At 20 V, about 99,9 % the size of flocs fluctuated from 150 – 350 nm, and around 0.1% the size of flocs was larger than 6500 nm. When applied voltage increased 40V, the size of flocs within 280 – 440 nm that occupied about 99 % and about 1% for bigger size of the flocs (>6500 nm). This size sharply increases to 6579.3 nm (make up 74.5 %) at applied voltage of 50 V. The other size is distributed range of 8111.3 – 10000 nm with the percentage from 20.1 – 5.4 %.

5.4.2. Interaction between the applied voltage and SEC

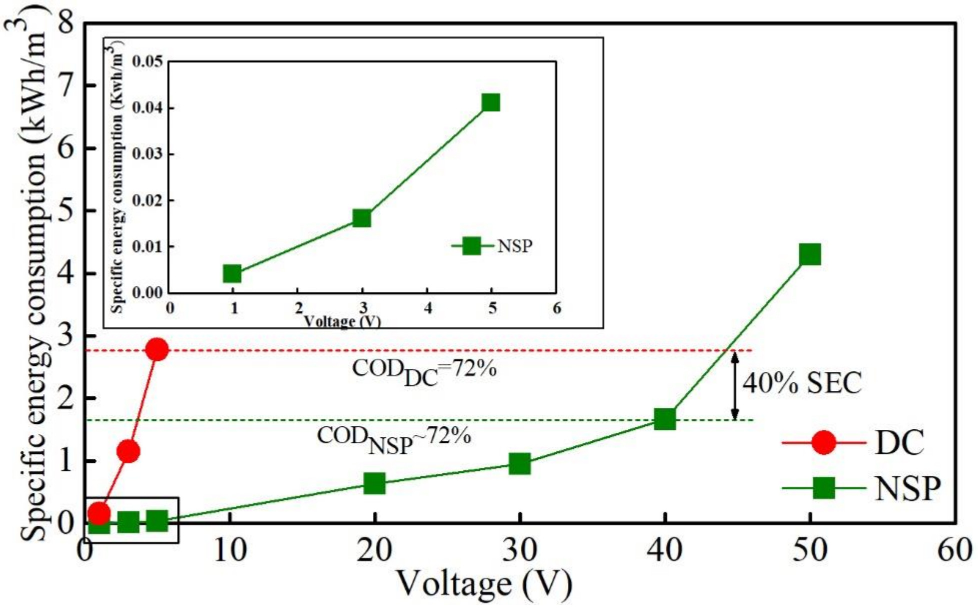

Fig 5.6. The relation between applied voltage and SEC, treatment time = 90 min.

The results from the Fig 5.6 shows the changing of the specific energy consumption with increases in the applied voltage. The strong relation between them was showed as applied voltage increased from 1 – 5 V in case of a DC power supply, and from 1 – 50 V in case of an NSP power supply, the specific energy consumption increased from 0.2-2.8 kWh/m^3 or 0.004-4.3 kWh/m^3, respectively. Moreover, from this figure that shows that in case of DC, the specific energy consumption increases faster than specific energy consumption in use of an NSP power supply. The results can be explained that in case of a DC power supply, the input voltage is constantly transferred to the electrocoagulation cell. In contrast, as using an NSP power supply, electrocoagulation is only active when a pulse is available that is equipment with time - on. Noticeably, the specific energy consumption of the an NSP power supply was always below the specific energy consumption of a DC power supply over the entire applied voltage range [114].

Moreover, in case of low applied voltage from 1 V to 5 V, the specific energy consumption just increasing from 0.004-0.041 kWh/m^3 for an NSP power supply. However, in case of DC power supply, the specific energy consumption is several orders of magnitude higher from 0.2-2.8 kWh/m^3 as shown in the Fig 5.6 and the Fig 5.6 inset. Therefore, in that above range of applied voltage, the SEC in case of NSP power supply was significantly lower than a DC power supply. These results are easy to understand that specific energy consumption is strong relation with applied voltage. While in use of a DC, the voltage is stable, using NSP the voltage only active as time-on. Moreover, the results are in excellent agreement with the results shown in the Fig 5.2. This agreement may be explained that the direct proportionality between the SEC and potential electrolysis. It implies that a high specific energy consumption leads to the generation of more ferrous or ferric ions in solution, promoting the formation of the ferrous or ferric hydroxides needed to coagulate soluble organic compounds and metal ions. As a result, the COD removal efficiency from municipal wastewater increased [42, 83]. The results could be showed by the data that in the case of the an NSP power supply, the COD removal efficiency was only 32% to 49 %. While, in case of a DC power supply, the COD removal efficiency from municipal wastewater was 62-72 %, as shown in the Fig 5.2.

The SEC values of DC 5 V and NSP 40 V were 2.8 and 1.7 kWh/m^3, respectively. The most important to conclude that at a similar COD removal efficiency (η ~ 72 %) from municipal wastewater as using Fe electrodes, the use of an nanosecond pulse required around 40 % less specific energy consumption than a DC power supply, as showed in Fig 5.6.

5.4.3. Influence of the treatment time on the SEC and the COD removal efficiency

The influence of treatment time on the specific energy consumption and COD removal efficiency as showed in the Fig 5.7. In this work, the treatment times were set up at 10 min, 30 min, 50 min, 70 min, 90 min, and 120 min to investigate for finding the optimum input conditions.

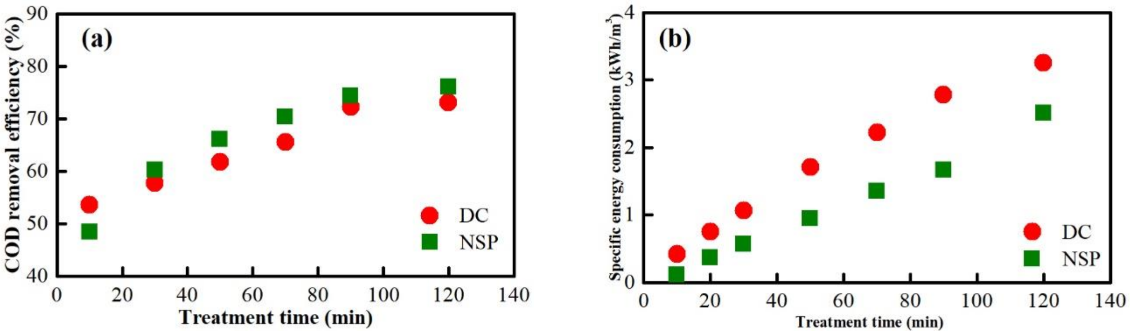

Fig 5.7. Influence of the treatment time on the SEC (b) and the COD removal efficiency (a), DC = 5 V and NSP = 40 V.

The Fig 5.7a shows the relation between treatment time and COD removal efficiency from municipal wastewater, from 10 -90 min of treatment time, the COD removal efficiency in case of a DC power supply increased from 53 % to 70 %. Whereas, in case of an NSP power supply, the COD removal efficiency increased from 48 % to 76 %. This interaction could be understood that the amount of ferric or ferrous ions that released from anodes increased. Meanwhile, the quantity of hydroxide ions from cathodes also increased. That led to increase the formation of ferrous or ferric hydroxide. Here was coagulant in solution. They promoted to enhance the removal pollutant from solution, as a result increasing COD removal efficiency from municipal wastewater [115]. Furthermore, in the fact the number of hydrogen bubbles were released from the cathodes that increased as increasing of treatment time. As a result, enhancing the flotation process efficiency. This led to increase COD removal efficiency from municipal wastewater [20, 84].

However, when the treatment time increased over 90 min, the COD removal efficiency from municipal wastewater was not significant increased, only < 2 %. This phenomenon could be explained that a sufficient number of flocs were available to remove the pollutants [85], and the cathodes reduction and new coagulant formation decreased [86].

On the other hand, regardless a DC power supply or an NSP power supply was applied, the specific energy consumption increased constantly with time as showed in the Fig 5.7b. Notably, the use of an NSP power supply produces a systematically higher COD removal efficiency from municipal wastewater and requires less specific energy than a DC power supply for the entire treatment time. That is vital point to conclude that using an NSP power supply is more advantage than a DC power supply to remove COD from municipal wastewater by using Fe electrodes [114].

5.4.4. Correlation between the SEC and COD removal efficiency

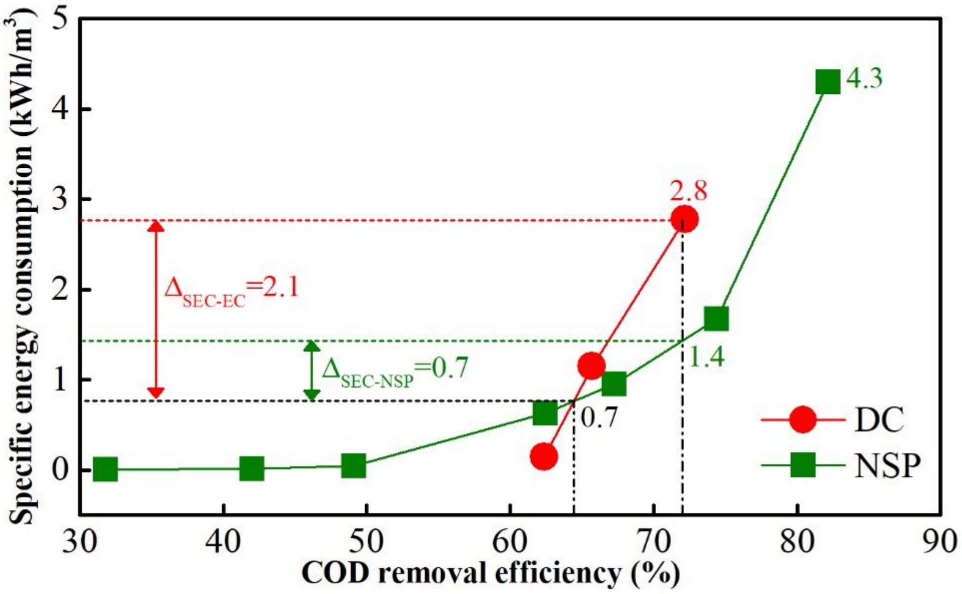

Fig 5.8. The correlation between the COD removal efficiency and SEC, treatment time = 90 min, and an applied voltage range from 1-50 V.

The variation in the COD removal efficiency from municipal wastewater and specific energy consumption was showed in the Fig 5.8. The specific energy consumption in used of a DC power supply fast increased than in case of an NSP power supply, which was used to operate electrocoagulation process [114]. To reach 64 % of COD removal efficiency from municipal wastewater, the specific energy consumption demanded 0.7 kWh/m^3 regardless a DC or an NSP power supply. On the other hand, to improve COD removal efficiency from 64 % to 72 %, in case of a DC power supply, the specific energy consumption needed to 2.8 kWh/m^3 ($\Delta_{SEC\text{-}DC}$ = 2.1 kWh/m^3). Whereas, in use of an NSP power supply, the specific energy consumption only demanded 1.4 kWh/m^3 ($\Delta_{SEC\text{-}NSP}$ = 0.7 kWh/m^3), as showed dashed line. Therefore, it is very important to conclude that in use of a DC power supply can require at least three times more specific energy than an NSP power supply that was applied.

From those results reveal that an NSP power supply could use energy more efficiency than a DC power supply for removing COD from municipal wastewater as using Fe electrodes. Furthermore, in case of an NSP power supply that can promote COD removal efficiency from municipal wastewater up to 82 % at a high specific energy consumption of 4.3 kWh/m^3.

Furthermore, Fig 5.8 also shows that for using of a DC power supply, which was recommended for use at low specific energy consumption because there was no significant increasing of COD removal efficiency from municipal wastewater ($\Delta\eta \sim 5$ %) as the specific energy consumption increased.

5.4.5. Characterization of the precipitation and surface of anode after electrocoagulation experiment

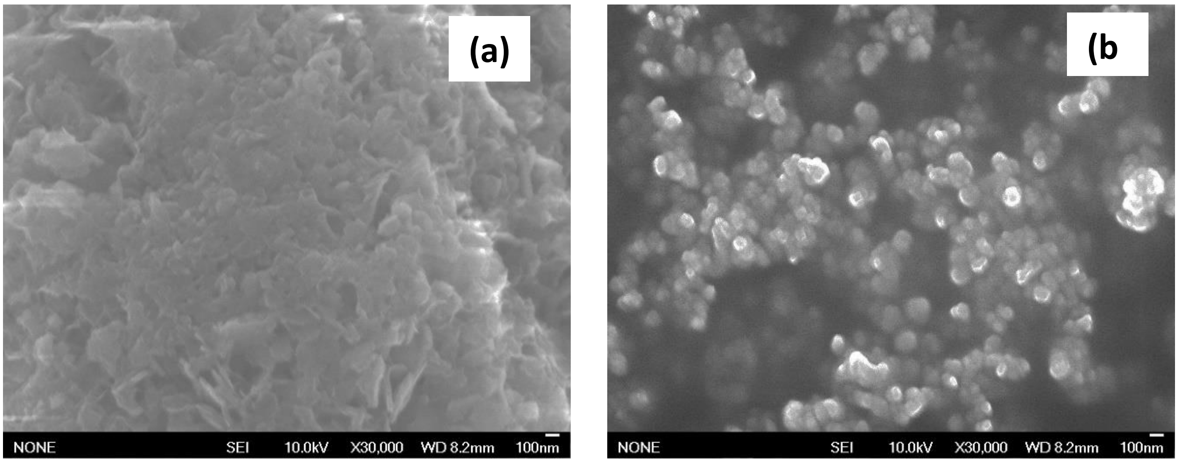

Fig 5.9. The images of precipitation were taken by FE-SEM, in case of a DC (a), and NSP (b).

Fig 5.9 reveals thar morphology of precipitation in case of a DC power supply and an NSP power supply. When use of a DC power supply, the morphology of precipitation showed a porous, as showed in the Fig 5.9a. However, regarding a precipitation released in solution as using an NSP power supply, which showed many smaller particles stacked over each other, as showed in the Fig 5.9b [114]. As a result, in case of an NSP power supply the precipitation was the higher surface area favours denser floc formation compared to the a DC power supply flocs [49].

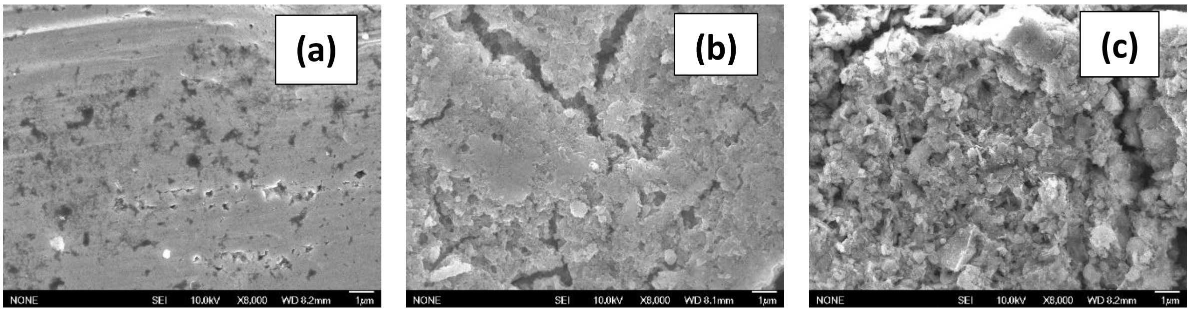

Fig 5.10. The surface of anode after EC process was taken by FE-SEM, before EC (a) and after using an NSP power supply (b) and DC power supply (c).

The way to operate in case of a DC power supply and an NSP power supply were different. Therefore, their effect on the anodes during electrocoagulation was diffident, which was showed in the Fig 5.10a, b and c. In case of an NSP power supply was used, the morphology of anode electrode after electrocoagulation process was few disordered pores and a smooth microstructure [114]. This state permitted to conclude that the iron electrodes was dissolved uniformly during electrocoagulation process, as showed in the Fig 5.10b. Whereas, the morphology of the iron anode electrode was rough and appeared many indentations in case of an NSP power supply, as showed in the Fig 5.10c. The indentations can be understood by consumption of the anode electrodes at active sites because of the generation of oxygen evolution at the surface [48].

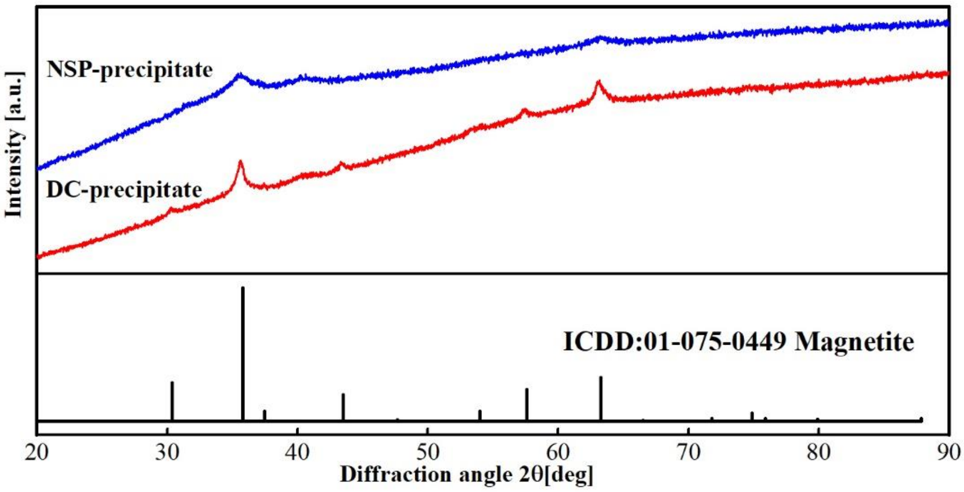

Fig 5.11. X-ray diffraction of the precipitation after EC process in case of using a DC and NSP power supplies.

X-ray diffraction of precipitation in case of a DC power supply and an NSP power supply were showed in the Fig 5.11. For using an NSP power supply, the X-ray diffraction of precipitation was a little lower than that of the precipitation in case of a DC power supply. This state could be understood the precipitation as used of an NSP power supply was better at adsorbing organic pollutants during settling than precipitation generated in case of a DC power supply, which was used as a main power supply [49, 114].

On the other hand, based on the X-Ray signal of precipitation as used a DC power supply and an NSP power supply, which were fix the ICDD values of magnetite (ICDD: 01-075-0449). The magnetite phase has also been reported elsewhere in case of electrocoagulation used a Fe electrode [104, 116, 117].

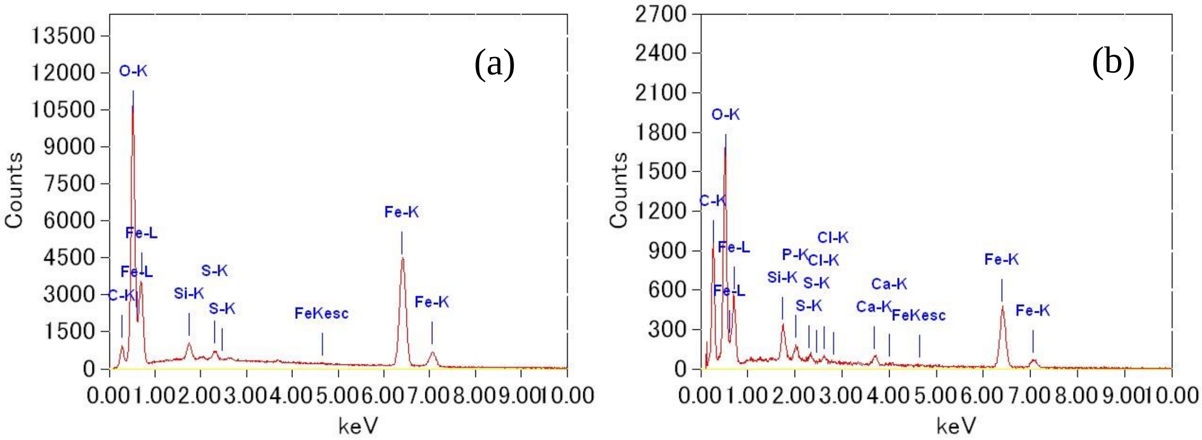

Fig 5.12. Type of elements in precipitation in case of a DC (a), and an NSP (b).

The type of elements that were adsorbed by coagulant during settling, as showed in the Fig 5.12. The EDS methods was used to determine that elements. The elements in precipitation included S, Si, C, and O regardless a DC power supply or an NSP power supply. Furthermore, beside of above elements, the other elements such as Cl, P and Ca that existed in the precipitation that generated from electrocoagulation process in use of an NSP power supply, as showed in the Fig 5.12b. Therefore, the results were showed in the Fig 5.11 and Fig 5.12 that indicated that coagulants in cased of using an NSP power supply was better performance than that in case of a DC power supply [114].

5.5. CONCLUSIONS OF CHAPTER

In this work, the efficiency of a DC power supply and an NSP power supply for application in electrocoagulation process was investigated. In case of a DC power supply, the COD removal efficiency could be up to 72 % at applied voltage 5 V. Whereas, this value was up to 82 % at applied voltage 50 V in case of an NSP power supply that was used to operate electrocoagulation process. On the other hand, in case of an NSP power supply, specific energy consumption could reduce 40 % compared with a DC power supply at the similar COD removal efficiency from municipal wastewater. The results from analysis of XRD, FE-SEM and EDS methods indicated that coagulants from electrocoagulation process in case of an NSP power supply was better performance than that in case of a DC power supply. The results permit me to conclude that the using of an NSP power supply was not only increase COD removal efficiency but also reducing the operation cost of wastewater treatment facilities. Therefore, it promotes the using of the EC process that should ideally to combine with renewable energy to reduce the carbon footprint of wastewater treatment technologies.

CHAPTER 6. FINAL CONCLUSIONS

In chapter 1, the characteristics of electrocoagulation technology were described. Including, general points of electrocoagulation were considered. The development of EC process was shown following the history milestones. In addition, the advantages and disadvantages of EC technology also included, which was showed to evaluate the feasible EC process as scale up. On the other hand, in this study that focused to remove COD from wastewater. Therefore, in this chapter the previous researches on removal COD from many wastewaters were listed. From that point, this study focused to deal with some existing problems such as using NSP instead of DC for improving COD removal from wastewater at low specific energy consumption. Moreover, the objectives and scope of study also described in this chapter.

In chapter 2, using EC process to remove COD from artificial wastewater. In this chapter, DC was used as main power supply for entire experiments. The results showed that highest COD removal efficiency (51 %) was achieved by using Al electrodes, and changing the influent pH = 4.1. Additionally, the optimum of applied voltage was determined at 15 V. Moreover, this chapter found that hydrogen bubble size around 42 µm may be suitable to promote the flotation process. As a result, enhancing COD removal efficiency from artificial wastewater.

In chapter 3. Comparisons between NSP and DC power supply were investigated. The efficiency of NSP power supply was revealed in this chapter. The vitality points in this chapter showed that at the similar COD removal efficiency, the specific energy consumption in case of an NSP power supply demanded at least 15 % less than a DC power supply. Furthermore, to improve COD removal efficiency from municipal wastewater over 60 %, the SEC in case of nanosecond pulse can reduce two or three times in respected to a DC power supply.

In chapter 4, NSP and DC power supply were used for EC process with aluminum electrodes to compare COD removal from textile wastewater. From this chapter, the advantages of NSP power supply affirmed based on the final results. This chapter showed that at the similar COD removal efficiency, an NSP could reduce at least 24% specific energy consumption compared with a DC power supply. Furthermore, to enhance COD removal efficiency from textile wastewater from 56 –

60 %, an NSP power supply required less than three times the SEC compared with a DC power supply. In addition, the reason for above results also made clearly.

In chapter 5, the efficiency of an NSP power supply as using Fe electrodes was investigated when it was compared with a DC power supply to remove COD from municipal wastewater. In this chapter, the results showed that maximum COD removal efficiency from municipal wastewater were different between NSP and DC, 82 % at 50 V and 72 % at 5 V, respectively. Moreover, at the similar COD removal efficiency of 72 %, SEC of an NSP power supply required at least 40 % less than a DC power supply. In addition, the better performance of NSP compared with a DC power supply was also explained in this chapter.

To remove COD from municipal wastewater, in case of using Al electrodes, the maximum COD removal efficiency was 80% at 5.2 kWh/m^3 with V = 50 V. At the similar COD removal efficiency (68 %) as used DC and NSP, NSP can save 15 % SEC compared with DC. Whereas, regarding Fe electrodes, the maximum COD removal efficiency was 82 % at 4.3 kWh/m^3 with V = 50 V. At the similar COD removal efficiency (72 %), NSP can save 40 % compared with DC. Therefore, in use of Fe electrodes was better performance than Al electrodes to remove COD from municipal wastewater regardless SEC or COD removal efficiency.

From the obtained results, an NSP power supply proved that it is better performance than a DC power supply when it is used as a main power supply for electrocoagulation process. Therefore, it is believed that an NSP power supply could have a net impact on reducing the operation cost of wastewater treatment facilities. Therefore, provoking the use of electrocoagulation processing; ideally in couple with renewable energy, to contribute to reduction of carbon emission footprint during the wastewater processing.

REFERENCES

[1] United Nations Environment Programe. Progress on intergrated water resources management. Global baseline for SDG 6 Indicator 6.5.1. degree of IWRM implementation, 2018.

[2] Crini G, Lichtfouse E. Advantages and disadvantages of techniques used for wastewater treatment. Environmental Chemistry Letters. 2018;17:145-155.

[3] Adelaide Dura. Electrocoagulation for water treatment: the Removal of Pollutants using Aluminium Alloys, Stainless Steels and Iron Anodes. National University of Ireland Maynooth; 2013.

[4] Chen G. Electrochemical technologies in wastewater treatment. Separation and Purification Technology. 2004;38:11-41.

[5] Holt PK. Electrocoagulation: unravelling and synthesising the mechanisms behind a water treatment process. 2002.

[6] Fayad N. The application of electrocoagulation process for wastewater treatment and for the separation and purification of biological media 2017.

[7] Holt PK, Barton GW, Mitchell CA. The future for electrocoagulation as a localised water treatment technology. Chemosphere. 2005;59:355-367.

[8] Bennajah M. Traitement des rejets industriels liquide par électrocoagulation/électroflottation en réacteur airlift: Institut National Polytechnique de Toulouse; 2007.

[9] Bensaïd J. Contribution à la dépollution des eaux usées par électrocoagulation et par adsorption sur les hydroxydes d’aluminium. 2009.

[10] Mollah MY, Morkovsky P, Gomes JA, Kesmez M, Parga J, Cocke DL. Fundamentals, present and future perspectives of electrocoagulation. Journal of hazardous materials. 2004;114:199-210.

[11] Hosny A. Separation of oil from oil/water emulsions using an electroflotation cell with insoluble electrodes. Filtration & separation. 1992;29:419-423.

[12] Chen G, Chen X, Yue PL. Electrocoagulation and electroflotation of restaurant wastewater. Journal of environmental engineering. 2000;126:858-863.

[13] Rossini M, Garrido JG, Galluzzo M. Optimization of the coagulation–flocculation treatment: influence of rapid mix parameters. Water Research. 1999;33:1817-1826.

[14] Holt PK, Barton GW, Wark M, Mitchell CA. A quantitative comparison between chemical dosing and electrocoagulation. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2002;211:233-248.

[15] Butler E, Hung Y-T, Yeh RY-L, Suleiman Al Ahmad M. Electrocoagulation in wastewater treatment. Water. 2011;3:495-525.

[16] Ascón EAA. Elimination of chemical oxygen demand from domestic residual water by electrocoagulation with aluminum and iron electrodes. Revista Ambiente & Água. 2018;13.

[17] Mollah MYA, Schennach R, Parga JR, Cocke DL. Electrocoagulation (EC)—science and applications. Journal of hazardous materials. 2001;84:29-41.

[18] Moreno-Casillas HA, Cocke DL, Gomes JAG, Morkovsky P, Parga JR, Peterson E. Electrocoagulation mechanism for COD removal. Separation and Purification Technology. 2007;56:204-211.

[19] Mollah MY, Morkovsky P, Gomes JA, Kesmez M, Parga J, Cocke DL. Fundamentals, present and future perspectives of electrocoagulation. J Hazard Mater. 2004;114:199-210. Epub 2004/10/30.

[20] Tak B-y, Tak B-s, Kim Y-j, Park Y-j, Yoon Y-h, Min G-h. Optimization of color and COD removal from livestock wastewater by electrocoagulation process: application of Box–Behnken design (BBD). Journal of Industrial and Engineering Chemistry. 2015;28:307-315.

[21] Balla W, Essadki AH, Gourich B, Dassaa A, Chenik H, Azzi M. Electrocoagulation/electroflotation of reactive, disperse and mixture dyes in an external-loop airlift reactor. J Hazard Mater. 2010;184:710-716. Epub 2010/09/28.

[22] Hakizimana JN, Gourich B, Chafi M, Stiriba Y, Vial C, Drogui P, Naja J. Electrocoagulation process in water treatment: A review of electrocoagulation modeling approaches. Desalination. 2017;404:1-21.

[23] Vepsäläinen M. Electrocoagulation in the treatment of industrial waters and wastewaters: VTT Technical Research Centre of Finland; 2012.

[24] Lu J, Wang Z, Ma X, Tang Q, Li Y. Modeling of the electrocoagulation process: A study on the mass transfer of electrolysis and hydrolysis products. Chemical Engineering Science. 2017;165:165-176.

[25] Abdel-Fatah MA, Awad AM, Ahmed EM, El-Aref AT. Comparison of Different Electrocoagulation Processes for Real Wastewater Degradation. International Journal of Scientific & Engineering Research. 2015;6:1133-1140.

[26] Vlyssides A, Karlis P, Zorpas A. Electrochemical oxidation of noncyanide strippers wastes. Environment international. 1999;25:663-670.

[27] Mouedhen G, Feki M, Wery Mde P, Ayedi HF. Behavior of aluminum electrodes in electrocoagulation process. J Hazard Mater. 2008;150:124-135. Epub 2007/06/01.

[28] Chen X, Chen G, Yue PL. Separation of pollutants from restaurant wastewater by electrocoagulation. Separation and purification technology. 2000;19:65-76.

[29] Moussa DT, El-Naas MH, Nasser M, Al-Marri MJ. A comprehensive review of electrocoagulation for water treatment: Potentials and challenges. J Environ Manage. 2017;186:24-41. Epub 2016/11/12.

[30] Heidmann I, Calmano W. Removal of Zn (II), Cu (II), Ni (II), Ag (I) and Cr (VI) present in aqueous solutions by aluminium electrocoagulation. Journal of Hazardous Materials. 2008;152:934-941.

[31] Bhaskar Raju G, Khangaonkar P. Electroflotation-a critical review. Transactions of the Indian Institute of Metals. 1984;37:59-66.

[32] Wills BA, Finch J. Wills' mineral processing technology: an introduction to the practical aspects of ore treatment and mineral recovery: Butterworth-Heinemann; 2015.

[33] Oecd. OECD Guidelines for the Testing of Chemicals September 2009/JA.

[34] Abràmoff MD, Magalhães PJ, Ram SJ. Image processing with ImageJ. Biophotonics international. 2004;11:36-42.

[35] Inan H, Dimoglo A, Şimşek H, Karpuzcu M. Olive oil mill wastewater treatment by means of electro-coagulation. Separation and Purification Technology. 2004;36:23-31.

[36] Kobya M, Ciftci C, Bayramoglu M, Sensoy MT. Study on the treatment of waste metal cutting fluids using electrocoagulation. Separation and Purification Technology. 2008;60:285-291.

[37] Kobya M, Can OT, Bayramoglu M. Treatment of textile wastewaters by electrocoagulation using iron and aluminum electrodes. Journal of Hazardous Materials. 2003;100:163-178.

[38] Zaroual Z, Chaair H, Essadki AH, El Ass K, Azzi M. Optimizing the removal of trivalent chromium by electrocoagulation using experimental design. Chemical Engineering Journal. 2009;148:488-495.

[39] Ghosh D, Solanki H, Purkait M. Removal of Fe (II) from tap water by electrocoagulation technique. Journal of Hazardous Materials. 2008;155:135-143.

[40] Chou W-L, Huang Y-H. Electrochemical removal of indium ions from aqueous solution using iron electrodes. Journal of Hazardous Materials. 2009;172:46-53.

[41] Bukhari AA. Investigation of the electro-coagulation treatment process for the removal of total suspended solids and turbidity from municipal wastewater. Bioresour Technol. 2008;99:914-921. Epub 2007/05/15.

[42] Aoudj S, Khelifa A, Drouiche N, Belkada R, Miroud D. Simultaneous removal of chromium(VI) and fluoride by electrocoagulation–electroflotation: Application of a hybrid Fe-Al anode. Chemical Engineering Journal. 2015;267:153-162.

[43] Verma SK, Khandegar V, Saroha AK. Removal of chromium from electroplating industry effluent using electrocoagulation. Journal of Hazardous, Toxic, and Radioactive Waste. 2013;17:146-152.

[44] Canizares P, Carmona M, Lobato J, Martinez F, Rodrigo M. Electrodissolution of aluminum electrodes in electrocoagulation processes. Industrial & engineering chemistry research. 2005;44:4178-4185.

[45] da Cruz SG, Dutra AJB, Monte MBM. The influence of some parameters on bubble average diameter in an electroflotation cell by laser diffraction method. Journal of Environmental Chemical Engineering. 2016;4:3681-3687.

[46] Hacha RR, LeonardoTorem M, Gutiérrez Merma A, da Silva Coelho VF. Electroflotation of fine hematite particles with Rhodococcus opacus as a biocollector in a modified Partridge–Smith cell. Minerals Engineering. 2018;126:105-115.

[47] Nguyen Q, Watari T, Yamaguchi T, Takimoto Y, Niihara K, Wiff J, Nakayama T. COD Removal from Artificial Wastewater by Electrocoagulation Using Aluminum Electrodes. Int J Electrochem Sci. 2020;15:39-51.

[48] Vasudevan S, Kannan BS, Lakshmi J, Mohanraj S, Sozhan G. Effects of alternating and direct current in electrocoagulation process on the removal of fluoride from water. Journal of Chemical Technology & Biotechnology. 2011;86:428-436.

[49] Govindan K, Oren Y, Noel M. Effect of dye molecules and electrode material on the settling behavior of flocs in an electrocoagulation induced settling tank reactor (EISTR). Separation and Purification Technology. 2014;133:396-406.

[50] Tandukar M, Ohashi A, Harada H. Performance comparison of a pilot-scale UASB and DHS system and activated sludge process for the treatment of municipal wastewater. Water Res. 2007;41:2697-2705. Epub 2007/04/10.

[51] Kolb M, Bahadir M, Teichgraber B. Determination of chemical oxygen demand (COD) using an alternative wet chemical method free of mercury and dichromate. Water Res. 2017;122:645-654. Epub 2017/06/27.

[52] Mulrow J, Machaj K, Deanes J, Derrible S. The state of carbon footprint calculators: An evaluation of calculator design and user interaction features. Sustainable Production and Consumption. 2019;18:33-40.

[53] Rittmann BE, Lee H-s, Zhang H, Alder J, Banaszak JE, Lopez R. Full-scale application of focused-pulsed pre-treatment for improving biosolids digestion and conversion to methane. Water Science and Technology. 2008;58:1895-1901.

[54] Gusbeth C, Frey W, Volkmann H, Schwartz T, Bluhm H. Pulsed electric field treatment for bacteria reduction and its impact on hospital wastewater. Chemosphere. 2009;75:228-233. Epub 2009/01/27.

[55] Morren J, Roodenburg B, de Haan SW. Electrochemical reactions and electrode corrosion in pulsed electric field (PEF) treatment chambers. Innovative Food Science & Emerging Technologies. 2003;4:285-295.

[56] Arjona N, Guerra-Balcázar M, Trejo G, Álvarez-Contreras L, Ledesma-García J, Arriaga L. Staircase and pulse potential electrochemical techniques for the facile and rapid synthesis of Pt and PtAg materials. Electrochim Acta. 2014;115:46-55.

[57] Keshmirizadeh E, Yousefi S, Rofouei MK. An investigation on the new operational parameter effective in Cr(VI) removal efficiency: a study on electrocoagulation by alternating pulse current. J Hazard Mater. 2011;190:119-124. Epub 2011/05/03.

[58] Kuokkanen V, Kuokkanen T, Rämö J, Lassi U. Recent Applications of Electrocoagulation in Treatment of Water and Wastewater—A Review. Green and Sustainable Chemistry. 2013;03:89-121.

[59] Cerqueira AA, Souza PSA, Marques MRC. Effects of direct and alternating current on the treatment of oily water in an electroflocculation process. Brazilian Journal of Chemical Engineering. 2014;31:693-701.

[60] Un UT, Koparal AS, Ogutveren UB. Electrocoagulation of vegetable oil refinery wastewater using aluminum electrodes. Journal of Environmental Management. 2009;90:428-433.

[61] Muthukumar K, Sundaram PS, Anantharaman N, Basha CA. Treatment of textile dye wastewater by using an electrochemical bipolar disc stack reactor. Journal of

Chemical Technology & Biotechnology: International Research in Process, Environmental & Clean Technology. 2004;79:1135-1141.

[62] Orkun MO, Kuleyin A. Treatment performance evaluation of chemical oxygen demand from landfill leachate by electro-coagulation and electro-fenton technique. Environmental Progress & Sustainable Energy. 2012;31:59-67.

[63] El-Naas MH, Al-Zuhair S, Al-Lobaney A, Makhlouf S. Assessment of electrocoagulation for the treatment of petroleum refinery wastewater. Journal of environmental management. 2009;91:180-185.

[64] Yavuz Y, Öcal E, Koparal AS, Öğütveren ÜB. Treatment of dairy industry wastewater by EC and EF processes using hybrid Fe□ Al plate electrodes. Journal of Chemical Technology & Biotechnology. 2011;86:964-969.

[65] Chou W-L, Wang C-T, Chang W-C, Chang S-Y. Adsorption treatment of oxide chemical mechanical polishing wastewater from a semiconductor manufacturing plant by electrocoagulation. Journal of Hazardous Materials. 2010;180:217-224.

[66] Janpoor F, Torabian A, Khatibikamal V. Treatment of laundry waste-water by electrocoagulation. Journal of Chemical Technology & Biotechnology. 2011;86:1113-1120.

[67] Bejankiwar RS. Electrochemical treatment of cigarette industry wastewater: feasibility study. Water research. 2002;36:4386-4390.

[68] Kurt U, Gonullu MT, Ilhan F, Varinca K. Treatment of domestic wastewater by electrocoagulation in a cell with Fe–Fe electrodes. Environmental Engineering Science. 2008;25:153-162.

[69] Mahajan R, Khandegar V, Saroha AK. Treatment of hospital operation theatre effluent by electrocoagulation. International Journal. 2013;4.

[70] Boudjemaa N, Drouichec N, Mameria N. Electro coagulation for the pathogenic and microorganism removal from Oued El-Harrach, Algeria wastewater. DESALINATION AND WATER TREATMENT. 2017;68:129-136.

[71] Boudjema N, Drouiche N, Abdi N, Grib H, Lounici H, Pauss A, Mameri N. Treatment of Oued El Harrach river water by electrocoagulation noting the effect of the electric field on microorganisms. Journal of the Taiwan Institute of Chemical Engineers. 2014;45:1564-1570.

[72] Boudjema N, Drouiche N, Kherat M, Mameri N. Wastewater disinfection by electrocoagulation process and its interaction with abiotic parameters. Desalination and Water Treatment. 2016;57:28151-28159.

[73] Shanmuganathan P, Ramachandra Murthy A, Rajasulochana P, Vishwalingam K. Exploitation and optimization of a microbial fuel cell for the treatment of whey wastewater and the power generation. Desalination and Water Treatment. 2017;72:156-161.

[74] Moreno H, Parga JR, Gomes AJ, Rodríguez M. Electrocoagulation treatment of municipal wastewater in Torreon Mexico. Desalination and Water Treatment. 2013;51:2710-2717.

[75] Nawarkar CJ, Salkar VD. Solar powered Electrocoagulation system for municipal wastewater treatment. Fuel. 2019;237:222-226.

[76] Que NH, Kawamura Y, Watari T, Takimoto Y, Yamaguchi T, Suematsu H, Niihara K, Wiff JP, Nakayama T. Nanosecond pulse used to enhance the electrocoagulation of municipal wastewater treatment with low specific energy consumption. Environ Technol. 2019:1-9.

[77] Linares-Hernandez I, Barrera-Diaz C, Roa-Morales G, Bilyeu B, Urena-Nunez F. A combined electrocoagulation-sorption process applied to mixed industrial wastewater. J Hazard Mater. 2007;144:240-248. Epub 2006/11/23.

[78] Chafi M, Gourich B, Essadki AH, Vial C, Fabregat A. Comparison of electrocoagulation using iron and aluminium electrodes with chemical coagulation for the removal of a highly soluble acid dye. Desalination. 2011;281:285-292.

[79] Cañizares P, Jiménez C, Martínez F, Rodrigo MA, Sáez C. The pH as a key parameter in the choice between coagulation and electrocoagulation for the treatment of wastewaters. Journal of Hazardous Materials. 2009;163:158-164.

[80] Ren M, Song Y, Xiao S, Zeng P, Peng J. Treatment of berberine hydrochloride wastewater by using pulse electro-coagulation process with Fe electrode. Chemical Engineering Journal. 2011;169:84-90.

[81] Chavalparit O, Ongwandee M. Optimizing electrocoagulation process for the treatment of biodiesel wastewater using response surface methodology. Journal of Environmental Sciences. 2009;21:1491-1496.

[82] Kumar A, Dixit CK. Methods for characterization of nanoparticles. Advances in Nanomedicine for the Delivery of Therapeutic Nucleic Acids: Elsevier; 2017. p. 43-58.

[83] Zaroual Z, Azzi M, Saib N, Chainet E. Contribution to the study of electrocoagulation mechanism in basic textile effluent. J Hazard Mater. 2006;131:73-78. Epub 2005/10/26.

[84] Khandegar V, Saroha AK. Electrochemical Treatment of Distillery Spent Wash Using Aluminum and Iron Electrodes. Chinese Journal of Chemical Engineering. 2012;20:439-443.

[85] Khandegar V, Saroha AK. Electrocoagulation for the treatment of textile industry effluent--a review. J Environ Manage. 2013;128:949-963. Epub 2013/07/31.

[86] Akyol A. Treatment of paint manufacturing wastewater by electrocoagulation. Desalination. 2012;285:91-99.

[87] Hashim KS, Shaw A, Al Khaddar R, Pedrola MO, Phipps D. Iron removal, energy consumption and operating cost of electrocoagulation of drinking water using a new flow column reactor. J Environ Manage. 2017;189:98-108. Epub 2016/12/25.

[88] Kotlyar L, Sparks B, LePage Y, Woods J. Effect of particle size on the flocculation behaviour of ultra-fine clays in salt solutions. Clay Minerals. 1998;33:103-107.

[89] Dixon JB, Weed SB, Parpitt R. Minerals in soil environments. Soil Science. 1990;150:562.

[90] Mahmad MKN, Rozainy MMR, Abustan I, Baharun N. Electrocoagulation process by using aluminium and stainless steel electrodes to treat total chromium, colour and turbidity. Procedia Chemistry. 2016;19:681-686.

[91] Zaidi S, Chaabane T, Sivasankar V, Darchen A, Maachi R, Msagati TAM. Electro-coagulation coupled electro-flotation process: Feasible choice in doxycycline removal from pharmaceutical effluents. Arabian Journal of Chemistry. 2015.

[92] Gupta A, Balomajumder C. Simultaneous Adsorption of Cr(VI) and Phenol from Binary Mixture Using Iron Incorporated Rice Husk: Insight to Multicomponent Equilibrium Isotherm. International Journal of Chemical Engineering. 2016;2016:1-11.

[93] Gładysz-Płaska A, Majdan M, Pikus S, Sternik D. Simultaneous adsorption of chromium(VI) and phenol on natural red clay modified by HDTMA. Chemical Engineering Journal. 2012;179:140-150.

[94] Chen J, Liu M, Zhang J, Xian Y, Jin L. Electrochemical degradation of bromopyrogallol red in presence of cobalt ions. Chemosphere. 2003;53:1131-1136.

[95] Lin SH, Peng CF. Treatment of textile wastewater by electrochemical method. Water research. 1994;28:277-282.

[96] Khorram AG, Fallah N. Treatment of textile dyeing factory wastewater by electrocoagulation with low sludge settling time: Optimization of operating parameters by RSM. Journal of Environmental Chemical Engineering. 2018;6:635-642.

[97] Wang T, Liu T. Pulse electro-coagulation application in treating dibutyl phthalate wastewater. Water Science and Technology. 2017;76:1124-1131.

[98] Mao X, Hong S, Zhu H, Lin H, Wei L, Gan F. Alternating pulse current in electrocoagulation for wastewater treatment to prevent the passivation of al electrode. Journal of Wuhan University of Technology-Mater Sci Ed. 2008;23:239-241.

[99] Ghanbari F, Moradi M, Eslami A, Emamjomeh MM. Electrocoagulation/Flotation of Textile Wastewater with Simultaneous Application of Aluminum and Iron as Anode. Environmental Processes. 2014;1:447-457.

[100] Ghanbari F, Moradi M, Mohseni-Bandpei A, Gohari F, Mirtaleb Abkenar T, Aghayani E. Simultaneous application of iron and aluminum anodes for nitrate removal: a comprehensive parametric study. International Journal of Environmental Science and Technology. 2014;11:1653-1660.

[101] Bayramoglu M, Eyvaz M, Kobya M. Treatment of the textile wastewater by electrocoagulation. Chemical Engineering Journal. 2007;128:155-161.

[102] Can OT, Kobya M, Demirbas E, Bayramoglu M. Treatment of the textile wastewater by combined electrocoagulation. Chemosphere. 2006;62:181-187. Epub 2005/07/06.

[103] Latha A, Partheeban P, Ganesan R. Treatment of Textile Wastewater by Electrochemical Method. International Journal of Earth Sciences and Engineering. 2017;10:146-149.

[104] Gomes JA, Daida P, Kesmez M, Weir M, Moreno H, Parga JR, Irwin G, McWhinney H, Grady T, Peterson E, Cocke DL. Arsenic removal by electrocoagulation

using combined Al-Fe electrode system and characterization of products. J Hazard Mater. 2007;139:220-231. Epub 2006/11/23.

[105] Garhwal S. Fourier transform infrared (ft-ir) spectroscopy in an-overview. Res J Med Plant. 2011;5:127-135.

[106] Kulkarni P, Dutari G, Weingeist D, Adin A, Haught R, Biswas P. Capture of water-borne colloids in granular beds using external electric fields: improving removal of Cryptosporidium parvum. Water Res. 2005;39:1047-1060. Epub 2005/03/16.

[107] Ganesan P, Lakshmi J, Sozhan G, Vasudevan S. Removal of manganese from water by electrocoagulation: Adsorption, kinetics and thermodynamic studies. The Canadian Journal of Chemical Engineering. 2013;91:448-458.

[108] Topare NS, Attar S, Manfe MM. Sewage/wastewater treatment technologies: a review. Sci Revs Chem Commun. 2011;1:18-24.

[109] Sommariva C, Converti A, Del Borghi M. Increase in phosphate removal from wastewater by alternating aerobic and anaerobic conditions. Desalination. 1997;108:255-260.

[110] Song P, Yang Z, Zeng G, Yang X, Xu H, Wang L, Xu R, Xiong W, Ahmad K. Electrocoagulation treatment of arsenic in wastewaters: A comprehensive review. Chemical Engineering Journal. 2017;317:707-725.

[111] Malakootian M, Mansoorian HJ, Moosazadeh M. Performance evaluation of electrocoagulation process using iron-rod electrodes for removing hardness from drinking water. Desalination. 2010;255:67-71.

[112] Wang T, Liu T. Pulse electro-coagulation application in treating dibutyl phthalate wastewater. Water Sci Technol. 2017;76:1124-1131. Epub 2017/09/07.

[113] Morgan B, Lahav O. The effect of pH on the kinetics of spontaneous Fe(II) oxidation by O2 in aqueous solution--basic principles and a simple heuristic description. Chemosphere. 2007;68:2080-2084. Epub 2007/03/21.

[114] Nguyen Q, Kawamura Y, Watari T, Niihara K, Yamaguchi T, Nakayama T. Electrocoagulation with a nanosecond pulse power supply to remove COD from municipal wastewater using iron electrodes. Int J Electrochem Sci. 2020;15:493-504.

[115] Al-Shannag M, Al-Qodah Z, Bani-Melhem K, Qtaishat MR, Alkasrawi M. Heavy metal ions removal from metal plating wastewater using electrocoagulation: Kinetic study and process performance. Chemical Engineering Journal. 2015;260:749-756.

[116] Mollah MY, Pathak SR, Patil PK, Vayuvegula M, Agrawal TS, Gomes JA, Kesmez M, Cocke DL. Treatment of orange II azo-dye by electrocoagulation (EC) technique in a continuous flow cell using sacrificial iron electrodes. J Hazard Mater. 2004;109:165-171. Epub 2004/06/05.

[117] Moreno C HA, Cocke DL, Gomes JA, Morkovsky P, Parga J, Peterson E, Garcia C. Electrochemical reactions for electrocoagulation using iron electrodes. Industrial & Engineering Chemistry Research. 2009;48:2275-2282.

LIST OF PUBLICATIONS

1. Comparison Between Nanosecond Pulse and Direct Current Electrocoagulation for Textile Wastewater Treatment, Que Ho NGUYEN, Takahiro WATARI, Takashi AMAGUCHI, Yuta KAWAMURA, Hisayuki SUEMATSU, Juan Paulo WIFF, Koichi NIIHARA, and Tadachika NAKAYAMA, Journal of Water and Environment Technology, No.3, Vol 18, pp.147-156.
2. COD Removal from Artificial Wastewater by Electrocoagulation Using Aluminum Electrodes, Q.H.Nguyen, T.Watari, T. Yamaguchi, Y.Takimoto, K.Niihara, J.P. Wiff and T.Nakayama, Int. J. Electrochem. Sci., 15 (2020)39-51.
3. Electrocoagulation with a nanosecond pulse power supply to remove COD from municipal wastewater using iron electrodes, Q.H.Nguyen, Y. Kawamura, T. Watari, K. Niihara, T. Yamaguchi and T. Nakayama, Int. J. Electrochem. Sci., 15 (2020) 493-504.
4. Nanosecond pulse used to enhance the electrocoagulation of municipal wastewater treatment with low specific energy consumption, Nguyen Ho Que, Yuta Kawamura, Takahiro Watari, Yuya Takimoto, Takashi Yamaguchi, Hisayuki Suematsu, Koichi Niihara, Juan Paulo Wiff & Tadachika Nakayama, Environmental technology (2019) 1-9.

LIST OF INTERNATIONAL CONFERENCES

Oral presentation

1. Using nanosecond pulse power supply for electrocoagulation to clean wastewater at low specific energy consumption, Q.H.Nguyen, T.Watari, T.Yamaguchi, K. Niihara, T. Nakayama, 21st anniversary of International Symposium on Eco-materials Processing and Design (ISEPD), China (2020).
2. Nanosecond pulse for enhancing electrocoagulation wastewater treatment at a low specific power consumption, Q.H. Nguyen, Y. Kawamura, T. Watari, Y. Takimoto, T. Yamaguchi, H.Suematsu, K. Niihara, J.P. Wiff and T. Nakayama, Green Energy and Environmental Technology, Paris (2019).
3. A Nanosecond Pulsed Electrocoagulation for Using in Textile Wastewater Treatment at a Low Specific Energy Consumption, Que Ho Nguyen, Takahiro Watari, Takashi Yamaguchi, Yuta Kawamura, Hisayuki Suematsu, Juan Paulo Wiff, Koichi Niihara and Tadachika Nakayama, Osaka (2019).

Poster presentations

1. Removal COD in artificial wastewater by electrocoagulation method using aluminum electrodes, Q.H.Nguyen, T. Watari, T. Yamaguchi, T. Nakayama, J.P. Wiff, H. Suematsu, K. Niihara, 12th International Conference on Ceramic Materials and Components for Energy and Environmental Applications, Singapore (2018).