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ชื่อโครงการ Probability of TDS reduction in effluent from electronic industry using adsorption, coagulation-flocculation, photocatalytic, and ion exchange processes

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คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

SENIOR PROJECT

Title	**Probability of TDS reduction in effluent from electronic industry using adsorption, coagulation-flocculation, photocatalytic, and ion exchange processes**	
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ความเป็นไปได้ในการลดทีดีเอสในน้ำทิ้งจากโรงงานอุตสาหกรรมอิเล็กทรอนิกส์ด้วยกระบวนการดูดซับ โคแอกกูเลชัน-ฟล็อคคูเลชัน โฟโตแคตาไลติก และการแลกเปลี่ยนไอออน

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Miss Sirima Sarewattana

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หัวข้อ ความเป็นไปได้ในการลดทีดีเอสในน้ำทิ้งจากโรงงานอุตสาหกรรมอิเล็กทรอนิกส์ด้วยกระบวนการดูดซับ โคแอกกูเลชัน-ฟล็อคคูเลชัน โฟโตแคตาไลติก และการแลกเปลี่ยนไอออน
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บทคัดย่อ

งานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาความเป็นไปได้ในการกำจัดทีดีเอสในน้ำทิ้งจากโรงงานอุตสาหกรรมอิเล็กทรอนิกส์เพื่อช่วยลดภาระของระบบรีเวอร์สออสโมซิสด้วย 4 กระบวนการบำบัด ได้แก่ 1) กระบวนการดูดซับที่พีเอช 5, 6 และ 7 ด้วยปริมาณถ่านกัมมันต์ 1 กรัมต่อน้ำทิ้งปริมาณ 50 มิลลิลิตร นำไปเขย่าเป็นเวลา 0.5, 1, 1.5, 6, 24 และ 48 ชั่วโมง 2) กระบวนการโคแอกกูเลชัน-ฟล็อคคูเลชัน ที่พีเอช 5, 6, 7, 8 และ 9 โดยใช้ปริมาณโพลีอลูมินัมคลอไรด์ 1 มิลลิลิตรต่อน้ำทิ้งปริมาณ 150 มิลลิลิตร ตามด้วยแอนไอออนิกโพลีอะคริลาไมด์ปริมาณ 0.1 มิลลิลิตร 3) กระบวนการโฟโตแคตาไลติกโดยใช้หลอดยูวีขนาด 7 วัตต์ ในการเร่งปฏิกิริยาด้วยแสง ด้วยไทเทเนียมไดออกไซด์ปริมาณ 1 มิลลิลิตรต่อลิตร ที่พีเอช 5, 6, 7 และ 8 เป็นเวลา 1 ชั่วโมง และ 4) การแลกเปลี่ยนไอออนโดยใช้เรซินแบบผสม ทั้งในการทดลองแบบกะ ด้วยปริมาณเรซินแบบผสม 1 กรัมต่อน้ำทิ้งปริมาณ 50 มิลลิลิตร และการทดลองแบบคอลัมน์ ด้วยปริมาณเรซินแบบผสม 10 กรัม ในคอลัมน์ที่มีอัตราการไหล 1 มิลลิลิตรต่อนาที เป็นเวลา 0.5-4 ชั่วโมง ผลการศึกษาพบว่า ในการหาสภาวะที่เหมาะสมด้วยกระบวนการดูดซับ โคแอกกูเลชัน-ฟล็อคคูเลชัน และโฟโตแคตาไลติก ไม่สามารถลดปริมาณของแข็งละลายในน้ำทั้งหมดได้ ต่างจากการหาสภาวะที่เหมาะสมในการแลกเปลี่ยนไอออนโดยใช้เรซินแบบผสม ซึ่งพบว่าเวลาที่เหมาะสมในการกำจัดทีดีเอสในการทดลองแบบกะ คือ 0.5 ให้ประสิทธิภาพในการกำจัดร้อยละ 25.5 และแบบคอลัมน์ ตั้งแต่เริ่มต้นจนถึงระยะเวลา 3 ชั่วโมง โดยให้ประสิทธิภาพในการกำจัดมากกว่าร้อยละ 99.0

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ABSTRACT

This research aimed to determine the probability of TDS reduction in effluent from electronic industry prior to intake to reverse osmosis via 4 treatment processes. 1) In adsorption process, pH was varied at 5, 6 and 7. At each pH, dose of granular activated carbon of 1 g/ 50 ml effluent with 100 rpm shaking for 0.5, 1, 1.5, 6, 24 and 48 hours were investigated. 2) In coagulation-flocculation process, pH was varied at 5, 6, 7, 8 and 9. One ml per 150 ml effluent was added, followed by 0.1 ml of coagulant aid. 3) In photocatalytic process, pH was varied at 5, 6, 7 and 8. One ml per L of photocatalyst (TiO_2) was added with UV lamp (7 watts) for an hour. 4) In ion exchange process, two systems i.e., batch and column were approached. Dose of mixed resin used in batch was 1 g/ 50 ml effluent, and 10 g at flow rate 1 ml/min in column for 0.5-4 hours. The results found that adsorption, coagulation-flocculation and photocatalytic processes showed very low TDS removal performance, on the other hand, ion exchange presented satisfactory efficiency. The results found that optimum reduction time for batch system of ion exchange was 0.5 hours with TDS removal efficiency of 25.5% whereas column system performed very high removal efficiency of more than 99.0% from initial to 3 hours of experimental period.

Key words: Activated carbon, Polyaluminium chloride, Titanium dioxide, UV lamp, Mixed resin

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Sirima Sarewattana

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Chapter 1

Introduction

1.1 Background and rationale

Electronic industry is one of the worldwide industries worth billions of dollars. Nowadays, people are increasingly involved with many electronics which making the cause of expanded capacity of electronic industry, where the processes and activities involve various steps which further generated wastewater (Yadav, 2016). For the sustainability of the manufacturing, the treated water from wastewater treatment system (normally called effluent) is subjected to the most popular system which is reverse osmosis (RO) to recycle the effluent for using in related processes and activities. Although the objective of using RO system is normally to treat total dissolved solids (TDS), too high TDS can cause several problems to RO e.g., membrane fouling which is the main cause of permeate flux reduction, block off the porous of membrane and loss of product quality in the system. Recommendation of TDS value before intake to the RO system is less than 1,000 mg/l; however, TDS from electronic effluent normally remained higher than that. This problem can be solved by pre-treatment of TDS from the effluent prior to intake to the RO system.

There are several methods to remove TDS, such as adsorption, coagulation, oxidation, nanofiltration, electrodialysis, high rate activated sludge system, or photocatalytic. For example, Vasanthy *et al.* (2008) studied the treatment of dyeing industry effluent with oxidation, coagulation and adsorption processes using sodium hypochlorite as an oxidizing agent, alum as a coagulating agent and commercial activated carbon as an adsorbent. The results showed that efficiency of TDS removal is more than 80% in oxidation, 90% in coagulation and 80% in adsorption process. Mortula and Shabani (2012) studied treatment of synthetic industrial wastewater via adsorption with different types of adsorbents which are limestone aggregate, activated carbon, steel slag and activated alumina. The most effective adsorbent was limestone aggregate which can remove up to 76.76% of TDS. Pokharna and

Shrivastava (2013) studied on photocatalytic treatment of textile industry effluent using titanium oxide. It was found that TDS removal efficiency up to 98.55%.

Thus, the aim of this project is based on the principle of adsorption, coagulation-flocculation, photocatalytic, and ion exchange using activated carbon, polyaluminium chloride, titanium dioxide, and mixed resin, respectively, to reduce the amount of TDS in the effluent of electronic industry. These four methods might be relatively inexpensiveness, effectiveness and easiness to be a pre-treatment of RO system.

1.2 Objective

To determine the probability of TDS reduction in effluent from electronic industry using adsorption, coagulation-flocculation, photocatalytic, and ion exchange processes.

1.3 Benefits

1.3.1 Get the most effective condition from each process to remove TDS from the electronic effluent.

1.3.2 Apply the optimum conditions to treat the electronic effluent prior to intake to the RO system.

Chapter 2
Theory and literature review

2.1 Theory

2.1.1 Electronic industry in Thailand

Thailand is also a major player in the hard disk and integrated circuits industry. The electronic manufacturing industry is currently growing rapidly. Being driven by technology, sensors and integrated circuits are smaller and more complex. This has led to the promotion of more advanced technology-based sub-industries, including the upgrading of the integrated circuits manufacturing industry. Production of electronic systems used in automotive and equipment with high-tech products, such as telecommunications equipment, design and manufacture of intelligent residential systems, smart appliances that connect to the Internet, electronic components, as well as the production of micro-electronic substances or plates (Eastern Economic Corridor, 2018).

Production of electronic products in the second quarter of 2018 shows a production index of 105.6, slightly increased by 3.23% (% QoQ) from the first quarter and 6.4% (YoY) in compared with the same quarter last year. Monolithic IC, HDD, PCBA and semiconductor increased by 18.1%, 17.8%, 7.8% and 6.4%, respectively. IC has grown as a key component in its development and parts of high technological products including smart phone and tablet. Meanwhile HDD has been developed to be more scalable for usage in cloud storage. Exportation of electronic products in the second quarter of 2018 were 308,739.84 million baht, slightly decreased from last quarter 2.2% (% QoQ), while increasing from quarter in the same period last year, 7.6% (YoY). Export to the market, including China, the United States, Japan, ASEAN, and the European Union increased by 12.8%, 10.5%, 10.1% , 6.4% and 6.2% respectively, compared to the same period of last year (Office of Industrial Economics, Ministry of Industry, 2018).

As mentioned above, the electronic industry in Thailand is likely to grow. Due to the demand of people in electronic goods, including the advancement of technology which being developed all the time.

2.1.2 Effluent from Electronic Industry

Electronic products and components processes produce large loading (huge amount and high concentration) of wastewater generated from various industrial activities and many chemicals (Yadav, 2016). Organic, inorganic, acids, alkalis, heavy metals, oil and grease, and some biological wastes consisted in electrics wastewater which are in the forms of suspended or dissolved solids. All above wastewater parameters can be treated by typical wastewater treatment system i.e., physical, chemical and biological treatments. However, total dissolved solids (TDS) is the main problematic parameter that remains in the effluent. TDS was found to be 589 mg/l in the effluent from electronic industry (Yadav, 2016). This value is high for suitable RO operation, causing the harder running system. As the result, more pre-treatment methods are needed to eliminate this overloaded TDS before intake water to RO system.

TDS is the amount of the dissolved solid, such as salts, minerals, colloids or all dissolved inorganic and organic substances contained in the effluent, which increasing the electrical conductivity (EC). For the TDS analysis, the direct method of measuring TDS is to evaporate water sample and weigh the remains with a precision analytical balance. Furthermore, because TDS has some of ionized solids, electrical conductivity meter can be used to estimate TDS.

2.1.3 Adsorption

Adsorption is one of the most important processes in the wastewater treatment system. It is used in various fields, such as in industry segment like water filter manufacturing which is used absorbable materials in filtration process, food and drug administration which adsorption involves in many processes, or petroleum and chemical industry that make various use of adsorption.

Adsorption is a process of trapping of suspended or dissolved substances in water onto the solid substances. The suspended or dissolved substances that was trapped on the solid substances called “adsorbate” and the solid substances which handling the suspended or dissolved substances called “adsorbent”. Adsorption is the sorption between three different phases which are solid, liquid and gas in the form of solid with liquid, solid with gas, or liquid with gas. Molecule of solution or suspensions are removed from the water and trapped on the adsorbent. Therefore, the adsorbent is usually a solid with a large cavity to increase the specific surface of the adsorbent. This will result in more absorbable, as the specific surface area of the adsorbent increases. Forces between molecule of the adsorbate and the adsorbent can be classified into two types: physical and chemical, according to the types of the forces (Chatsirivech, 2009).

2.1.3.1 Physical adsorption

Physical adsorption, also called physisorption, is the adsorption on the surface of the adsorbent with one or more physical forces. The physical forces of this type of adsorption are 1) the attraction between the poles of the adsorbate and the poles on the adsorbent surface, 2) the attraction between the charges or ions of the adsorbate and the charges on the adsorbent surface and 3) The mass attraction between the adsorbate and the adsorbent (Chatsirivech, 2009).

2.1.3.2 Chemical adsorption

Chemical adsorption, also called chemisorption, is the chemical bonding or sharing of electrons between molecule of the adsorbate and the adsorbent surface as same as chemical reaction. This type of adsorption requires the same amount of energy as the general chemical reaction, so the adsorption is usually good or rapid at high temperatures and it only occurs on the adsorbent surface. This type of adsorption takes place in only one layer called “monolayer adsorption” (Chatsirivech, 2009).

2.1.4 Coagulation-Flocculation

Coagulation-Flocculation are processes which are the addition of coagulant into the water to neutralize or stabilize charges of colloidal particles, causing them to clump together and lump up to a larger size for rapidly precipitated. In general, the system consists of rapid stirring tank which coagulant is added to mix with the water for precipitation of particles and slow stirring tank for aggregation which coagulation aid is added to increase the size of precipitated particles to a larger particle. Because the coagulation aid is a high molecular weight and high charge polymer used to make the bridge, strengthen and thickening the precipitated particles become to settlings. The precipitation and aggregation of particles also requires the interaction with chemical precipitation by adjusting the pH value to optimum condition for achievement of high removal efficiency. Moreover, to make the effective coagulation and flocculation, an optimum dosage of coagulant and a rapid mixing with an optimum contact time are necessary.

2.1.5 Photocatalysis

Photocatalysis is one of the advanced oxidation processes (AOPs) for industrial wastewater treatment with less residual waste. The most common use of semiconductors for photocatalysis such as TiO_2, ZnO, MgO, CdS etc. The photocatalyst should be photoactive and suitable towards visible or UV light. When a photon with an energy more than the band gap of the photocatalyst is absorbed on its surface, it causes excitation of an electron from valence band (vb) to conduction band (cb), forming a positive hole in the valence band then valence band holes can migrate to the surface and participate in interfacial oxidation-reduction reactions (Pokharna and Shrivastava, 2013).

Titanium dioxide (TiO_2), also known as titanium oxide, is one of the most studied semiconductors due to appropriate properties of it, such as high physical and chemical stability, non-toxicity, non-environmental impact, relatively low cost and photocatalytic efficiency. It is well established that conduction band electrons (e^-) and valence band holes (h^+) are generated when irradiating TiO_2 suspension aqueous with light energy greater than its band gap energy. The photogenerated electrons can reduce the organic such as dye or react with electron acceptors such as oxygen (O_2) adsorbed on the Ti(III)-surface or dissolved in water, reducing it to superoxide radical anion ($O_2^{\bullet -}$). The photogenerated holes can oxidize the organic molecule to form organic radical (R^+) or react with hydroxide (OH^-) oxidizing them into OH• radicals. According to this, the reactions at the semiconductor surface causing the degradation of the organic can be expressed as follows: (Konstantinou and Albanis, 2004).

$$TiO_2 + hv\ (UV) \rightarrow TiO_2\ (e_{CB}^- + h_{VB}^+) \tag{2.1}$$

$$TiO_2\ (h_{VB}^+) + H_2O \rightarrow TiO_2 + H^+ + OH\bullet \tag{2.2}$$

$$TiO_2 + (h_{VB}^+) + OH^- \rightarrow TiO_2 + OH\bullet \tag{2.3}$$

$$TiO_2\ (e_{CB}^-) + O_2 \rightarrow TiO_2 + O_2^{\bullet -} \tag{2.4}$$

$$O_2^{\bullet -} + H^+ \rightarrow TiO_2 + HO_2\bullet \tag{2.5}$$

2.1.6 Ion exchange

Ions are electrically charged atoms or molecules found in water. Ion exchange are used to exchange non-desirable ions with hydrogen and hydroxyl to form deionized or demineralized water. Ion exchange is a process of mobile ions between liquid phase and solid matrix which is insoluble and being in the form of microbeads such as zeolite and resins. Resins are most commonly used in water softening in order to replace magnesium and calcium ions found in hard water. Being made of crosslinked polystyrene, there are several types of resins. Most in commercial are made of polystyrene sulfonate. Types of resins are differed in their functional group within resins, the exchange will involve opposite charges between functional group and liquid phase (Braun *et al.*, 2002). Removal of both charged ions from liquid phase need to use an intermixed of two types of resins, strong acid cation ($R\text{-}SO_3H_2$) and strong base anion (R-NOH) resins called mixed bed system for an ion exchange. For example, in NaCl solution the process will be:

$$\text{R-H} + Na^+ \longleftrightarrow \text{R-Na} + H^+ \quad (2.6)$$

$$\text{R-OH} + Cl^- \longleftrightarrow \text{R-Cl} + OH^- \quad (2.7)$$

$$2H^+ + OH^- = H_2O \quad (2.8)$$

The reactions are driven to the right-hand side of equations because H_2O is weakly dissociated (Braun *et al.*, 2002). Ion exchange is similarly to adsorption process than chemical process because it is a redistribution of ions between two phases by diffusion, and chemical factors are less significant or even absent (Inglezakis and Poulopoulos, 2006). The exchange of ions depended on its ability which are valency and atom weight. High valency and atom weight are better replaced ions on the resins than lower (Areejitranusorn, 2001). Capacity of resins depend on cross linkage within resin. In general, the quality of resins is measured by the crosslinked percentage of polystyrene (divinylbenzene: DVB). Resins with low crosslinked percentage are low ability of ion exchange. The ability of resins with 6% crosslinked is 1.6 or 1.7 meq/ml at 54-56% of water capacity. This type of resin has cheaper cost than high crosslinked percentage (Samornkraisorakit, 2010).

2.1.7 Relationship between Electrical conductivity (EC) and Total Dissolved Solids (TDS)

Electrical conductivity (EC) is a measurement of ability to conduct an electrical current in liquid by ions, charged particles. The more ions, the higher ability of a liquid to conduct electricity. EC measurement can be used to provide some value in liquid such as total dissolved solids (TDS). TDS is a measurement of all dissolved organic and inorganic substances in the form of ionized, colloidal suspended, or molecular. TDS in ionized form can creates the ability in conduction of electrical current.

Two principal methods in measurement of TDS are gravimetric and conductivity. Although gravimetric is more accurate, but conductivity (EC) is usually used to estimate. As the result, according to a definition of both EC and TDS, EC can be used to estimate dissolved solids with the calculation from the equation below:

$$\text{TDS} = \text{EC} \times \text{Factor}$$

2.2 Literature review

Basha *et al*. (2008) studied on performance of four electrochemical ion exchange (EIX) cells run for a maximum of 7 hours for TDS (Cl^-, SO_4^{2-}, PO_4^{3-}, Ca^{2+}, Fe^{2+} and Mg^{2+}) removal in synthetic wastewater. Each EIX cell is different in resins between cathode, middle and anode chamber. Almost complete removal of TDS occurred in 4.5-7 hours under one or more test conditions. Removal efficiency is around 92.4-100%.

Vasanthy *et al.* (2008) studied dyeing industry effluent treatment with oxidation, coagulation and adsorption using oxidizing agent (sodium hypochlorite), coagulating agent (alum) and adsorbent (commercial activated carbon). The TDS of the effluent was 3,860 mg/L. The most TDS removal efficiency were using 0.25 grams of sodium hypochlorite, 1 gram of alum and 0.75 gram of commercial activated carbon and the results showed 80%, 90% and 80% removal of TDS respectively.

Nkwonta and Ochieng (2010) studied on TDS removal in wastewater using roughing filters. Gravel and charcoal were used to evaluate roughing filtration treatment system. Gravel was used as roughing filter media and to provide a media for bacteria growth and charcoal was used as an alternative filter media to enhance sedimentation and other filtration processes like adsorption. The result shown that roughing filter give 97% TDS removal after 90 days.

Mishra and Mohapatra (2012) researched on treatment of rice mill wastewater by six chemical treatment with bleaching powder, ferric alum, lime, activated charcoal and rice husk charcoal. The optimized experimental condition was the treatment with activated charcoal followed by adding bleaching powder, ferric alum and lime together. TDS values for the two natural rice mill wastewater samples were 2,324 and 2,145 mg/L and the optimum condition of TDS removal was 75.1% and 74.5%.

Mortula and Shabani (2012) determined treatment of synthetic industrial wastewater via adsorption with different adsorbent (e.g., activated carbon, activated alumina, steel slag, limestone aggregate). TDS of the wastewater was 1,150 mg/L. The most effective one which could remove up to 76.76%TDS presented in using limestone aggregate, while activated carbon, steel slag and activated alumina removed only 47.68%, 45.94% and 44.8%, respectively.

Pokharna and Shrivastava (2013) worked on photocatalytic treatment of textile industry effluent using titanium oxide. The TDS value of textile effluent is 3,540 mg/l. After adding 1.2 ml of 0.2M titanium oxide in 25 ml of sample and placed in sunlight for photolysis for 96 hours. Result of photocatalysis showed the removal efficiency of TDS up to 98.55%.

Khatmode and Thakare (2015) studied on textile effluent treatment using via adsorption. The textile effluent characteristic showed high dissolved solids value 2,900 - 3,100 mg/L. After the treatment with sawdust, the textile effluent was decreased 27%TDS after 24 hours.

Table 2.1 Summary of TDS removal by adsorption process

Name	**Type of wastewater**	**Initial TDS (mg/l)**	**Adsorbent**	**Adsorption time**	**% Removal**
Vasanthy *et al*. (2008)	Dyeing wastewater	3,860	Commercial activated carbon (CAC)	30-60 minutes	79%
Nkwonta and Ochieng (2010)	Municipal wastewater	28.12	Charcoal	90 days	97%
Mishra and Mohapatra (2012)	Rice mill wastewater	2,324	Activated charcoal and Rice husk charcoal	96 hours	75.10% and 60%
Mortula and Shabani (2012)	Synthetic wastewater as food processing industry	1,150	Activated carbon, Activated alumina, Steel slag and Limestone aggregate	1 hour	47.68%, 44.28%, 45.94% and 76.76%
Khatmode and Thakare (2015)	Textile effluent	1,700	Sawdust	24 hours	27%

Table 2.2 Summary of TDS removal by coagulation-flocculation process

Name	**Type of wastewater**	**Initial TDS (mg/l)**	**Reagent**	**Treatment time**	**% Removal**
Vasanthy *et al*. (2008)	Dyeing wastewater	3,860	Alum	30-60 minutes	90%
Mishra and Mohapatra (2012)	Rice mill wastewater	2,324	Ferric alum	96 hours	31%

Table 2.3 Summary of TDS removal by photocatalytic process

Name	**Type of wastewater**	**Initial TDS (mg/l)**	**Reagent**	**Treatment time**	**% Removal**
Pokharna and Shrivastava (2013)	Textile effluent	3,540	Titanium oxide	96 hours	98.55%

Table 2.4 Summary of TDS removal by ion exchange process

Name	**Type of wastewater**	**Initial TDS (mg/l)**	**Material**	**Treatment time**	**% Removal**
Basha *et al*. (2008)	Synthetic wastewater	859	Resin	4.5-7 hours	92.4-100%

Chapter 3

Materials and methods

3.1 Materials

3.1.1 Water sample

The electronic effluent was collected from an electronic industry and stored at 4°C in a refrigerator. The pH, electrical conductivity (EC) and total dissolved solids (TDS) of the electronic effluent were measured using pH meter, EC meter and oven drying (180^{o}C), respectively.

3.1.2 Equipments

1) Electrical conductivity meter (EC meter)
2) Drying oven
3) Evaporating dishes
4) Hotplate stirrer
5) Incubator
6) Jar test
7) Reciprocating shaker
8) Steam bath
9) UV lamp 7 Watts
10) pH meter
11) Glass microfiber filter GF/C
12) Analytical balance (4 digits)
13) Burette
14) Burette clamp

3.1.3 Chemicals

1) Granular activated carbon: GAC (Commercial grade)
2) Polyaluminium chloride 10%: PACl (Commercial grade)

3) Anionic polyacrylamide 0.01% (Commercial grade)

4) Anatase titanium dioxide 1%: TiO_2

5) Hydrochloric acid: HCl

6) Sodium hydroxide: NaOH

7) Mixed resin (Commercial grade)

3.2 Experimental procedure

The overall of four processes i.e., adsorption, coagulation-flocculation, photocatalytic, and ion exchange to remove TDS in this experiment were illustrated in Figures 3.1-3.4.

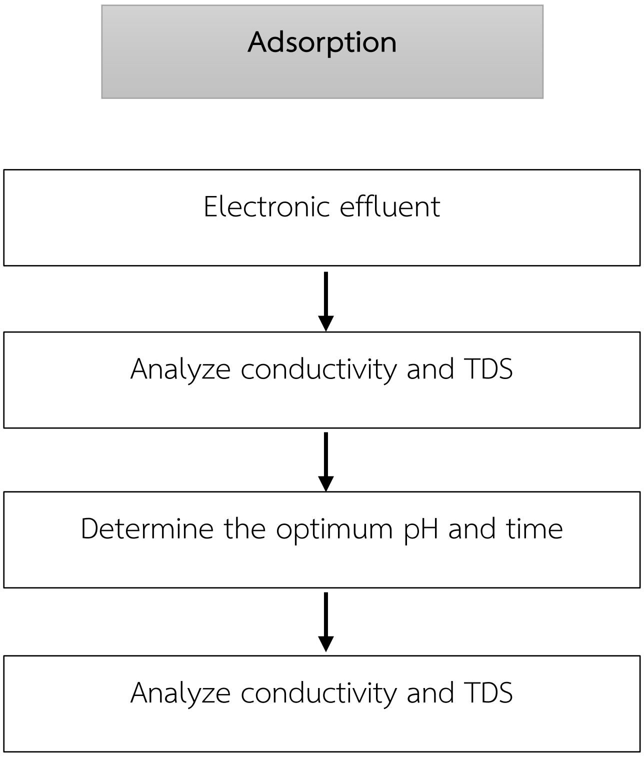

Figure 3.1 Adsorption process

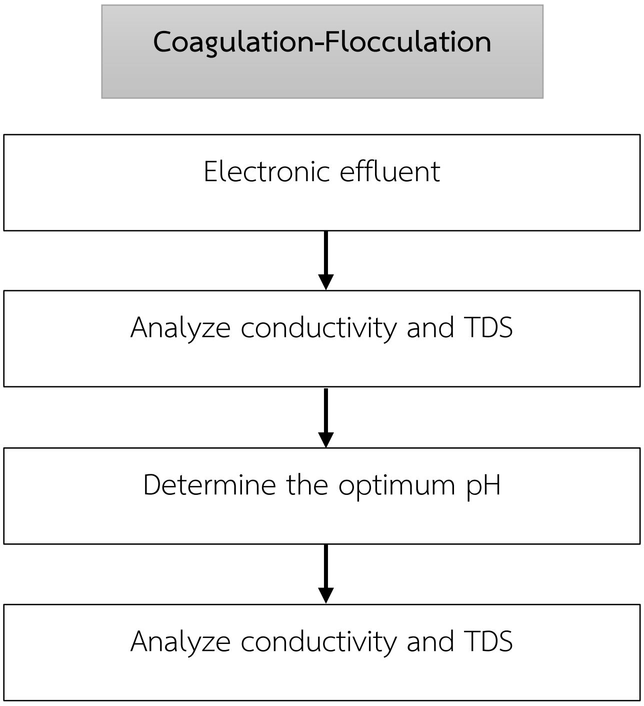

Figure 3.2 Coagulation-Flocculation process

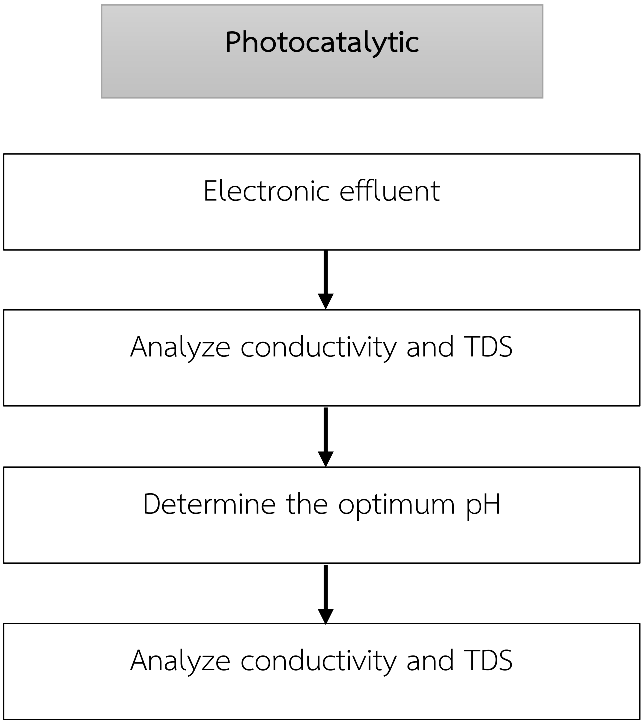

Figure 3.3 Photocatalytic process

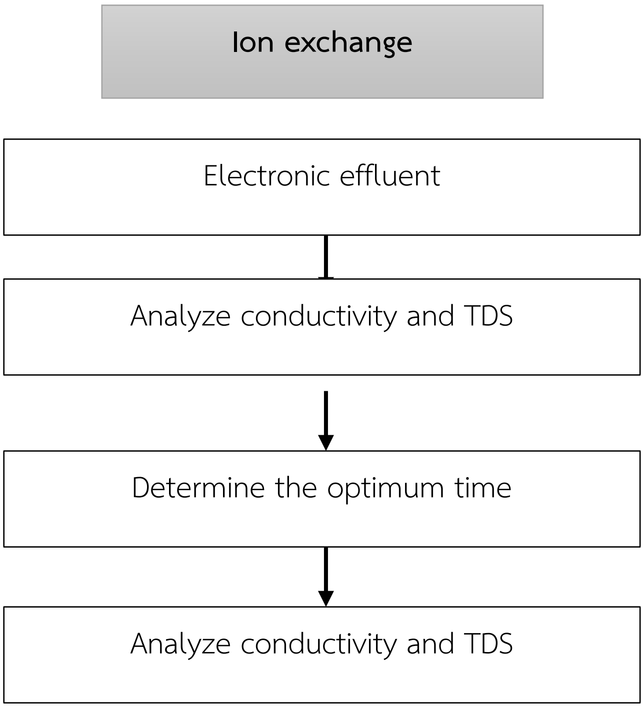

Figure 3.4 Ion exchange process

3.2.1 Adsorption process

3.2.1.1 The adsorption experiment is shown in Figure 3.5 and described below.

Figure 3.5 Electronic effluent shaken for adsorption using GAC

1) Fill 50 ml of electronic effluent in beakers
2) Adjust pH of each beaker to 5, 6 and 7
3) Add 1 g of GAC in each beaker
4) Shake all beakers in shaker with 100 rpm mixing
5) Sampling effluent after a mixing at 0.5, 1, 1.5, 6, 24 and 48 hours
6) Analyze conductivity of all samples

3.2.2 Coagulation-Flocculation process

3.2.2.1 The coagulation-flocculation experiment is shown in Figure 3.6 and described below.

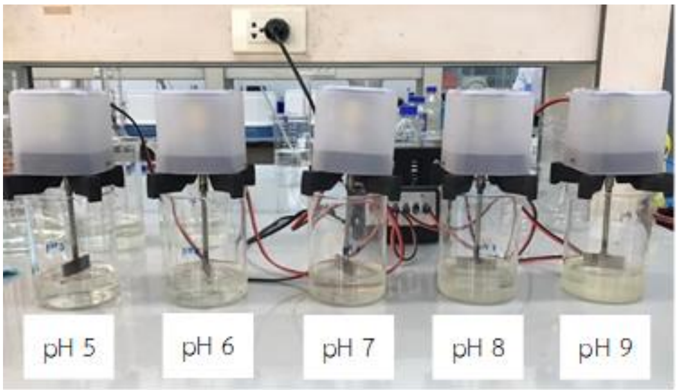

Figure 3.6 Electronic effluent treated by coagulation-flocculation using PACl

1) Fill 150 ml of electronic effluent in beakers
2) Adjust pH of each beaker to 5, 6, 7, 8 and 9
3) Add 1 ml of 1% PACl with 150 rpm mixing for 1 minute
4) Add 0.1 ml of 0.01% coagulant aid with slow mixing at 60 rpm for 15 minutes
5) Settle effluent for 20 minutes
6) Analyze conductivity of all samples

3.2.3 Photocatalytic process

3.2.3.1 The photocatalytic experiment is shown in Figure 3.7 and described below.

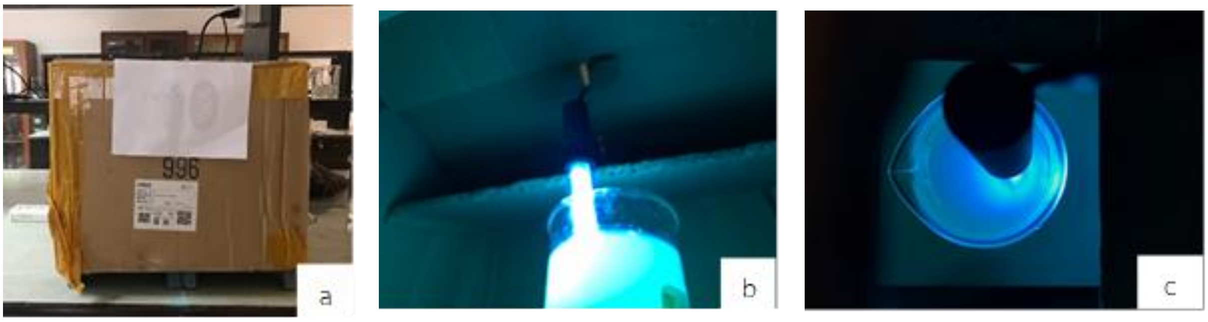

Figure 3.7 Electronic effluent treated by photocatalytic using TiO_2 in (a) front, (b) below and (c) top

1) Fill 100 ml of electronic effluent in beakers
2) Adjust pH of effluent to pH 5, 6, 7 and 8
3) Add 0.1 ml of 1% TiO_2 with rapid mixing at 200 rpm and turned on the UV light (closed system) for 60 minutes
4) Settle effluent for 5 minutes
5) Analyze conductivity of all samples

3.2.4 Ion exchange process

3.2.4.1 The ion exchange in batch experiment is shown in Figure 3.8 and described below.

Figure 3.8 Electronic effluent shaken for ion exchange using resin

1) Fill 50 ml of electronic effluent in beakers
2) Add 1 g of resins in each beaker
3) Shake all beakers in shaker with 100 rpm mixing
4) Sampling effluent after a mixing at 0.5, 1 and 2 hours
5) Analyze conductivity of all samples

3.2.4.2 The ion exchange in column experiment is shown in Figure 3.9 and described below.

Figure 3.9 Electronic effluent flow out from column for ion exchange using resin

1) Fill 10 g of resins in burette
2) Fill a burette with electronic effluent
3) Allow the effluent flow out at flow rate 1 ml/min
4) Sampling effluent every 30 minutes for 4 hours
5) Analyze conductivity of all samples

Chapter 4

Results and discussion

4.1 Relationship between Electrical conductivity (EC) and Total Dissolved Solids (TDS)

Electronic effluent was taken for EC measuring using 1 L of effluent with varying pH (5, 6 and 7) in order to make a difference in three samples. EC meter was used to measure EC of each beaker. 20 ml of effluent in each beaker was taken to evaporate and dry for TDS measuring. The result illustrates in Figure 4.1 (a) and (b).

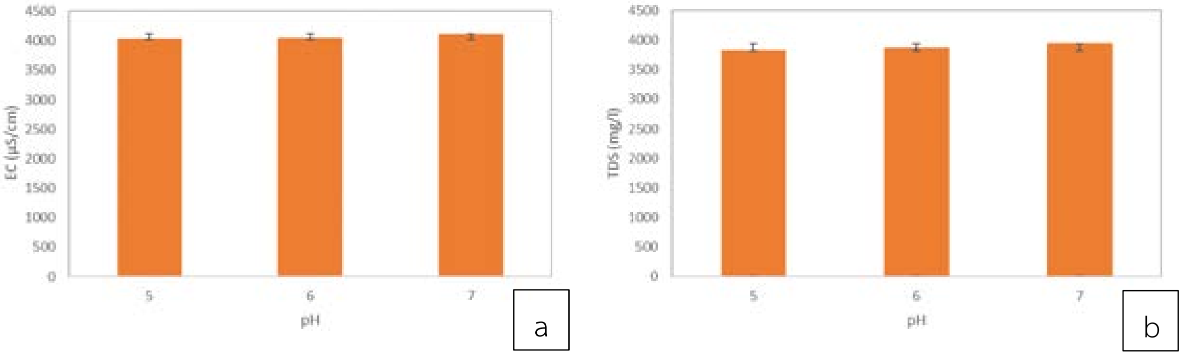

Figure 4.1 (a) Electrical conductivity (EC) values and (b) Total dissolved solids (TDS) values in electronic effluent

From Figure 4.1, measuring EC in each beaker was found that the values in sample pH 5, 6 and 7 are 4,030, 4,040 and 4,110 µS/cm, respectively. Moreover, the results from evaporating and drying in TDS measuring from the same samples found 3,820, 3,863 and 3,940 mg/l, respectively. The calculation based on relationship between EC and TDS revealed that the factor between EC and TDS in this electronic effluent was 0.96±0.007. Thus, 0.96 will be used as a converting factor throughout this experiment.

4.2 Efficiency of TDS removal by adsorption

The optimum condition for TDS removal in electronic effluent was determined by varying pH (5, 6 and 7) and contact time (0.5, 1, 1.5, 6, 24 and 48 hours) in each pH of adsorption with 100 rpm shaking. The result shows in Figures 4.2.

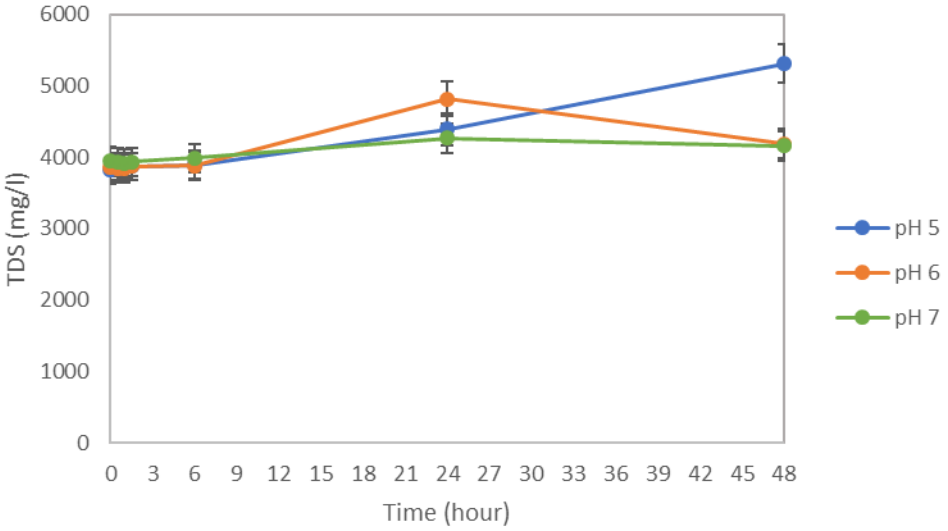

Figure 4.2 Effect of pH and time on TDS removal after treatment by adsorption process at pH 5, 6 and 7

From Figure 4.2, it was found that trend of TDS removal in each pH were not slightly difference in the period of 6 hours experiment. TDS was increased after 24 hours of treatment. After 48 hours of adsorption, the increase of TDS in pH 5, 6 and 7 were 38.97%, 8.34% and 5.50%, respectively. The results showed that pH and time significantly affected on the TDS removal. Principally, high adsorption efficiency occurs in long adsorption time. However, in this experiment, TDS was significant increased despite adsorption time increased. The reason behind might be a point of zero charge (pH_{pzc}) of adsorbent (Granular activated carbon, GAC). pH_{pzc} was used to describe adsorption mechanism. The pH_{pzc} of GAC used in this work is shown in Figure 4.3.

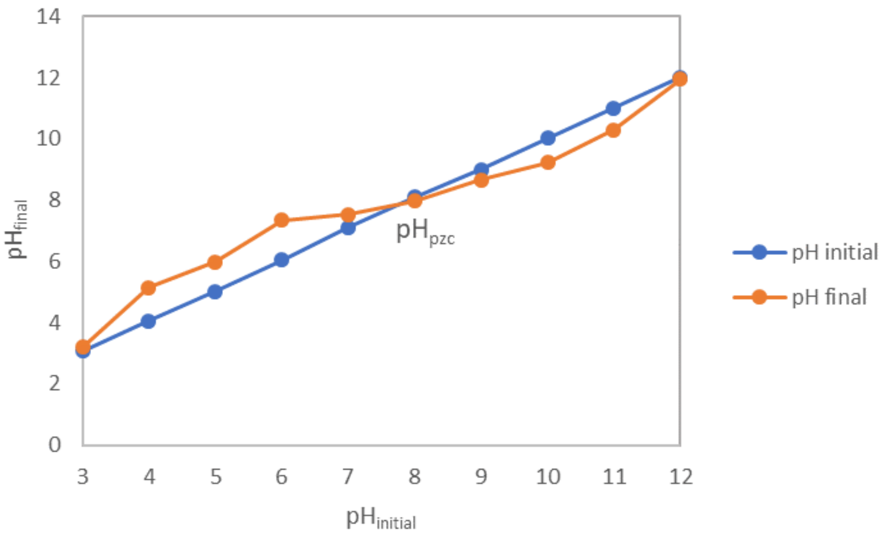

Figure 4.3 pH_{pzc} of GAC

The analysis of the pH_{pzc} experimental data was focused on the effect of pH on GAC surface described the condition when the electrical charge density on GAC surface is zero. The results show that pH_{pzc} of GAC used in this experiment is pH 8, the GAC surface is scarcely or not active when $pH < pH_{pzc}$. The same experimental result from Iovino *et al*. (2015) explained that effect of equilibrium pH plays a major role in determining the chemical equilibria in solution. As the pH decreases, the excess H^+ determines the coincidental occurrence of hydrogen bonds between carbon and ibuprofen (IBP) molecules and reduces π-π interaction because of the decrease in electron density of the basal planes of carbon. The affinity of carbon with water molecules is likely to increase effected the formation of surface complexes, which can partially compete with IBP adsorption. This effect of this mechanism explains the slightly increase in adsorption capacity when the pH is more than 8, makes this mechanism is more active.

In accordance with extra experiment to prove adsorption mechanism in this work, adsorption experiment in electronic effluent at pH 8 and 9 was done. The results show that TDS removal efficiency were slightly increased 1.88% and 0.83% from the initial.

Another possible reason is that at low pH may cause the falling out of some functional group from GAC resulting in increase of TDS after treatment. Thus, efficiency of TDS removal in this process is not as effective as it should be.

4.3 Efficiency of TDS removal by coagulation-flocculation

Electronic effluent was treated by coagulation-flocculation with constant dose of 1 ml coagulant (polyaluminium chloride, PACl), followed by constant dose of 0.1 ml coagulant aid (anionic polyacrylamide) in 150 ml effluent at each pH. The optimum condition for TDS removal was determined by varying pH (5, 6, 7, 8 and 9). The results show in Figures 4.4.

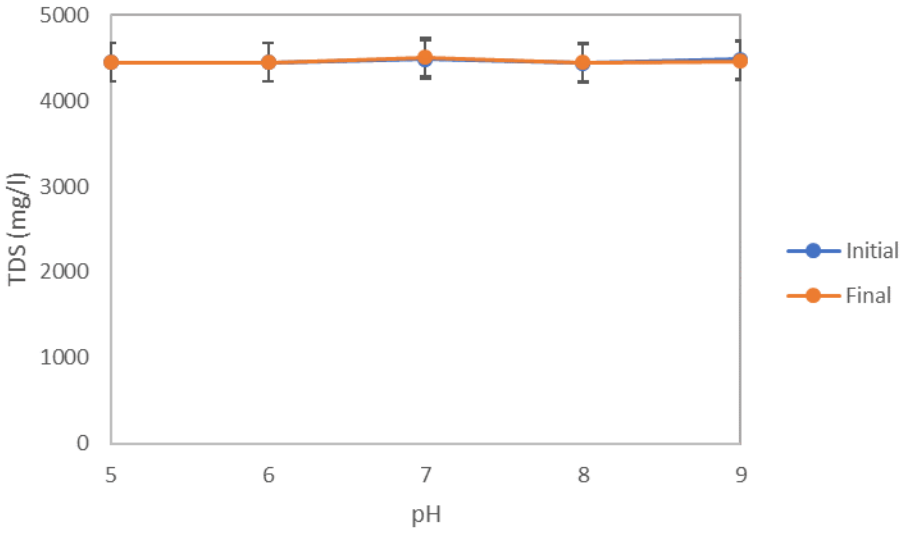

Figure 4.4 Effect of pH on TDS removal after treatment by coagulation-flocculation at pH 5, 6, 7, 8 and 9

At all pH range in this experiment, it was found that the TDS before and after treatment was unchanged. The highest efficiency of TDS removal was found in pH 9 that decreased only 0.43% after treatment. The results are not similarly to the study of Vasanthy *et al*. (2008) that treated TDS from dyeing industry effluent via coagulation process with shows high efficiency in TDS removal about 90%. The satisfactory of TDS removal from Vasanthy *et al*. (2008) may be explained according to the colloidal theory.

In general, colloidal particles have sizes from 1 nanometer to 1 micrometer, while, in TDS measurement usually used filter paper with 1.2 micrometer of pore size. Hence, some of colloidal particles can pass through the filter paper resulting in colloidal particles being in component of TDS analysis. In accordance with coagulation-flocculation theory, colloidal particles in form of TDS can be coagulated by PACl. PACl causes aluminium complex that can be adsorbed on colloidal particles to overcome the repulsive charges for neutralization.

Hence, attraction of PACl (positively charged) and colloidal particles (negatively charged) by the Van der Waals forces causes colloidal particles to cling together and settling down.

This means there are two possible causes of very low TDS treatment efficiency in this work. The first is the effluent presented none or little of colloidal particles in form of TDS. The second is the colloidal particles have the same charges as PACl.

4.4 Efficiency of TDS removal by photocatalytic

Electronic effluent was treated by photocatalytic using 1 ml/L of TiO_2 with varying pH (5, 6, 7 and 8) and 1 hour of contact time. Each pH was stirred in closed system. The result shows in Figures 4.5.

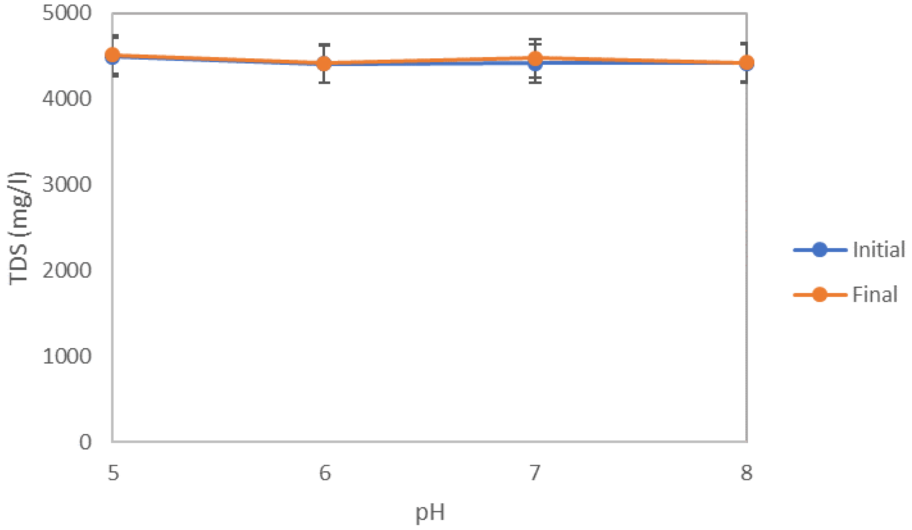

Figure 4.5 Effect of pH on TDS removal after treatment by photocatalytic at pH 5, 6, 7 and 8

From Figure 4.5, it was found that trend of TDS removal efficiency is slightly different although pH was changed. Unexpectedly, TDS values were slightly increased at every pH of treatment up to 0.22-1.30% compared to the initial. This result is very different from the study of Pokharna and Shrivastava (2013) that treated TDS in textile industry effluent via photocatalytic treatment and the efficiency was up to 98.55%.

The slightly increase of TDS after photocatalytic process might due to the fact that photocatalytic process cannot be oxidized inorganic matter and wastewater sample used in this work composed mainly of inorganic matter. In contrast with the sample in the study of

Pokharna and Shrivastava that showed large amount of organic matter and can be easily oxidized.

In order to prove the above presumption, additional experiment was taken by analyzing chemical oxygen demand (COD) in the sample. COD is the amount of oxygen required to oxidize organic matter into carbon dioxide, ammonia and water under acidic conditions. COD can be used to quantify the amount of organic in water, therefore, COD analysis in this experiment can be used as a representative of total organic matter in this sample. Experimental result showed that COD in this sample was 34.04 mg/l, which verified that the sample had small amount of organic matter.

Furthermore, the increase of TDS values may be caused by the reaction between TiO_2 and H_2O molecules, produced more ions in the effluent resulting in very low efficiency in TDS removal.

4.5 Efficiency of TDS removal by ion exchange

The study of ion exchange to reduce TDS was done by two systems i.e., batch and column. The results were described as follows:

4.5.1 Ion exchange using resins in batch

Electronic effluent was treated by ion exchange using 1 g of mixed resin in 50 ml of water with 100 rpm shaking and varying contact time (0.5, 1 and 2 hour(s)). The result shows in Figures 4.6.

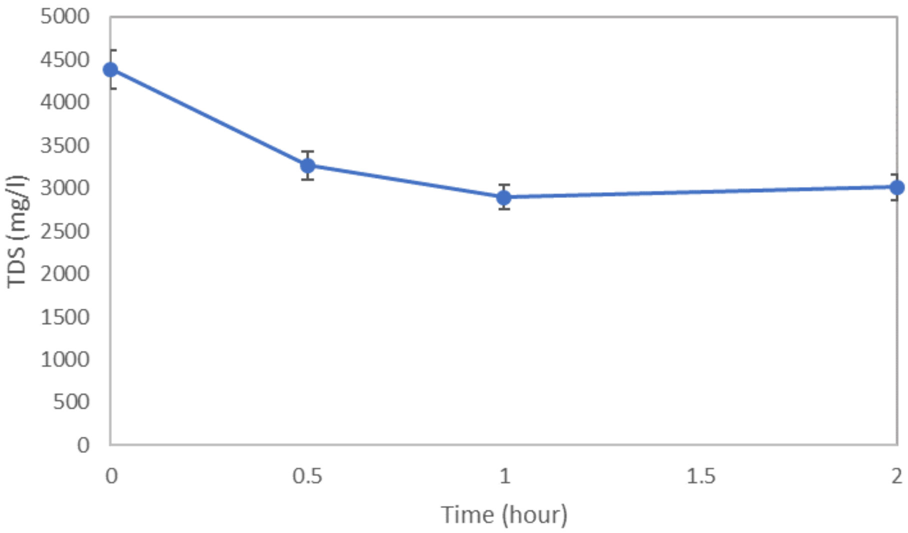

Figure 4.6 Effect of time on TDS removal after treatment by ion exchange (batch) using resin

After adding mixed resin, it was found that trend of TDS reduced rapidly in the first half hour and then slightly increased after 1 hour. The maximum TDS removal efficiency at 0.5 hours. was 25.53%. Mixed resin can immediately remove TDS because there are a lot of capacity within resin according to its cross linkage. H^+ and OH^- are less atomic weight than other ions in the effluent. These ions in this effluent, in form of TDS has a greater ability to replace ions within resin, resulting in the decrease of TDS values. However, the experimental results are not high effective as expectation. The reason may be caused by the amount of resin used in this experiment is not enough for 50 ml effluent.

4.5.2 Ion exchange using resins in column

Electronic effluent was treated by 10 g of mixed resin in column with down flow effluent at flow rate 1 ml/min and collecting the effluent every 30 minutes for 4 hours. The results show in Figures 4.7.

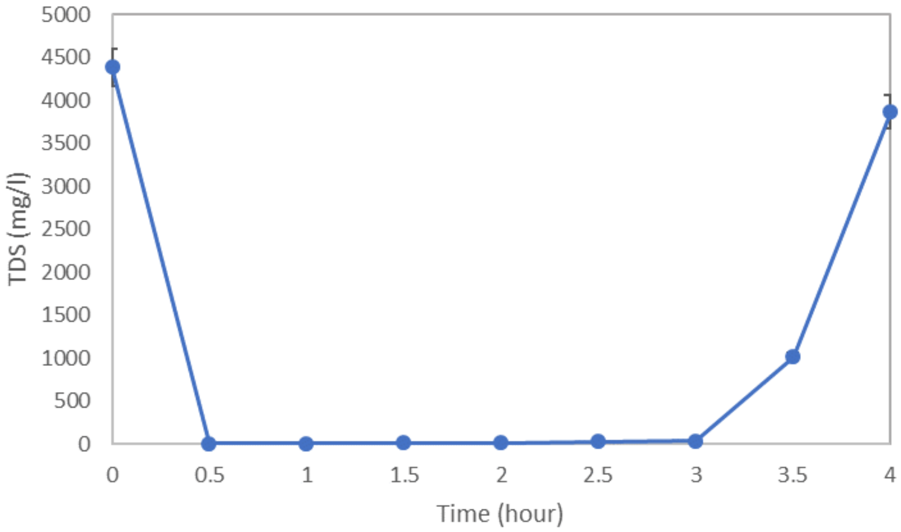

Figure 4.7 Effect of time on TDS removal after treatment by ion exchange (column) using resin

After the water passed the column, it was found that resin has an efficiency in TDS removal immediately in the first half hour and remaining until 3 hours of treatment. At first 3 hours, the highest efficiency of TDS removal was found at 99.98%. However, after 3.5 hours of column study, TDS values began increase greater than the third hour of treatment.

The cause of the increase in TDS values since the third hour of treatment may be affected by the performance of resin after treatment for a period. Losing of performance in resin means there are none of its space called cross linkage to be replaced by ions in the effluent. Resin lose its effectiveness and need to be regenerated before it was used again.

Furthermore, another reason of the increase in TDS after 3.5 hours of column study should be the effect of pH as shown in Figure 4.8

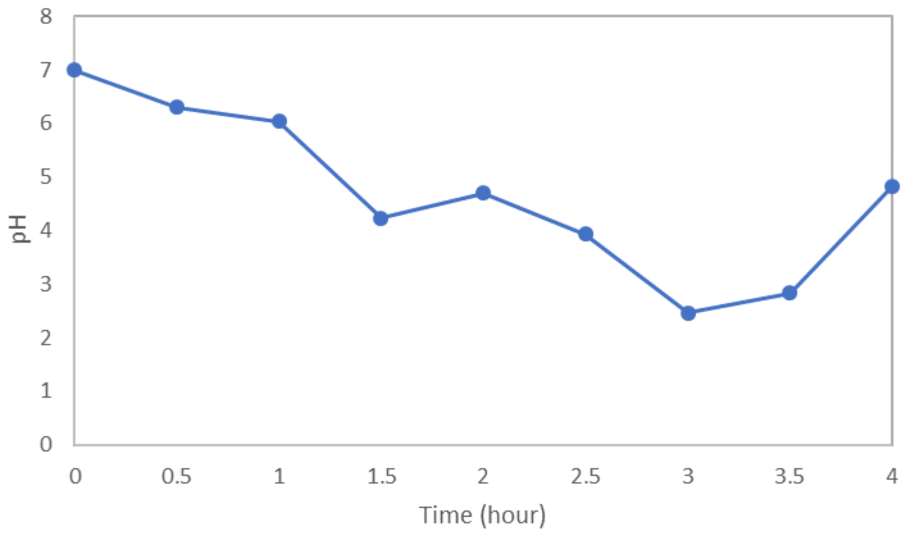

Figure 4.8 Effect of time on pH after treatment by ion exchange (column) using resin

Figure 4.8 shows pH of the elution was slightly decreased until the fourth hour of treatment. Basic principle of pH measurement is the comparison of the voltage potential of hydrogen ions in solution between glass electrode and reference electrode, which is a standard cell that already knows the voltage potential. The overall concentration of hydrogen ions is inversely related to its pH. Therefore, the decreased pH showed in Figure 4.8 means an increase in the number of hydrogen ions in the effluent.

Hydrogen ions are good in conduct electricity, which can be measured with EC meter. Increase of hydrogen ions resulted in high EC, related TDS values due to the relationship between EC and TDS mentioned above. As the result, slightly decreased pH in Figure 4.8 causes the slightly increase of TDS in Figure 4.7

Chapter 5

Conclusions and recommendation

5.1 Conclusions

This study focused on determination of probability for TDS reduction by adsorption, coagulation-flocculation, photocatalytic, and ion exchange processes. The conclusions can be summarized as follows:

1) The efficiency of TDS removal by adsorption, coagulation-flocculation, and photocatalytic processes were less than 1%.
2) The efficiency of TDS removal by ion exchange in batch system at 1 g of mixed resin in 50 ml of electronic effluent with 0.5 hours of contact time was 25.53%.
3) The efficiency of TDS removal by ion exchange in column system at 10 g with flow rate of 1 ml/min was more than 99.00% from the beginning to 3 hours.
4) Ion exchange in column system was suggested to apply in TDS reduction before treated with RO system.

5.2 Recommendation

1) In further study, the characteristics of electronic effluent should be analyzed before experiment. The compositions within the effluent will indicate the probability of TDS reduction processes.
2) The physical and chemical characteristics of granular activated carbon (GAC) should be analyzed in order to know the process and mechanism of adsorption.
3) The pH value obtained from ion exchange (column) experiment can be used to determine the ability of mixed resin to be regenerated.

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Table 1 Statistic test of samples after treatment by adsorption process at pH 5

Tests of Between-Subjects Effects

Dependent Variable: TDS

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	5089331.802[a]	5	1017866.360	3.745	.032
Intercept	1729890.462	1	1729890.462	6.365	.028
Hour	5089331.802	5	1017866.360	3.745	.032
Error	2989608.960	11	271782.633		
Total	9724815.360	17			
Corrected Total	8078940.762	16			

a. R Squared = .630 (Adjusted R Squared = .462)

Table 2 Statistic test of samples after treatment by adsorption process at pH 6

Tests of Between-Subjects Effects

Dependent Variable: TDS

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	1612440.960[a]	5	322488.192	30.209	.000
Intercept	553069.714	1	553069.714	51.809	.000
Hour	1612440.960	5	322488.192	30.209	.000
Error	106752.000	10	10675.200		
Total	2016000.000	16			
Corrected Total	1719192.960	15			

a. R Squared = .938 (Adjusted R Squared = .907)

Table 3 Statistic test of samples after treatment by adsorption process at pH 7

Tests of Between-Subjects Effects

Dependent Variable: TDS

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	264332.951[a]	5	52866.590	16.124	.000
Intercept	116494.966	1	116494.966	35.531	.000
Hour	264332.951	5	52866.590	16.124	.000
Error	36065.280	11	3278.662		
Total	383754.240	17			
Corrected Total	300398.231	16			

a. R Squared = .880 (Adjusted R Squared = .825)

Table 4 Statistic test of samples between pH 5, 6, 7, 8 and 9 at 1 hour of treatment by adsorption process

Tests of Between-Subjects Effects

Dependent Variable: TDS

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	12189.696[a]	4	3047.424	16.000	.000
Intercept	22861.824	1	22861.824	120.032	.000
Hour	12189.696	4	3047.424	16.000	.000
Error	1904.640	10	190.464		
Total	36956.160	15			
Corrected Total	14094.336	14			

a. R Squared = .865 (Adjusted R Squared = .811)

Table 5 Statistic test of samples after treatment by coagulation-flocculation process at pH 5, 6, 7, 8 and 9

Tests of Between-Subjects Effects

Dependent Variable: TDS

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	3170.304[a]	4	792.576	9.214	.002
Intercept	24.576	1	24.576	.286	.605
Hour	3170.304	4	792.576	9.214	.002
Error	860.160	10	86.016		
Total	4055.040	15			
Corrected Total	4030.464	14			

a. R Squared = .787 (Adjusted R Squared = .701)

Table 6 Statistic test of samples after treatment by photocatalytic process at pH 5, 6, 7 and 8

Tests of Between-Subjects Effects

Dependent Variable: TDS

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	3502.080[a]	3	1167.360	21.714	.000
Intercept	7864.320	1	7864.320	146.286	.000
Hour	3502.080	3	1167.360	21.714	.000
Error	430.080	8	53.760		
Total	11796.480	12			
Corrected Total	3932.160	11			

a. R Squared = .891 (Adjusted R Squared = .850)

Table 7 Statistic test of samples in the relationship between electrical conductivity (EC) and total dissolved solids (TDS) test

Tests of Between-Subjects Effects

Dependent Variable: Relationship

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	.000[a]	2	.000	2.784	.154
Intercept	7.003	1	7.003	190988.636	.000
pH	.000	2	.000	2.784	.154
Error	.000	5	3.667E-5		
Total	7.277	8			
Corrected Total	.000	7			

a. R Squared = .527 (Adjusted R Squared = .338)

BIOGRAPHICAL DATA

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