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**Project Title** **Column adsorption of chemical oxygen demand (COD) in sugar wastewater using filter cake**

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# Column adsorption of chemical oxygen demand (COD) in sugar wastewater using filter cake

# การใช้คอลัมน์ดูดซับซีโอดีในน้ำเสียโรงงานน้ำตาลด้วยกากหม้อกรอง

Thanikjara Sangphirom

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## บทคัดย่อ

งานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาการนำกากหม้อกรองซึ่งเป็นของเสียจากการผลิตน้ำตาล มาใช้เป็นวัสดุดูดซับในกระบวนการดูดซับ เพื่อลดค่าสารอินทรีย์ในน้ำเสียจากกระบวนการผลิตน้ำตาลของโรงงานน้ำตาลเดียวกัน ศึกษาถึงสมดุลการดูดซับสารอินทรีย์ในรูปซีโอดีด้วยกากหม้อกรองที่มีการปรับปรุงคุณสมบัติเพื่อให้เหมาะสมต่อการเป็นวัสดุดูดซับ โดยการคัดแยกขนาดในช่วง 0.5-2 มิลลิเมตร และเผาที่อุณหภูมิ 550 องศาเซลเซียส เป็นเวลา 3 ชั่วโมง ในส่วนแรกทำการศึกษาสมดุลการดูดซับแบบกะที่อุณหภูมิห้อง โดยใช้วัสดุดูดซับ 1 กรัมต่อน้ำเสีย 50 มิลลิลิตร เขย่าที่ความเร็ว 150 รอบต่อนาที เป็นเวลา 120 นาที ผลการทดลองพบว่า สามารถลดค่าซีโอดีในน้ำเสียได้ 82.5 มิลลิกรัมต่อวัสดุดูดซับ 1 กรัม คิดเป็นประสิทธิภาพร้อยละ 25 ในส่วนที่สองเป็นการศึกษาการดูดซับในคอลัมน์ขนาดเส้นผ่านศูนย์กลาง 2.54 เซนติเมตร ความสูงของวัสดุดูดซับ 20 เซนติเมตร คิดเป็นน้ำหนักของวัสดุดูดซับ 14.75 กรัม อัตราการไหลของน้ำเสีย 0.5 1 และ 2 มิลลิลิตรต่อนาที ผลการศึกษาพบว่า เวลาเบรคทรูจะลดลงตามอัตราการไหลที่เพิ่มขึ้น อธิบายกลไกการดูดซับตามแบบจำลองของโทมัสพบว่า อัตราการไหลที่เหมาะสมคือ 1 มิลลิลิตรต่อนาที สามารถลดค่าซีโอดีในน้ำเสียได้ 35.2 มิลลิกรัมต่อวัสดุดูดซับ 1 กรัม ค่าคงที่ของโทมัส เท่ากับ $1.53 \times 10^{-6}$ ลิตรต่อมิลลิกรัม-นาที (R-square เท่ากับ 0.9008 และ sum of squares error เท่ากับ 0.0237) ในส่วนแบบจำลองของยูน-เนลสันพบว่า อัตราการไหลที่เหมาะสมคือ 1 มิลลิลิตรต่อนาที ค่าคงที่ของยูน-เนลสัน เท่ากับ 0.01 ต่อนาที ค่าสัมประสิทธิ์แสดงการตัดสินใจ (R-square) เท่ากับ 0.9268 และผลรวมของความเบี่ยงเบนออกจากจุดอ้างอิงยกกำลังสอง (sum of squares error)เท่ากับ 0.0172 จากค่าสัมประสิทธิ์แสดงการตัดสินใจของแบบจำลองทั้งสองพบว่าแบบจำลองยูน-เนลสันมีความเหมาะสมมากกว่าแบบจำลองของโทมัส ซึ่งอธิบายได้ว่าอัตราการลดลงของการดูดซับเป็นสัดส่วนกับปริมาณตัวดูดซับ และเบรคทรูของตัวดูดซับ

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## Abstract

The objective of this research was to determine the filter cake which is a waste from sugar production use as an adsorbent material via adsorption process to reduce the organic matter in wastewater from the sugar process in the same sugar factory. The adsorption equilibrium of organic matter in form of COD by modified filter cake was studied. Adsorbent from filter cake was prepared by sieving size between 0.5-2 mm and then carbonized at 550°C for 3 hours. Firstly, batch adsorption was conducted under room temperature using 1 g of adsorbent with 50 ml wastewater and shook at mixing speed of 150 rpm. The result found that it can reduce COD for 82.5 mg per 1 g of adsorbent or 25 percent efficiency. Secondly, COD adsorption in 2.54 cm diameter packed bed column with 20 cm high of adsorbent (or 14.75 g weight of adsorbent) at wastewater flow rates of 0.5, 1, and 2 mL/min was tested. The result showed that higher flow rates resulted in lower breakthrough times. According to the principle of Thomas model, it was found that the optimum flow rate is 1 mL/min, which reduced COD in wastewater for 35.2 mg per 1 g of adsorbent. This flow rate presented lowest Thomas's constant ($K_{th}$), highest coefficient of determination (R-square) and bottommost the sum of square error (SSE) which were 1.53 x $10^{-6}$ L/mg.min, 0.9008 and 0.0237, respectively. With respect to Yoon and Nelson model, it was found that the fitted flow rate was 1 mL/min with highest Yoon and Nelson's constant, maximum R-square and lowest SSE were 0.01 $min^{1}$, 0.9268 and 0.0172, respectively. Based on the R-square of both models, Yoon and Nelson model was more appropriate than Thomas model to explain the reduction rate of this adsorption is proportion of the number of adsorbents and breakthrough of the adsorbent.

**Keyword**: adsorbent, organic matter removal, Thomas model, Yoon-Nelson model

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# Chapter I

# INTRODUCTION

## 1.1 Background and rationale

Thailand is the world's second largest sugar exporter (15.06%) after Brazil. There are 55 sugar factories in Thailand located in the North (10 factories), East (20 factories), South (5 factories), and Northeast (20 factories) (Office the Cane and Sugar Board [OCSB], 2017). The working period of sugar factory is divided into 3 seasons i.e., 1) conversion of sugarcane into sugar in November to April, 2) production of white sugar from raw sugar in May to August and 3) maintenance to repair machine for preparing production. The main process in the production of sugar is milling, defecation, evaporation, sugar boiling and crystallization. Bagasse, molasses and filter cake are three by-products of the sugar industry. Bagasse accounts for 29% of sugarcane and its characteristics are moisture content 48-53%, density 160 kg/$m^3$, low heating value 7.53 MJ/kg and flammable (Office the Cane and Sugar Board [OCSB], 2018). This means it prefers to use as fuel to generate electricity. Molasses are generated in the final step by separating the sugar by centrifuge. Normally, molasses can be used as raw materials to produce alcohol, monosodium glutamate. Filter cake is waste of the sugarcane juice that is passed through the milling before delivering sugarcane to the boiler. The sugarcane juice must be filtered to removed dirt. The filtered residue is quite elaborate, called filter cake. Recently, filter cake is used as a soil conditioner which is a low cost material. Fortunately, filter cake comprises of a lot of carbon and porous structure. These characterizations show an interesting sign to produce an adsorbent material which can be used in the adsorption process to treat organic matter in wastewater.

Wastewater from sugar industry contains mainly of organic matter which cannot directly be measured by chemical oxygen demand (COD). COD is a measurement of oxygen required to oxidize soluble and particulate organic matter in water. A COD test can be used to easily quantify the amounts of organics in water. COD exceeds the standard means a greater

amount of oxidizable organic material in the water, which caused of dissolved oxygen (DO) reduction in watershed. A depletion in oxygen can lead to anaerobic condition, which is detrimental to higher aquatic life forms, brownish color, odor, and visual pollution. Therefore, COD removal is required. Several methods to reduce COD in water include coagulation and flocculation, microbiology process, oxidation and reduction, Fenton reaction, advanced oxidation process, filtration, and adsorption.

The principle of treating wastewater from factory by waste from its plant should be a good approach to reach sustainable development. This means filter cake, by-product from sugar industry, can be applied in adsorption process to treat COD in wastewater from sugar factory.

## 1.2 Objective

To determine COD removal efficiency of filter cake from sugar factory via adsorption process.

## 1.3 Benefits

1) An alternative approach to treat industrial wastewater by using waste from its own industry.
2) Cost reduction for waste treatment and value added to industrial waste

# Chapter II

# THEORY AND LITERATURE REVIEW

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## 2.1 Theory

### 2.1.1 Sugar factories

The various steps involve for the production of sugar as shown in Figure 2.1:

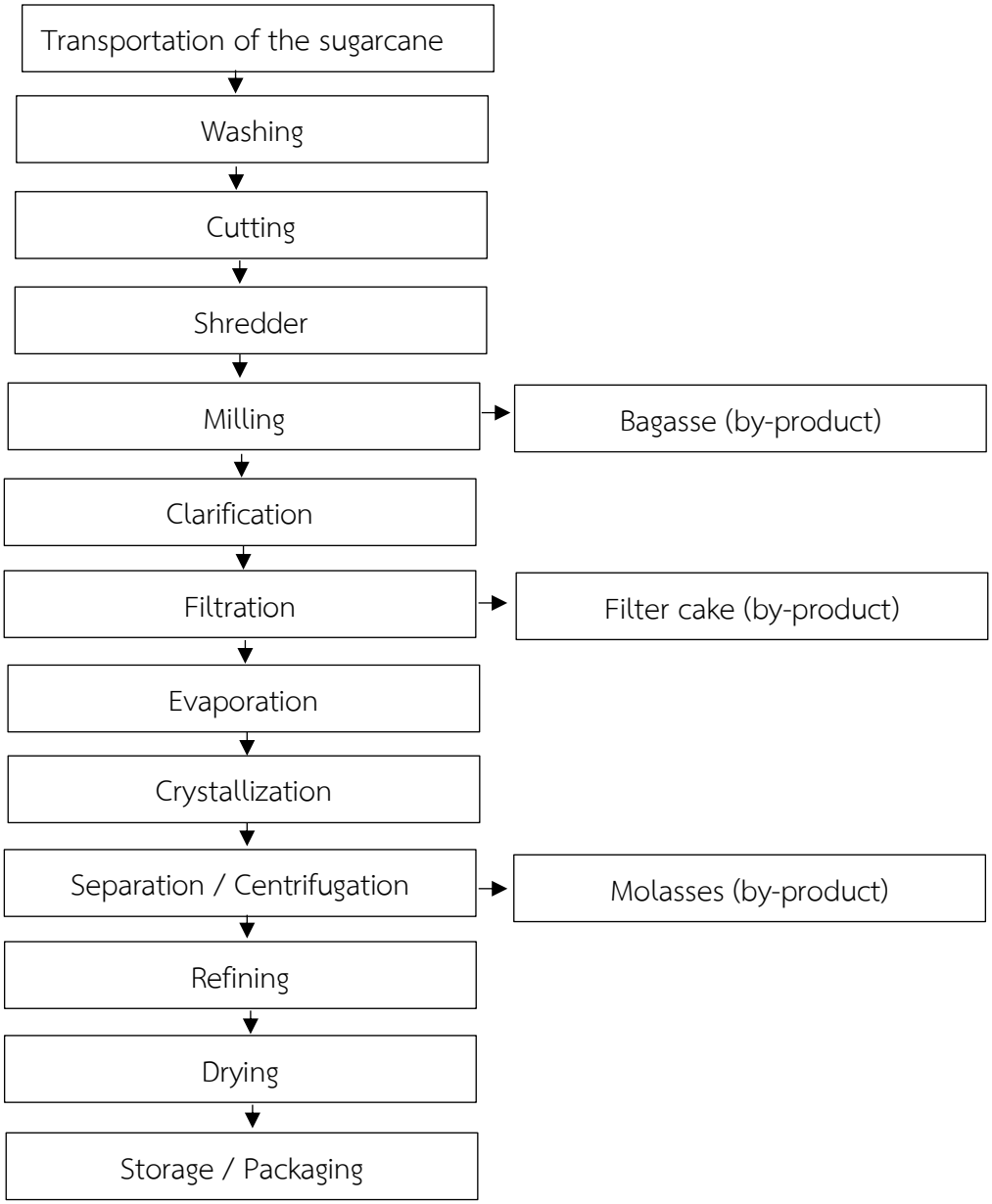


Figure 2.1 Sugar production process

Detail of sugar production is:

1. Sugarcane is transported to the sugar industries.
2. Sugarcane is washed before processing.
3. Cane is cut into desired size.
4. Shredder is used to remove leaves and undesired solid particles from cane.
5. Milling is process of crushing the sticks of sugar cane to extract the juice. The shredded cane is fed through a series of crushing mills to extract the sugar rich juice consists of, top roller, feed roller, and discharge roller. These use to extract the juice from crushing sticks. The poor juices of subsequent millings are re-process and hot water is applied in the last milling to increase extraction. Bagasse is produced as a by-product.
6. Clarification process sludge, mud, suspended and colloidal particles are removes by some chemical compounds. These are calcium phosphate (flocculent), Lime and $SO_2$ (bleaching agent), and $CO_2$ (acidifying agent). When these chemicals are mixed, suspended and colloidal particles are collected resulting settled down. Sludge and mud are collected in bottom and drainage to rotary filter.
7. Clarified mud from the clarifier further filtered in rotary filter. Mud and sludge are stick on the periphery of rotating drum by the action of suction. Filter cake is removed from the drum by doctor blade.
8. Evaporation are used in process industry to concentrate liquids. The operation is performed usually by use of low pressure, dry, and saturated steam. The evaporator feed inters at upper section and concentrated thick liquor exit at bottom section.
9. Crystallization is a purification process. The object of process is usually the recovery of the solute (crystal) form the solvent. The process consists of clustering, nucleation, and growth.
10. Separation is separate sugar from molasses by using centrifuge operation at 100-1800 rpm. Molasses pass through perforations and sugar crystals are washed with 85 degrees Celsius water (Negasi ,2016). Raw sugar and molasses are produced.

11. Refining is a processes raw sugar into white refined sugar. Refining process consists of 4 steps, these are affination, carbonatation, char filtration, and recovery. Affination is dissolving off some surface impurities. Carbonatation is removing further impurities that precipitate from solution with calcium carbonate. Char filtration is removing further impurities with activated carbon. Recovery, the liquor left over from the preparation of white sugar and the washings from at affination stage both contain sugar.

12. Drying is very essential mass transfer operation in processing sugar cane into sugar. The wet raw sugar from centrifuges goes to rotary drier to remove the water from the wet sugar to reduce moisture content to 0.5-2% and using hot air at 110 degrees Celsius which flow counter currently with sugar (Negasi, 2016).

13. Storage is final process. Factors affecting sugar storage are temperature, moisture, light, grain size and compression.

### 2.1.2 Wastewater from sugar factories

The water utilized in the sugar industry can be classified in to two categories. First, the external water which does not contact with the sugar manufacturing process directly. The external water is cooling water used for condensing and cooling power turbines, mill turbines, mill bearings, crystallizes sulfur burners, air compressors, vaccum pumps, hot liquor pump and water used for floor washing, vessel washing and domestic use. Second, the internal water is water comes along with sugarcane. Clean cane contains about 70% water (Sharma, 2015). The water from cane itself in form of condensate is more than sufficient for the internal process of sugar manufacturing such as condensate water used for imbibition, boiler, filter, cake washing, milk of lime preparation movement water at pans, molasses, dilutions, centrifugals, melting etc. The major units that consume water in the sugar factory are boiler feed water, cooling water for condenser, process water for maceration, lime preparation, dilution for control of brix, dilution in evaporators and massecuite dilution, filter mud, fly ash handling, and cane wastewater. There are many sources of wastewater generating in a sugar industry. The quantity of effluent as shown in Tables 2.1, 2.2 and 2.3:

Table 2.1 Quantity of water use from sugar factory based on factory size (Ashna, 2017)

| Crushing Capacity (tonne/day) | Effluent (Cubic metre/day) |
|---|---|
| < 1,500 | 300 - 500 |
| 1,500 - 3,000 | 800 - 1,200 |
| > 3,000 | 2,000 - 2,500 |

Table 2.2 Quantity of water use in each process of sugar factory (Ashna, 2017)

| Process | Effluent (Cubic metre/day) |
|---|---|
| Mill house | 50 - 80 |
| Boiling house | 150 - 200 |
| Boiler house (blow down) | 40 - 50 |
| Pump cooling water | 80 - 100 |
| Sulphur furnaces | 14 - 20 |
| Lime hydrator | 14 - 16 |
| Excess condensate | 20 - 30 |
| Final effluent | 400 - 500 |
| Spray pond over flow | 400 - 500 |

Table 2.3 The characteristics of wastewater from typical sugar factory.

| Parameter | Guven *et al*. (2009) | Hampannavar *et al*.(2011) | Shivayogimath *et al*. (2013) | Sahu et al. (2015) | Range |
|---|---|---|---|---|---|
| COD (mg/L) | 6,300 | 1,000-4,340 | 6,400 | 3682 | 1,000-6,400 |
| BOD (mg/L) | - | 350-2,750 | 2,250 | - | 350-2,750 |
| pH | - | 5.2-6.5 | 5.1 | 5.5 | 5.2-6.5 |
| Colour | - | Reddish yellow | Greenish yellow | Dark yellow | - |
| TSS (mg/L) | - | 760-800 | 380 | 540 | 380-800 |
| VSS (mg/L) | - | 173-2,190 | - | - | 173-2,190 |
| TKN (mg/L) | 53.23 | 15-40 | - | - | 15-53.23 |
| Phosphorous (mg/L) | 4.77 | 1.3-2.5 | - | 5.9 | 1.3-5.9 |
| TDS (mg/L) | - | - | 1,008 | 1,447 | 1008-1,447 |

From Table 2.3, the wastewater from sugar industry normally contains high COD, BOD, suspended solids, low nutrient and most acidic pH. The sugar industry operates on a seasonal basis, wastewater production is also obviously seasonal. When the untreated wastewater discharge into the environment, they destroy the ecological area of living organism.

### 2.1.3 Filter cake

Filter cake is a major residue of the sugarcane industry, that is obtained when the cane juice is clarified using calcium hydroxide, contains material originally suspended in the juice along with inorganic salts that precipitate during the classification process, and is removed from the juice using rotation vacuum filters. Its' characteristic is spongy, amorphous, dark or even black (as shown in Figure 2.2). The components and chemical composition of filter cake are 8.9% of cellulose, 2.4% of hemicellulose, 1.2% of lignin, 9.5% of fat and wax, 32.5% of

carbon, 2.2% of hydrogen, 2.2% of nitrogen, 2.4% of phosphorus, and 14.5% of ash. The filter cake contains 0.5-1.8% of sugar and about 70% of water (George *et al*., 2010). For every 100 tons of crushed sugarcane, approximately 3-3.3 tons of filter cake remain as a by-product (Sualam, 2017). Filter cake causes significant pollution and is considered to be a waste that poses management, handling, transportation, because of its high water content, its attraction on insects and other pests, and final disposal problems in sugar factory. It also ignites spontaneously when exposed to sunlight. Filter cake has also been applied as a structural soil amendment to counteract soil amendment to counteract soil degradation that leads to soil erosion and compaction. In agriculture, filter cake is used as a fertilizer, and is applied directly or indirectly on the sugarcane fields. A widespread use of filter cake is production of compost, a soil improver that reduces the amount or chemical fertilizer needed.

Figure 2.2 Filter cake (Jala and Chakhatrakan, 2016)

### 2.1.4 Adsorption

#### 1) Adsorption principle

Adsorption is a wastewater purification technique for removing low concentrations of organic or inorganic compound. Adsorption is defined as the adhesion of chemical species onto the surface of particles. When a solution containing absorbable solute comes into contact with a solid with a highly porous surface structure, liquid-solid intermolecular forces of attraction cause some of the solute molecules from the solution to be concentrated or deposited at the solid surface. Adsorption depends on surface energy. Surface atoms of the adsorbent are partially expose so they can attract the adsorbate molecules. Adsorption may

result from electrostatic attraction, chemisorption, and physisorption. Adsorption is operative in most natural physical, biological, and chemical system.

**2) Adsorption mechanism**

The adsorption mechanism can be divided into 3 steps. These are external diffusion, internal diffusion and surface reaction. The external diffusion is a mechanism by which the molecules of the adsorbent reach the adsorbent. The surface area of the adsorbent has a liquid encapsulated by molecules inserted through the layer of the liquid. Internal diffusion is mechanism which the molecules of the adsorbent are spread into the cavity. Surface reaction is a mechanism which the molecules are absorbed on the surface of the adsorbent. The adsorption rate is very important. The rapid adsorption rate will allow the system to enter the equilibrium quickly. The adsorption rate is controlled by the most resistance step. In moving molecules, the slowest step is the determination of the adsorption rate. The steps to adsorb are divided into 3 sub-steps. Firstly, bulk transport which is the fastest step. The molecules that are adsorbed in the liquid are sent to the surface of a thin layer of liquid or the water that adsorbs the adsorbent. Secondly, film transport which is a process where the molecules on the surface of the thin liquid layer penetrate to the surface of the adsorbent material. Transporting the film layer is a process in which the adsorbents are spread through the water film to the surface of the adsorbent. Finally, the interparticle transport is the diffusion of the solute molecules into the porosity of the adsorbent called pore diffusion.

**3) Adsorbent**

Adsorbent is a material that uses to remove the trace contaminants from liquid and gas stream. Adsorbents have small pore diameters so that there is a high surface area to facilitate adsorption. The pore size usually ranges between 0.25 and 5 mm (Anne, 2018). Industrial adsorbents have high thermal stability and resistance to abrasion. Depending on the application, the surface may be hydrophobic or hydrophilic. Both polar and nonpolar adsorbents exist. The adsorbents appear in many shapes including rods, pellet, and molded shapes. Carbon-based compounds (e.g., graphite, activated charcoal), oxygen- based

compounds (e.g., zeolites, silica), and polymer- based compounds are major classes of industrial adsorbents. Examples of adsorbents include silica gel, alumina, activated carbon or charcoal, zeolites, and biomaterials.

A large specific surface area is preferable for providing large adsorption capacity, but the creation of a large internal surface area in a limited volume inevitably gives rise to large numbers of small sized pores between adsorption surface. The size of the micropores determines the accessibility of adsorbate molecules to the internal adsorption surface, so the pore size distribution of micropores is another important property for characterizing absorptivity of adsorbents.

Activated carbon materials can be prepared by 2 main methods viz., physical activation and chemical activation. Physical activation is thermal process by carbonization at temperature below 700 $^{o}$C in anaerobic condition and then using oxidizing gases, $CO_2$ or steam as second step with temperature over than 800 $^{o}$C. This process uses to create a porous structure that increases the adsorption capacity. Chemical activation involves 2 major steps, which are heating process and chemical treatment process. Chemical agents such as calcium chloride, zinc chloride, phosphoric acid, etc. are added to improving the surface area or size of structure in materials (Ahmida, 2015).

**4) Adsorption operation**

**4.1) Batch-type adsorption**

In batch-type contact processes a quantity of carbon is mixed continuously with a specific volume of water until the contaminants have been decreased to a desired level. The carbon is then removed and either discarded or regenerated for use with another volume of solution. The finely powdered carbon is used in this type of system, separation of the spent adsorbent from the water may be difficult. The large particles of carbon which are removed more rapidly when exhausted, requires longer periods of contact between solution and adsorbent. Adsorption results in the removal of solutes from solution and their concentration at a surface, until the amount of solute remaining in solution is in equilibrium

with that at the surface. This equilibrium is described by expressing the amount of solute absorbed per unit weight of adsorbent and the concentration of solute remaining in solution. An expression of this type is termed an adsorption isotherm. Two equations, the Langmuir equation and the Freundlich equation.

**4.2) Column-type adsorption**

Column-type is a continuous-flow operation that has advantage over batch-type operation because rates of adsorption depend on the concentration of solute in the solution being treated. As column operation, the carbon is continuously contacted with polluted solution and slowly change the layer of carbon in the column. In contrast with batch treatment, the concentration of polluted solute is contacted with a specific quantity of carbon and rapidly decreased, thereby decreasing the effectiveness of the adsorbent for removing the solute. For column adsorption, the impurity is adsorbed most rapidly and effective by the first few layers of fresh carbon during the initial stage of operation. The first layer is contacted with the solution at its highest concentration capacity ($C_0$). The small amounts of polluted solute which leak from the first few layers are then removed from next adsorbent layer resulting in no pollution escapes from the adsorption column (C=0). Over time though, all adsorbent layers in column are full and cannot adsorb anymore. The plot of $C/C_0$ versus time (for a constant flow rate) or volume of water treated depicts the increase in the ratio of effluent to influent concentration as the zone moves through the column. The breakpoint on this curve represents that the column is in equilibrium can refer as a breakthrough curve. For most adsorption operations in water and wastewater treatment, breakthrough curves exhibit a characteristic as S-shape.

**5) Column adsorption model**

To predict the performance both shape and position of breakthrough curve of fixed-bed adsorption column, it can be explained by column adsorption model. The model estimates the adsorptive capacity of adsorbent and predict breakthrough curve. Several column adsorption models are created, however there are two favorite models as follows:

1) Thomas model

Thomas model which assumes Langmuir kinetics of adsorption-desorption and no axial dispersion is derived with the assumption that the rate driving force obeys second-order reversible reaction kinetics. It is suitable to estimate the adsorption process where external and internal diffusion resistances are extremely small. Thomas model can be used to determine the maximum solid phase concentration of solute on the adsorbent as well as the adsorption rate constant for an adsorption column.

2) Yoon and Nelson model

Yoon-Nelson model is less valuable or convenient to obtain process variables and to predict adsorption under variety conditions. This assumption of this model based on the rate of decrease in probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent.

Table 2.4 Nonlinear and linear equations of different kinetic column models.

| Kinetic models | Nonlinear equations | Linear equations |
|---|---|---|
| Thomas model | $\frac{C}{C_o} = \frac{1}{1+\exp\left[k_T\left[q_o m - C_o V_{eff}\right]/Q\right]}$ | $\ln\left(\frac{C_o}{C}-1\right) = \frac{k_T q_o m}{Q} - k_T C_o t$ |
| Yoon-Nelson model | $\frac{C}{Co} = \frac{1}{1+e^{K_{YN}(\tau - t)}}$ | $\ln \frac{C}{C_0 - C} = K_{YN} t - \tau K_{YN}$ |

**Where** $C_o$ $\left(\frac{mg}{dm^3}\right)$ is the initial sorbate concentration,

$C$ $\left(\frac{mg}{dm^3}\right)$ is the aqueous adsorbate concentration,

$k_T$ $\left(\frac{dm^3}{min\ mg}\right)$ is the rate constant,

$q_o$ (mg/g) represents the maximum solid-phase concentration of the adsorbate,

$Q\ (\frac{dm^3}{min})$ is the volumetric flow,

$V_{eff}$ ($dm^3$) is the throughput volume,

m (g) is the mass of adsorbent in the column,

t is the breakthrough time (min),

$K_{YN}$ is the rate constant ($min^{-1}$), and

**τ** is the time required for 50% adsorbate breakthrough (min)

**2.2 Literature review**

Halim *et al*. (2010) studied ammoniacal and COD removal from semi-aerobic landfill leachate using a carbon-mineral composite adsorbent in a fixed bed column. The breakthrough capacities for ammoniacal nitrogen and COD adsorption were 4.46 and 3.23 mg/g, respectively. The optimum empty bed contact time was 75 min. The column efficiency for ammoniacal nitrogen and COD adsorption using fresh adsorbent was 86.4% and 92.6%, respectively, and these values increased to 90.0% and 93.7%, respectively, after the regeneration process.

Low (2011) studied optimization of the adsorption conditions for the decolorization and COD reduction of methylene blue aqueous solution using low-cost adsorbent. The performance of raw bagasse and tartaric acid-modified bagasse as adsorbents on decolorization and COD reduction of methylene blue aqueous solution. Raw bagasse was achieved at 0.82 g, pH 9.4, 122 rpm of shaking speed, 44 min of contact time, and 55 degrees Celsius. The maximum decolorization (78.16%) and COD reduction (77.95%) for raw bagasse were appreared. Tartaric acid-modified bagasse was achieved at 0.78 g, pH 9.4, 120 rpm of shaking speed, 34 min of contact time, and 49 degrees Celsius. It found the maximum decolorization (99.05%) and COD reduction (98.45%) for tartaric acid-modified bagasse. Tartaric acid-modified bagasse was found to be more effective than raw bagasse in decolorization and COD reduction of methylene blue aqueous solution.

Li *et al*. (2016) studied effect of pyrolytic temperature on the adsorptive removal of p-benzoquinone, tetracycline, and polyvinyl alcohol by the biochars from sugarcane bagasse.

The sugarcane bagasse was pyrolyzed under oxygen-limited conditions from 100 to 600$^0$C. The carbon content increased from 57.7% of the raw bagasse to 75.3% of the biochar pyrolyzed at 600$^0$C, while the O content decreased from 13.2% to 6.1%. According, the biochar surface became more hydrophobic with increasing pyrolytic temperature. The adsorption affinity of biochars towards the three pollutants improved with an increase in the pyrolytic temperature.

Oguz (2017) studied fixed-bed column on the removal of $Fe^{3+}$and neural network modelling. The sorption potential of the particles of ignimbrite to uptake $Fe^{3+}$ ions from an aqueous solution was investigated using a fixed-bed sorption column. The effects of inlet $Fe^{3+}$concentration (20-75 mg/L), feed flow rate (5-15 mL/min), bed height (5-20 cm), initial solution pH (1.7-4), and particle size (0.25-0.5, 0.5-1, 1-2 mm) were investigated. The highest experimental theoretical bed capacities were obtained to 3.65 and 3.29 mg/g at inlet $Fe^{3+}$concentration of 75 mg/L, bed height of 5 cm and flow rate 5 mL/min, pH of 4 and particle size of 0.25-0.5 mm.

# Chapter III

# MATERIALS AND METHODS

## 3.1 Materials

### 3.1.1 Equipment

1) Orbital shaker
2) Filter paper
3) Scales
4) Column set
5) pump
6) Erlenmeyer flasks
7) Burette
8) Pipette
9) Glass wool
10) Incubator
11) Furnace
12) Parafilm
13) Volumetric flask
14) Vertex
15) Rubber tube
16) Digestion vessels
17) Sieve

### 3.1.2 Chemicals

1) Distilled water
2) Filter cake
3) Wastewater from sugar factory
4) Potassium dichromate (Carlo, 7778-50-9 CAS.NO, 3288 UN Class, grade AR)

5) Sulfate mercury (Merck, grade AR)

6) Sulfuric acid (Qrec)

7) Silver sulfate (Poch, 10294-26-5 CAS.NO, 3077 UN Class, grade AR)

8) Ferrous Ammonium Sulfate

9) Ferrous Sulfate (Ajax, 7782-63-0 CAS.NO, grade AR)

10) 1,10-Phenanthroline Monohydrate (Ajax)

## 3.2 Experiment procedure

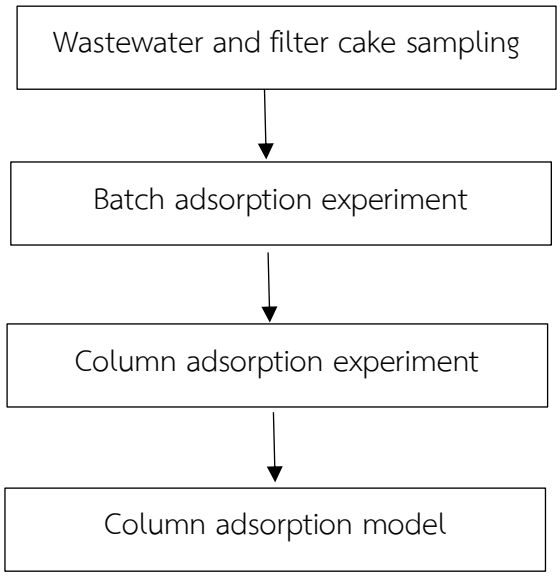


Figure 3.1 experiment procedure

### 3.2.1 Wastewater and filter cake sampling

Wastewater and filter cake samples were collected from one sugar factory in Phetchabun province. Wastewater sample was kept at a temperature below 4$^{o}$C. The wastewater was analyzed for chemical oxygen demand (COD) follows Standard methods 5220 C. Filter cake samples were prepared by screened with 0.5 to 2 mm sieves and carbonized at temperature of 550$^{o}$C for 3 hours and then washed with distilled water. The filter cake was dried at 105$^{o}$C for 1 hour and stored in tightly closed bottles (as shown in Figure 3.2).

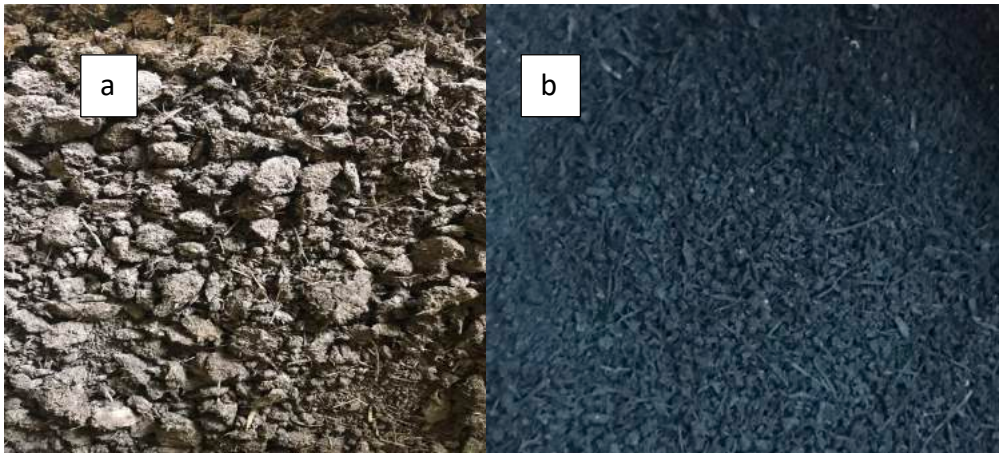


Figure 3.2 (a) filter cake from sugar factory (b) modified filter cake (adsorbent)

### 3.2.2 Batch adsorption experiment

To determine equilibrium time, which time to equilibrium determined the flow rate in the column adsorption. Batch adsorption experiment was done as follows:

1) Fill 50 ml wastewater and 1 g filter cake into 150 ml Erlenmeyer flasks
2) Shake in orbital shaker at mixing speed 150 rpm. for 30, 60, 120, 180, 240, and 300 minutes.
3) Filter through the filter paper for separating filter cake and wastewater.
4) Collect the samples at the time setting in 3) and adjust pH below 2 by adding conc. sulfuric acid
5) Analyze for COD
6) Plot graph of COD versus time to find equilibrium time.

### 3.2.3 Column adsorption experiment

To determine the breakthrough curve, column adsorption experiment (as shown in Figure 3.3) was done as follows:

1) Pack filter cake into columns (diameter 2.5 cm.) with 20 cm height (14.75 g.).
2) Feed wastewater into the column at flowrate of 0.5, 1 and 2 ml/min
3) Collect samples at the end of column at 10, 20, 30, 40, 55, 70, 85, 100, 115, 130, 145, 160, 175, 190, 210, 230, 250, 280, 310, 340, and 370 minutes.

4) Adjust pH below 2 by adding conc. sulfuric acid

5) Analyze for COD

6) Plot effluent COD / initial COD versus time to find breakthrough curve and equilibrium time

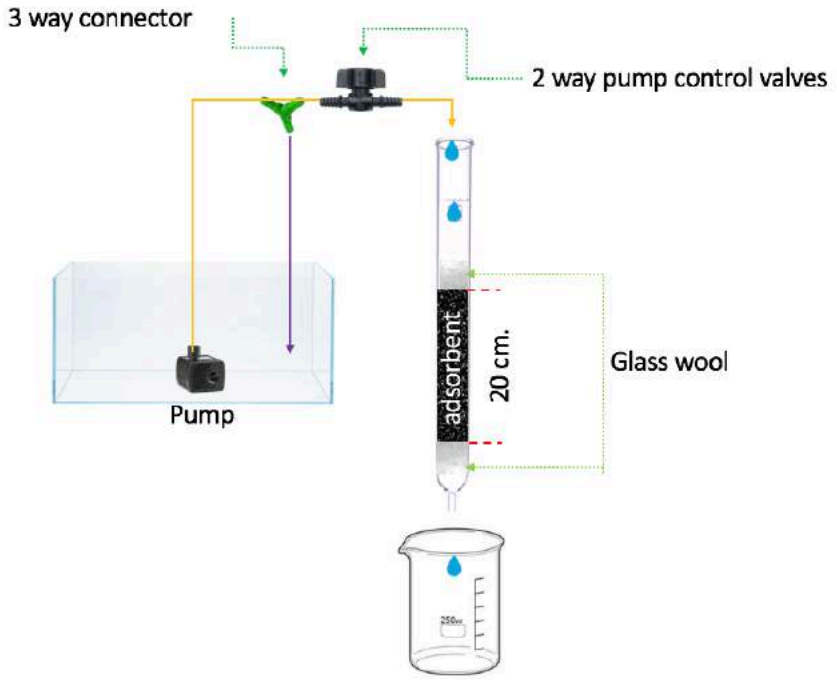


Figure 3.3 adsorption column experiment

### 3.2.4 Column adsorption model

The Thomas model and Yoon-Nelson models were selected to fit with the experimental breakthrough curves of column adsorption using linear or non-linear regression methods. There are two values that used to confirm the fitting model i.e., Coefficients of linearity ($R^2$), which describe the fit between experimental data and forms of Thomas and Yoon-Nelson equations and the sum of squares of the errors (SSE) by the following equation:

$$SSE= \sum_{i=1}^{n} (y_c - y_e)^2 \quad (3.1)$$

Where y is $C_t/C_0$, the subscripts ‘c’ and ‘e’ show the calculated and experimental values, respectively, and n is the number of measurements.

Compare data between the column adsorption experiment with Thomas model and Yoon-Nelson model.

1) The Thomas model was taken in the linearized form as follows:

$$\ln\left(\frac{C_0}{C_t}-1\right)=\frac{k_{th}q_0X}{V}-k_{th}C_0t \qquad (3.2)$$

Where $C_0$ is the influent COD (mg/L)

$C_t$ is the effluent COD at time t (mg/L)

t is the time (min)

X is the amount of adsorbent in the column (g)

V is the flow rate (mL/min)

$K_{Th}$ (l/min mg) is Thomas rate constant and

$q_0$ (mg/g) is the equilibrium COD uptake per gram of the adsorbent

The values of $k_{th}$ and $q_0$ can be determined from a plot of ln ($C_0/C_t$ -1) against t at a given flow rate using linear least-square regressive analysis or from a plot of $C_t/C_0$ against t using nonlinear regression analysis as described by the following equation:

$$\frac{C_t}{C_0}=\frac{1}{1+exp\left[\left(\frac{k_{th}Mq_0}{Q}\right)-(k_{th}C_0t)\right]} \qquad (3.3)$$

The excellent adsorption capacity predicted form Thomas model will reveal with high $q_0$ and $R^2$, and low $k_{th}$ and SSE values.

2) The Yoon-Nelson model was taken linearized form as follows:

$$\ln\frac{C}{C_0-C}=K_{YN}t-\tau K_{YN} \qquad (3.4)$$

Where $C_t$ is the effluent COD at time t (mg/L)

$C_0$ is the influent COD (mg/L)

t is the time (min)

$K_{YN}$ ($min^{-1}$) is the rate constant

$\tau$ (min) is the time required 50% breakthrough.

The values of $k_{YN}$ and $\tau$ can be determined from a plot of ln ($C_t/C_0$ -C) against t at a given flow rate using linear least-square regressive analysis or from a plot of $C_t/C_0$ against t using nonlinear regression analysis as expressed by the following equation:

$$\frac{C}{C_0} = \frac{1}{1+e^{k_{YN}(t-\tau)}} \quad (3.5)$$

The excellent adsorption capacity predicted form Yoon and Nelson model will reveal with high $\tau$ and $R^2$, and low $k_{YN}$ and SSE values.

# Chapter IV
# RESULTS AND DISCUSSION

## 4.1 Batch adsorption experiment

For investigating the effect of treatment time, 1 g adsorbent was mixed with 50 ml of wastewater sample at 150 rpm shaking speed with varied time 30 to 300 min. Initial COD of the samples was approx. 6,600 mg/L. The residual COD concentration was measured after treatment. The comparison between the filter cake adsorbents and COD reduction with various contact time is shown in Figure 4.1.

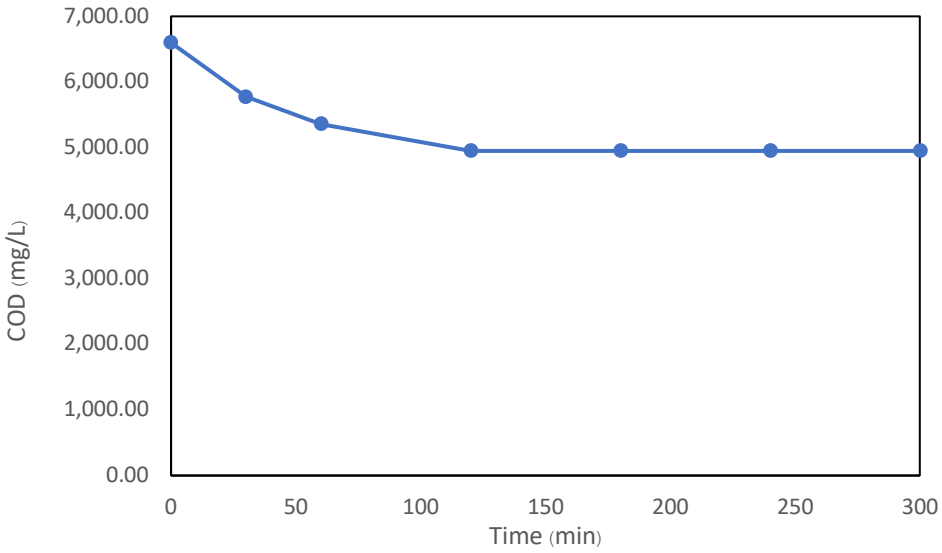


Figure 4.1 Effect of contact time on COD concentration (filter cake =1 g; wastewater = 50 ml; agitation rate = 150 rpm)

The adsorption reaction increased with the increasing in contact time. The maximum COD adsorption capacity occurred at 120 minutes was about 25% (approx. 6,600 mg/L). The $q_0$ with is the COD uptake per one gram of adsorbent at the equilibrium time was 82.5. In this batch experiment, 120 minutes was set as equilibrium time and will use to determine the flow rate for column adsorption test in the next experiment.

### 4.2 Column adsorption experiment

In packed column experiment, 2.54 cm inner diameter with 20 cm in height of adsorbent (14.75 g) was set and sugar wastewater was top-down fed until 370 minutes. The COD in wastewater of approx. 4,400, 6,300 and 6,500 mg/L were allowed to flow through the bed by pump at different flow rates of 0.5, 1, 2 mL/min, respectively. The eluents from the column were collected for the respective COD concentration. The breakthrough curve of $C_t/C_0$ ($C_t$ is the effluent COD at time t, and $C_0$ is the influent COD) at different flow rates is shown in Figure 4.2.

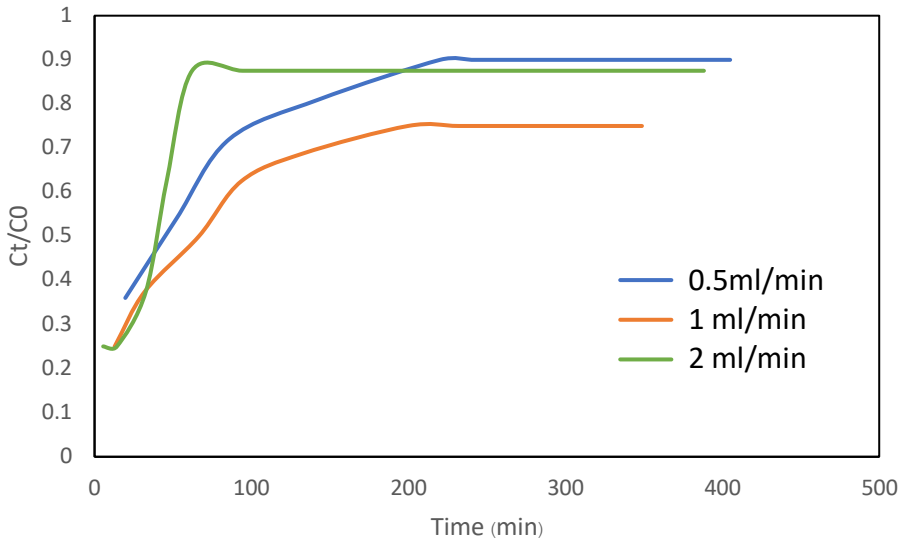


Figure 4.2 Breakthrough curves at 3 flowrates of COD adsorption with filter cake

As shown in Figure 4.2, the breakthrough times of 0.5, 1 and 2 ml/min flowrates occurred at 220, 200, 62 minutes, respectively. The flow rate 0.5 mL/min showed a longer time to exhaust the adsorption sites available in the column. Typically, high flowrate increases saturation reaching of breakthrough time. This means at low rate of influent, COD had more time to contract with adsorbent resulting in higher removal of COD from wastewater in column. It can be stated that feeding rate is one of the main factors on the effectiveness of continuous adsorption and column performance. This result is in line with El-Naas et al. (2017) who reported that the increase of flow rate from 5 – 20 mL/min caused the breakthrough of phenol occurs earlier and Sun et al. (2014) who revealed that higher flow rates resulted in lowered breakthrough times and provided for more efficient interaction between the adsorbent and adsorbate in the solution.

## 4.3 Column adsorption model

Two models namely Thomas model and Yoon-Nelson model were selected to fit with the breakthrough curves of column adsorption from previous part. The models were first shown in linear regression and then recalculated to non-linear regression for describing the adsorption mechanism of this experiment. There are two values that used to confirm the fitting result of each model i.e., $R^2$ and SSE. Coefficient of linearity ($R^2$) defines as the fit between experimental data and forms of Thomas and Yoon-Nelson equations, whereas the sum of squares of the errors (SSE) is the following equation:

$$SSE = \sum_{i=1}^{n} (y_c - y_e)^2$$

Where y is $C_t/C_0$, the subscripts 'c' and 'e' show the calculated and experimental values, respectively, and n is the number of measurements.

### 4.3.1 Thomas model

Thomas model is a model that uses to determine the maximum solid phase concentration of solute on the adsorbent as well as the adsorption rate constant for an adsorption column. The linearized form of the Thomas model (as described in Section 3.2.4) is illustrated in Figure 4.3.

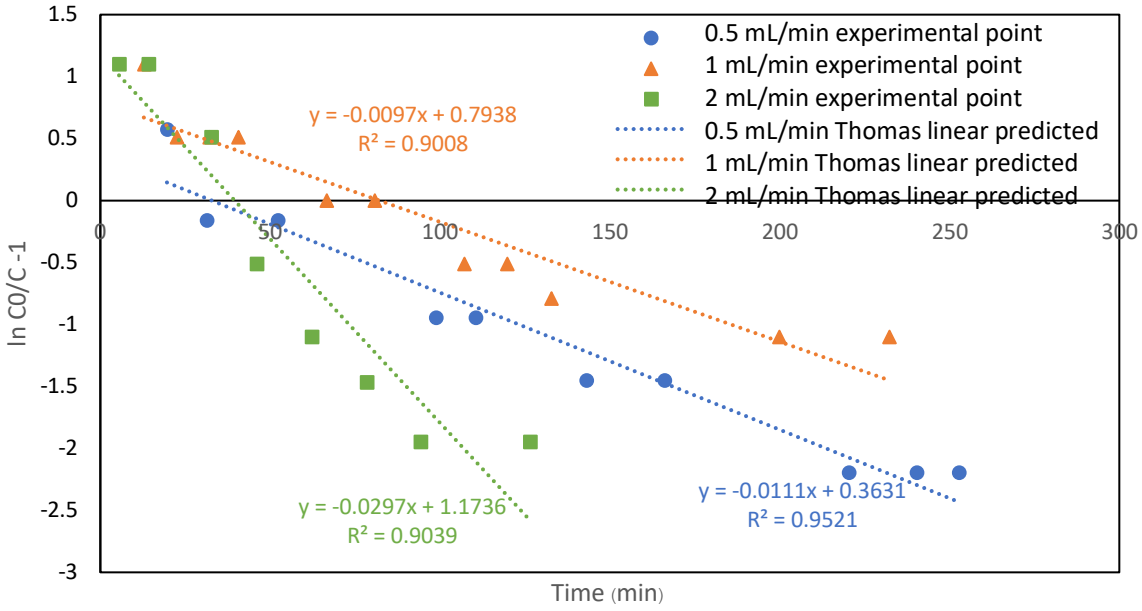


Figure 4.3 Linear predicted points of Thomas model (flow rate = 0.5, 1, 2 mL/min, mass of filter cake = 14.75 g)

The values of $k_{th}$ and $q_0$ can be determined from a plot of ln ($C_0/C_t$ -1) against t at a given flow rate using linear least-square regressive analysis or from a plot of $C_t/C_0$ against t using nonlinear regression analysis as shown in Figure 4.4.

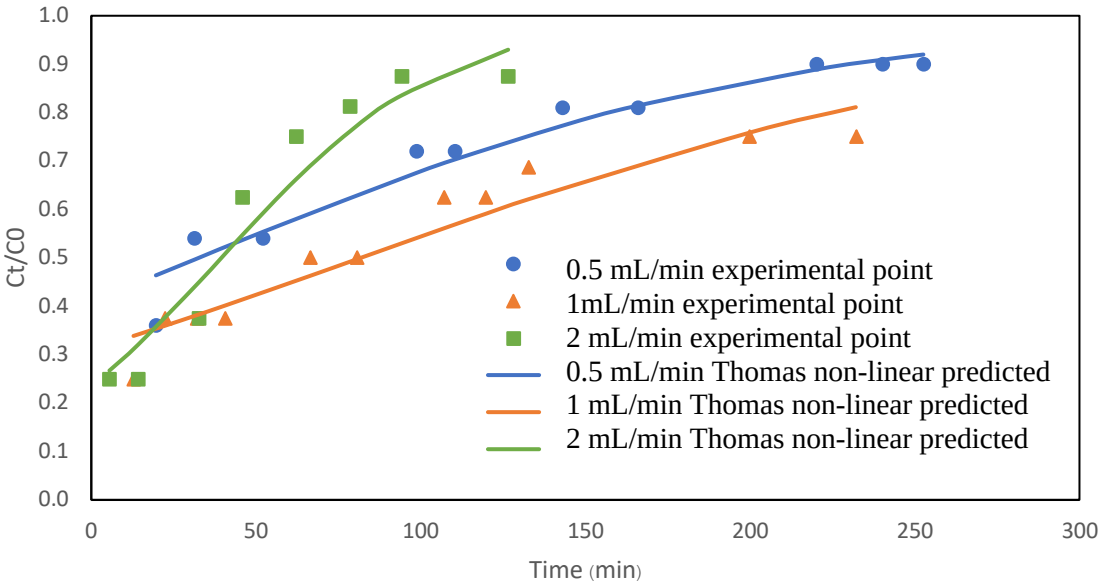


Figure 4.4 Thomas model fitting of the experiment data for COD adsorption using different flow rate (mass of filter cake = 14.25 g)

Thomas model was used to fit the experimental data (Figure 4.4) in order to determine the rate constant and the other fitted parameters, which are given in Table 4.1.

Table 4.1 Thomas parameters onto the column adsorption study

| flow rate | COD (mg/L) | Thomas | | | |
|---|---|---|---|---|---|
| | | $K_{th}$ (L/mg.min) | $q_0$ (mg/g) | $R^2$ | SSE |
| 0.5 | 4,356 | 2.55E-06 | 4.84 | 0.9521 | 0.0171 |
| 1 | 6,336 | 1.53E-06 | 35.2 | 0.9008 | 0.0237 |
| 2 | 6,465 | 4.59E-06 | 34.6 | 0.9039 | 0.0318 |

Table 4.1 lists the parameters of Thomas model and values of $R^2$ and SSE by linear and nonlinear regression analysis using least square method. Figure 4.3 shows the experimental points and linear predicted points in different flow rate condition. The values of equilibrium uptake per gram of adsorbent ($q_0$, mg/g) from experiment were also listed in Table

4.1. The excellent adsorption capacity predicted from Thomas model will reveal with high $q_0$ and $R^2$, and low $K_{th}$ and SSE values.

It can be observed that the simulation of whole breakthrough curve fitted well with the Thomas model. The flow rate at 0.5, 1 and 2 mL/min provided $q_0$ 4.84, 35.2 and 34.6 mg/g, respectively. This is attributed to the difference in driving force for adsorption that accompanies the concentration difference. Therefore, the higher driving force resulting from higher COD concentration in adsorbent led to a higher $q_0$ value. Lowest $k_{th}$ ($1.53 \times 10^{-6}$ L/mg.min) was also occurred in flow rate 1 mL/min. This can be concluded that the flow rate 1 mL/min was more suitable for predict the dynamic behavior of the column over than the flow rate 0.5 and 2 mL/min because of its higher $q_0$ and lower $K_{th}$ than others. Furthermore, the flow rate at 0.5, 1 and 2 mL/min provided $R^2$ 0.9521, 0.9008, and 0.9039, respectively, and SSE 0.0171, 0.0237, and 0.0318, respectively, revealed that Thomas model suitably described the COD adsorption in a fixed-bed column whereas the diffusion through the film/pores is not the rate-limiting step.

### 4.3.2 Yoon-Nelson model

Yoon-Nelson model based on an assumption that the rate of decrease in probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent. The linearized form of the Yoon-Nelson model (as described in Section 3.2.4) is illustrated in Figure 4.5.

The values of $k_{YN}$ and $\boldsymbol{\tau}$ can be determined from a plot of ln ($C_t/C_0$ -C) against t at a given flow rate using linear least-square regressive analysis or from a plot of $C_t/C_0$ against t using nonlinear regression analysis as shown in Figure 4.6.

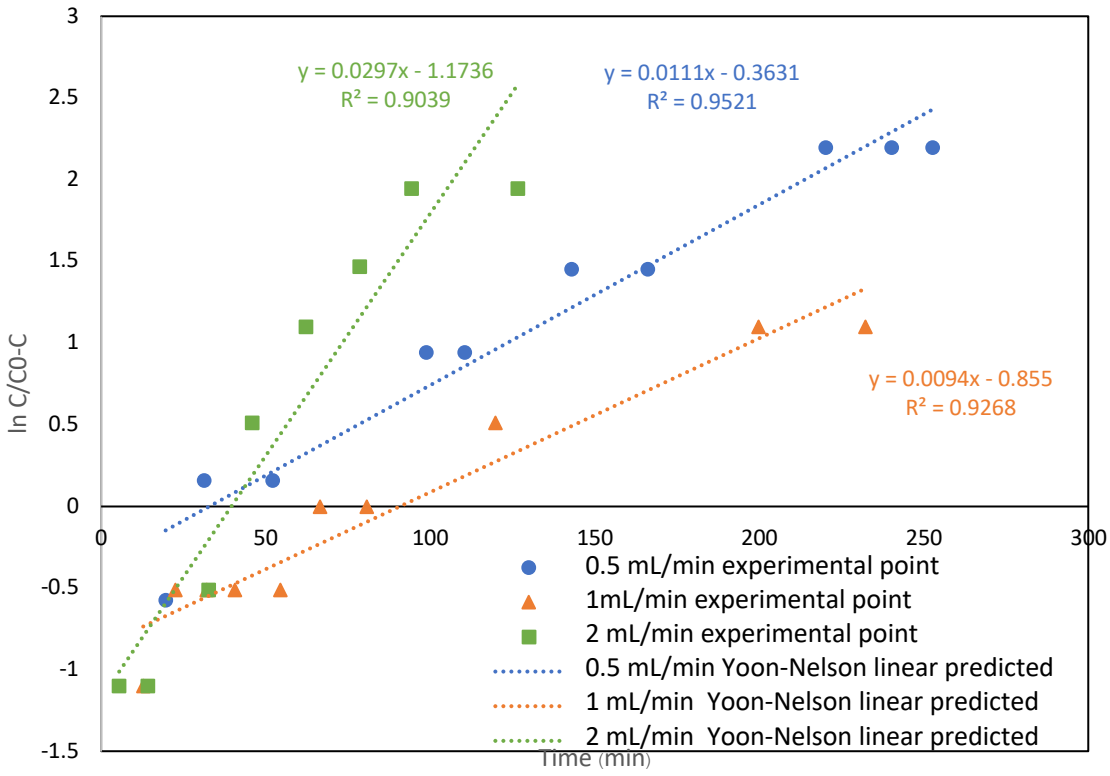


Figure 4.5 Linear predicted points of Yoon-Nelson model (flow rate = 0.5, 1, 2 mL/min, mass of filter cake = 14.75 g)

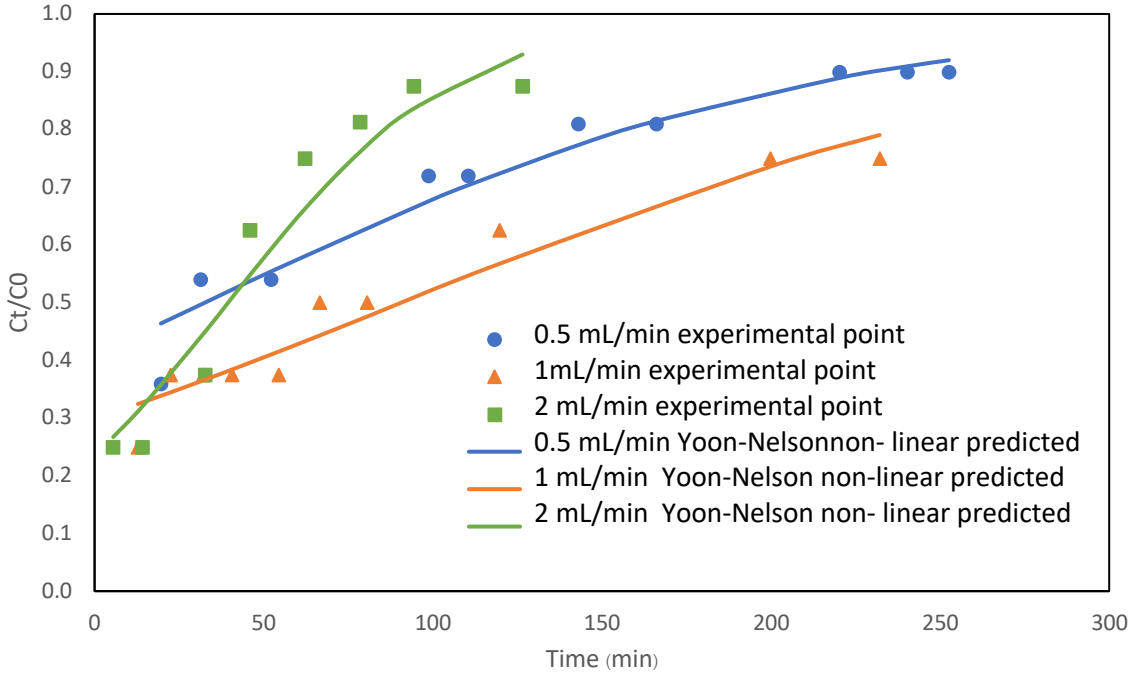


Figure 4.6 Yoon-Nelson model fitting of the experiment data for COD adsorption using different flow rate (mass of filter cake = 14.25 g)

Yoon-Nelson model was used to fit the experimental data (Figure 4.6) in order to determine the fitted parameters, which are given in Table 4.2.

Table 4.2 Yoon-Nelson parameters onto the column adsorption study

| flow rate | COD (mg/L) | Yoon-Nelson | | | |
|---|---|---|---|---|---|
| | | $K_{YN}$ ($min^{-1}$) | $\tau$ (min) | $R^2$ | SSE |
| 0.5 | 4,356 | 0.0111 | 32.7 | 0.9521 | 0.0171 |
| 1 | 6,336 | 0.0094 | 91.0 | 0.9268 | 0.0172 |
| 2 | 6,465 | 0.0297 | 39.5 | 0.9039 | 0.0318 |

A simple theoretical model was introduced to investigate the breakthrough behavior of COD adsorption on filter cake adsorbent. The values of $k_{YN}$, $\tau$ and other statistical parameters are listed in Table 4.2. The exceptional adsorption capacity predicted from Yoon-Nelson model will report with high $\tau$ and $R^2$, and low $K_{YN}$ and SSE values.

The flow rate at 0.5, 1 and 2 mL/min provided the time required to achieve 50% adsorbate breakthrough ($\tau$) 32.7, 91.0 and 39.5 minutes respectively. The flow rate at 0.5, 1 and 2 mL/min gave $K_{YN}$ 0.0111, 0.0094, and 0.0297 $min^{-1}$ respectively. Longer $\tau$ proved the superiority of the flow rate at 1mL/min over the flow rate at 0.5 and 2 mL/min. Higher $\tau$ fits with lower $K_{YN}$ value shows that the column performs longer time of adsorption and more sites available of adsorbent. This means the flow rate at 1 mL/min has better performance to remove COD under fix bed column adsorption than at 0.5 and 2 mL/min. Moreover, the flow rate at 0.5, 1 and 2 mL/min gave $R^2$ 0.9521, 0.9268, and 0.9039, SSE 0.0171, 0.0172, and 0.0318, respectively. The $R^2$ and SSE values also indicated good applicability of this model in column operations. From the results, it was found that flow rate at 1 mL/min is suitable for predict the dynamic behavior of the column.

# Chapter V
# CONCLUSIONS AND RECOMMENDATIONS

## 5.1 Conclusions

The performance of adsorbent modified by filter cake to adsorb COD in wastewater in the same sugar factory were studied. Conclusions are summarized as follows:

- From batch adsorption study, $q_0$ was 82.5 mg/g, which was about 25% at equilibrium time 120 minutes.
- Flow rate at 0.5 mL/min had longer service time (220 min.) compared to the flow rate at 1 and 2 mL/min (200 and 62 min).
- From Thomas model, $q_0$ achieved by flow rate at 1 mL/min was 35.2 mg/g while flow rates at 0.5 and 2 were 4.84 and 34.6 mg/g, respectively. The flow rate at 1 mL/min presented $K_{th}$, R-square, and SSE which are $1.53 \times 10^{-6}$ L/mg. min, 0.9008 and 0.0237, respectively.
- From Yoon and Nelson model, $\tau$ achieved by the flow rate at 1 mL/min was 91 min whilst the flow rates at 0.5 and 2 were 32.7 and 39.5 min, respectively. The flow rate at 1 mL/min showed $K_{YN}$, R-square, and SSE which are 0.0094 $min^{-1}$, 0.9268, and 0.0172, respectively.

In fixed-bed column adsorption of flow rate at 1 mL/min, Yoon and Nelson model was more suitable in predicting the sorption kinetics than Thomas model. Therefore, this column adsorption can explain that the rate of decrease in probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent.

## 5.2 Recommendations

The treated wastewater still does not pass the industrial effluent standard (which set COD 120 mg/L); therefore, it must be treated with next wastewater treatment units e.g., activated sludge or contact stabilization pond.

# References


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# APPENDICES

## Appendix A

## COD analysis

### Apparatus

1) Digestion Vessels
2) Incubator
3) Burette
4) Erlenmeyer flasks

### Chemicals

1) The standard solution of the potassium dichromate 0.1 N

   Dissolve potassium dichromate which was dried at 103 °C for 2 hours. Add 167 ml of sulfuric acid and 33.3 g of sulfate mercury to dissolve. Let it cool. And diluted with distilled water until the volume is 1000 ml.

2) Sulfuric acid and silver sulfate

   Silver sulfate 8.8 grams in 1 liter of sulfuric acid, set aside for 1-2 days to allow all silver sulfates to be dissolved before being used.

3) Ferrous Ammonium Sulfate Standard Solution (FAS) 0.05 N

   Dissolve Ferrous Ammonium Sulfate 19.6 g in distilled water, add 20 ml of conc. sulfuric acid and dilute to 1000 ml with distilled water.

4) Ferroin indicator solution

   Ferrous Sulfate 695 mg and 1,10-Phenanthroline Monohydrate 1.485 g in distilled water and diluted to 100 ml

### Determine the concentration of FAS solution

Pipette 5.0 ml of standard solution of the potassium dichromate 0.1 N in Erlenmeyer flask add 50 ml of distilled water, then gradually add 15 ml of sulfuric acid. 2-3 drops of ferroin indicator solution and titration with FAS until brown is the end point.

### Procedure

1) Put water sampling in digestion vessels add standard solution of the potassium dichromate 0.1 N followed by a slow sulfuric acid solution in the amount shown as the table 6.1, close the lid tightly and shake well. For Blank, use distilled water and make it like every example.

2) Place the digestion vessels in the incubator. Set the temperature at 150 $\pm$ 2 degrees Celsius for 2 hours and leave the incubator to cool.

3) Pour the solution from the digestion vessels into Erlenmeyer flask. Fill with 2-3 drops of Ferroin indicator solution, titration with standard FAS solution. The color of the solution will gradually change color from yellow to brown sugar. Which indicates the end.

Table A.1 The size of the digestion vessels and water sampling volume and chemical volume

| digestion vessels (mm.) | water sampling (mL) | potassium dichromate (mL) | Sulfuric acid (mL) | Total (mL) |
|---|---|---|---|---|
| 16 x 100 | 2.5 | 1.5 | 3.5 | 7.5 |
| 20 x 150 | 5.0 | 3.0 | 7.0 | 15.0 |
| 25 x 150 | 10.0 | 6.0 | 14.0 | 30.0 |

**Calculations**

1) $\text{FAS (N)} = \dfrac{5.0 \text{ X } 0.1}{\text{mL of FAS}}$

2) $\text{COD (mg/L)} = \dfrac{(\text{A-B}) \text{ X N X } 8000}{\text{mL of water sampling}}$

A = mL of FAS used in blank titration

B = mL of FAS used in water sampling

N = concentration of FAS (N)

## Appendix B

## Column adsorption experiment

Table 6.2 Actual flow rate of the column adsorption as setting at 0.5 mL/min

| Sampling | Time (min) | Volume (ml) | Flow rate (ml/min) |
|---|---|---|---|
| 0.1h | 10 | 9.8 | 0.98 |
| 0.2h | 10 | 5.9 | 0.59 |
| 0.3h | 10 | 10.4 | 1.04 |
| 0.4h | 10 | 8.8 | 0.88 |
| 0.55h | 15 | 8 | 0.53 |
| 1.1h | 15 | 6.5 | 0.43 |
| 1.25h | 15 | 5.8 | 0.39 |
| 1.4h | 15 | 5.2 | 0.35 |
| 1.55h | 15 | 11.1 | 0.74 |
| 2.1h | 15 | 11.5 | 0.77 |
| 2.25h | 15 | 9.5 | 0.63 |
| 2.4h | 15 | 17.6 | 1.17 |
| 2.55h | 15 | 10 | 0.67 |
| 3.1h | 15 | 6.2 | 0.41 |
| 3.3h | 20 | 6.4 | 0.32 |
| 3.5h | 20 | 29 | 1.45 |
| 4.1h | 20 | 24.3 | 1.22 |
| 4.4h | 30 | 16.5 | 0.55 |
| 5.1h | 30 | 12 | 0.40 |
| 5.4h | 30 | 11.6 | 0.39 |
| 6.1h | 30 | 11.5 | 0.38 |

Average flow rate= 0.68 ml/min

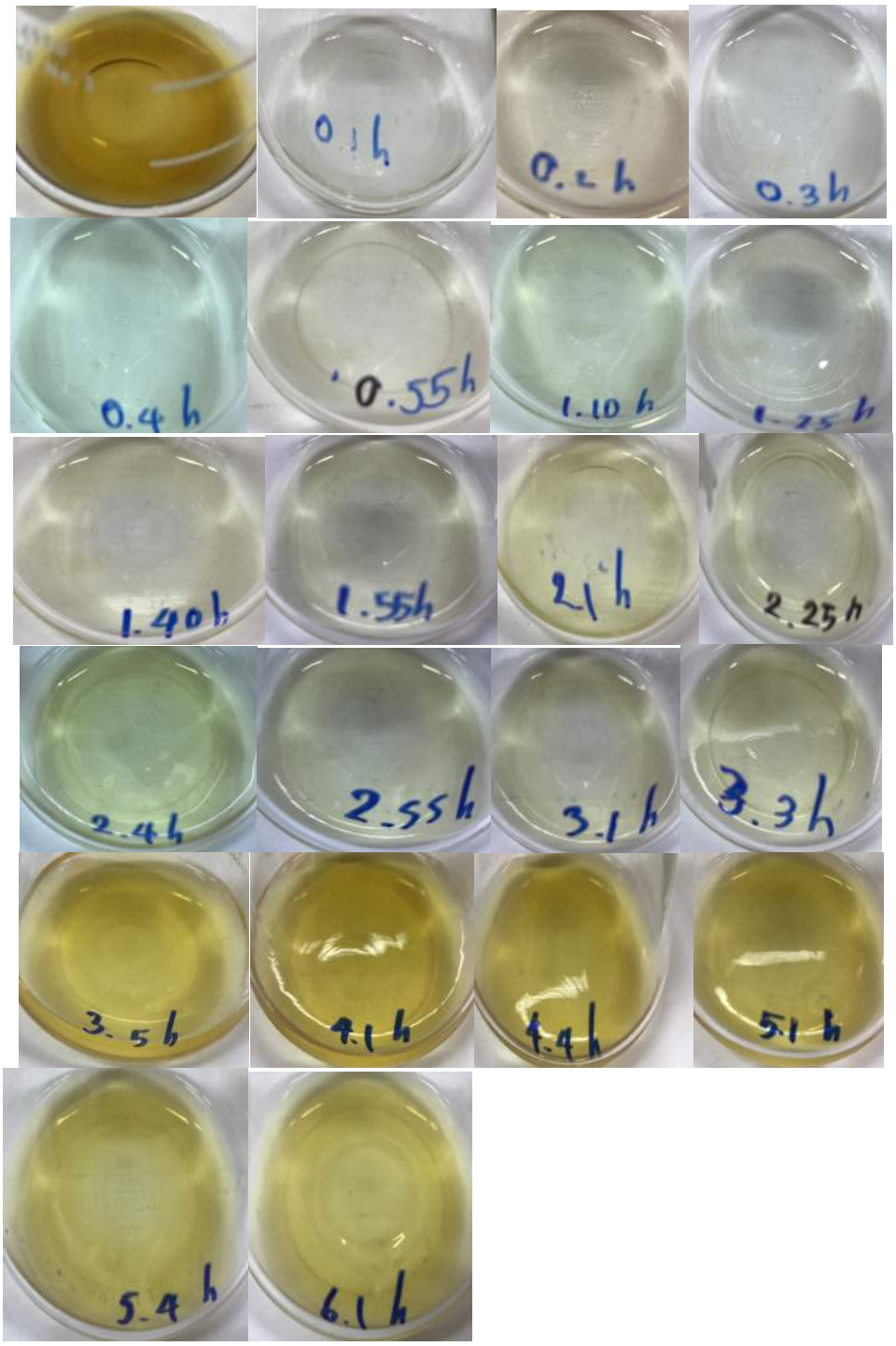


Figure 6.1 Eluents from column adsorption test at 10-370 minutes, flow rate at 0.5 mL/min and filter cake 14.75 g

Table 6.3 Actual flow rate of the column adsorption as setting at 1 mL/min

| Sampling | Time (min) | Volume (ml) | Flow rate (ml/min) |
|---|---|---|---|
| 0.1 | 10 | 12.8 | 1.28 |
| 0.2 | 10 | 9.7 | 0.97 |
| 0.3 | 10 | 9.6 | 0.96 |
| 0.4 | 10 | 8.5 | 0.85 |
| 0.55 | 15 | 13.8 | 0.92 |
| 1.1 | 15 | 12.1 | 0.81 |
| 1.25 | 15 | 14.1 | 0.94 |
| 1.4 | 15 | 13 | 0.87 |
| 1.55 | 15 | 13.4 | 0.89 |
| 2.1 | 15 | 12.7 | 0.85 |
| 2.25 | 15 | 13 | 0.87 |
| 2.4 | 15 | 13.9 | 0.93 |
| 2.55 | 15 | 16 | 1.07 |
| 3.1 | 15 | 15.7 | 1.05 |
| 3.3 | 20 | 21.4 | 1.07 |
| 3.5 | 20 | 16 | 0.80 |
| 4.1 | 20 | 16.4 | 0.82 |
| 4.4 | 30 | 39 | 1.30 |
| 5.1 | 30 | 40 | 1.33 |
| 5.4 | 30 | 37.7 | 1.26 |
| 6.1 | 30 | 37.7 | 1.26 |

Average flow rate= 0.99 mL/min

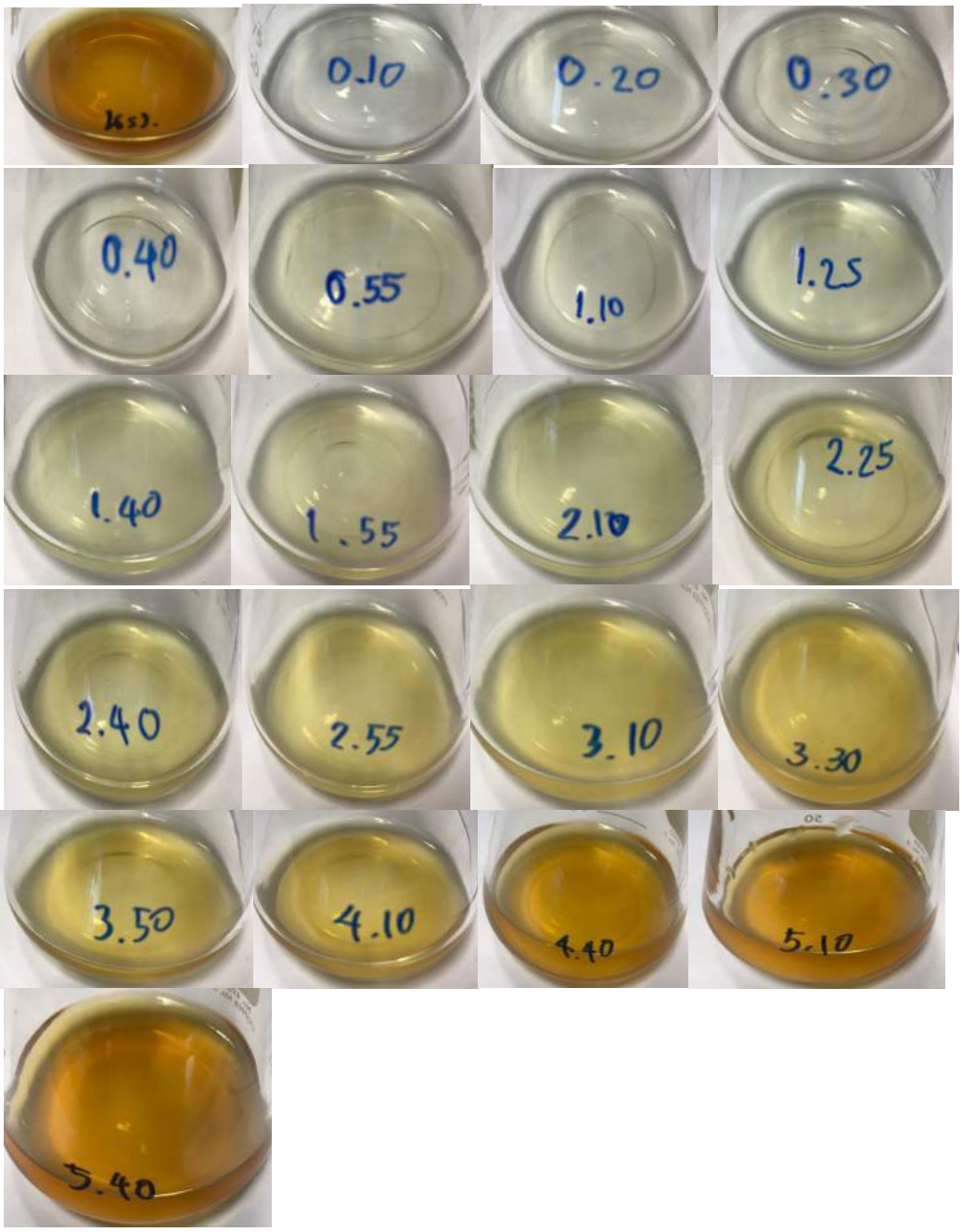


Figure 6.2 Eluents from column adsorption test at 10-370 minutes, flow rate at 1 mL/min and filter cake 14.75 g

Table 6.4 Actual flow rate of the column adsorption as setting at 2 mL/min

| Sampling | Time (min) | Volume (ml) | Flow rate (ml/min) |
|---|---|---|---|
| 0.1h | 10 | 11 | 1.10 |
| 0.2h | 10 | 17.5 | 1.75 |
| 0.3h | 10 | 37 | 3.70 |
| 0.4h | 10 | 26.4 | 2.64 |
| 0.55h | 15 | 32.4 | 2.16 |
| 1.1h | 15 | 32.7 | 2.18 |
| 1.25h | 15 | 31.6 | 2.11 |
| 1.4h | 15 | 32.9 | 2.19 |
| 1.55h | 15 | 31.6 | 2.11 |
| 2.1h | 15 | 31.2 | 2.08 |
| 2.25h | 15 | 34.8 | 2.32 |
| 2.4h | 15 | 31.7 | 2.12 |
| 2.55h | 15 | 29.7 | 1.98 |
| 3.1h | 15 | 31.2 | 2.08 |
| 3.3h | 20 | 41.4 | 2.07 |
| 3.5h | 20 | 42.2 | 2.11 |
| 4.1h | 20 | 41.5 | 2.08 |
| 4.4h | 30 | 60.5 | 2.02 |
| 5.1h | 30 | 58.9 | 1.96 |
| 5.4h | 30 | 60.8 | 2.03 |
| 6.1h | 30 | 59.6 | 1.99 |

Average flow rate= 2.13 mL/min

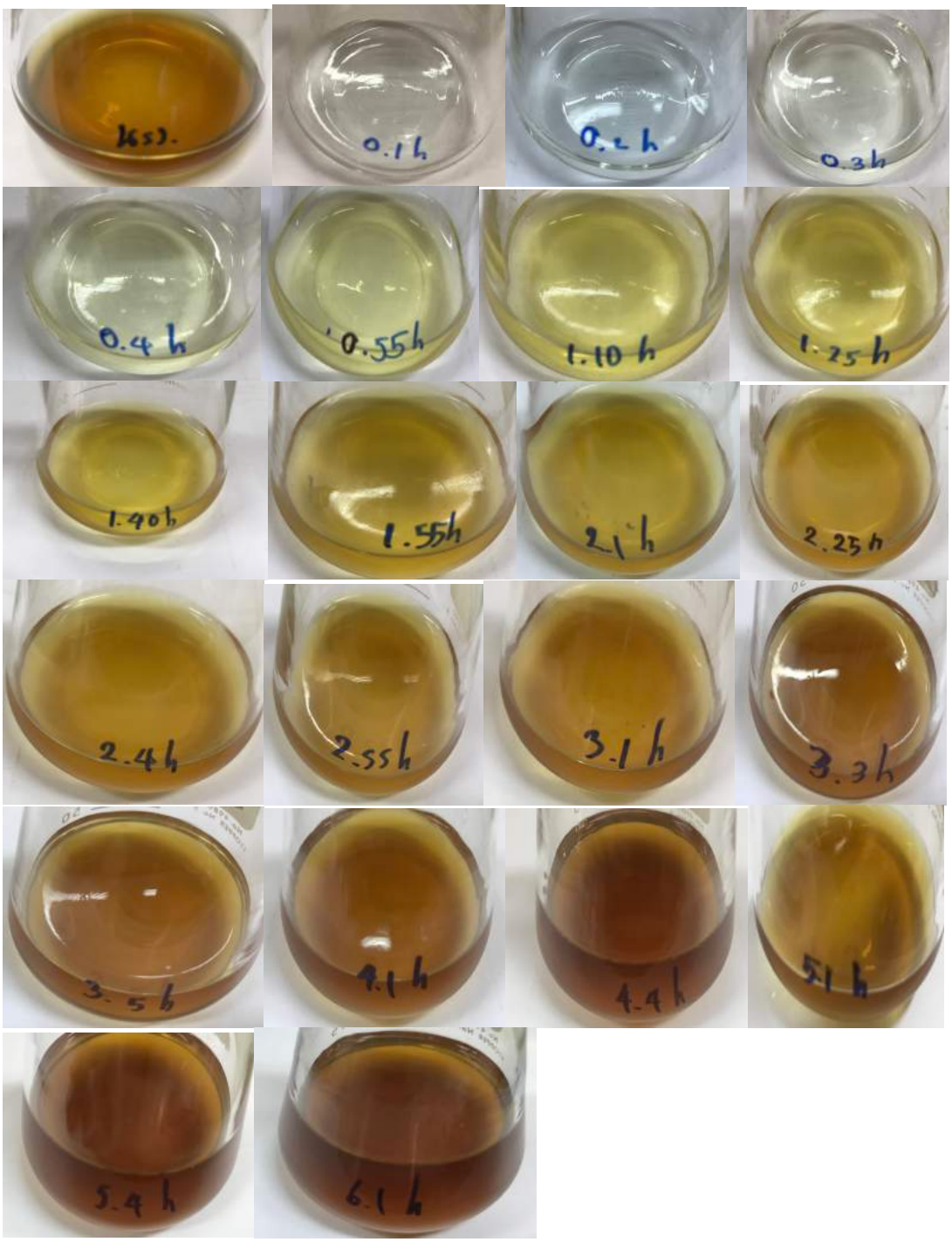


Figure 6.3 Eluents from column adsorption test at 10-370 minutes, flow rate at 2 mL/min and filter cake 14.75 g

# BIOGRAPHY

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