การดูดซับสารกำจัดวัชพืชพาราควอตในน้ำโดยใช้กรดฮิวมิกรองรับด้วยกากตะกอนจากการผลิตน้ำประปาที่เก็บกักในเม็ดแอลจิเนต

นางสาวมัลลิกา สุขใส

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาเคมี ภาควิชาเคมี
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2560

ADSORPTION OF PARAQUAT HERBICIDE IN WATER USING HUMIC ACIDS SUPPORTED ON SLUDGE FROM TAP WATER PRODUCTION ENTRAPPED IN ALGINATE BEADS

Miss Munlika Suksai

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Chemistry
Department of Chemistry
Faculty of Science
Chulalongkorn University
Academic Year 2017

Thesis Title	ADSORPTION OF PARAQUAT HERBICIDE IN WATER USING HUMIC ACIDS SUPPORTED ON SLUDGE FROM TAP WATER PRODUCTION ENTRAPPED IN ALGINATE BEADS
By	Miss Munlika Suksai
Field of Study	Chemistry
Thesis Advisor	Associate Professor Apichat Imyim, Ph.D.

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

....Dean of the Faculty of Science

(Professor Polkit Sangvanich, Ph.D.)

THESIS COMMITTEE

....Chairman

(Associate Professor Vudhichai Parasuk, Ph.D.)

....Thesis Advisor

(Associate Professor Apichat Imyim, Ph.D.)

....Examiner

(Associate Professor Pakorn Varanusupakul, Ph.D.)

....External Examiner

(Assistant Professor Woravith Chansuvarn, Ph.D.)

มัลลิกา สุขใส : การดูดซับสารกำจัดวัชพืชพาราควอตในน้ำโดยใช้กรดฮิวมิกรองรับด้วยกากตะกอนจากการผลิตน้ำประปาที่เก็บกักในเม็ดแอลจิเนต (ADSORPTION OF PARAQUAT HERBICIDE IN WATER USING HUMIC ACIDS SUPPORTED ON SLUDGE FROM TAP WATER PRODUCTION ENTRAPPED IN ALGINATE BEADS) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร.อภิชาติ อิ่มยิ้ม, 66 หน้า.

งานวิจัยนี้ ทำการศึกษาการดูดซับสารกำจัดวัชพืชพาราควอตในน้ำ โดยใช้กรดฮิวมิกรองรับด้วยกากตะกอนจากการผลิตน้ำประปาหรือกากตะกอนสารส้มที่เก็บกักในเม็ดแอลจิเนต หลังจากนั้นหาลักษณะเฉพาะของตัวดูดซับด้วยเทคนิคฟูเรียร์ทรานสฟอร์มอินฟราเรดสเปกโตรสโกปี พบว่าตัวดูดซับมีกรดฮิวมิก กากตะกอนสารส้ม และแอลจิเนตเป็นองค์ประกอบ จากนั้นทำการศึกษาชนิดและปริมาณของตัวดูดซับ ได้แก่ เม็ดแอลจิเนตเพียงอย่างเดียว, กรดฮิวมิก-เม็ดแอลจิเนต, กากตะกอนสารส้ม-เม็ดแอลจิเนต, กากตะกอนสารส้ม-กรดฮิวมิก-เม็ดแอลจิเนต-1 และ กากตะกอนสารส้ม-กรดฮิวมิก-เม็ดแอลจิเนต-2 ทำการทดสอบการดูดซับพาราควอตในสารละลายพบว่าตัวดูดซับทั้งหมดสามารถดูดซับพาราควอตได้ โดยเฉพาะกากตะกอนสารส้ม-กรดฮิวมิก-เม็ดแอลจิเนตสามารถดูดซับพาราควอตได้สูงที่สุด ร้อยละ 93.6 หลังจากนั้นนำกากตะกอนสารส้ม-กรดฮิวมิก-เม็ดแอลจิเนตมาทดสอบประสิทธิภาพการดูดซับพาราควอตในระบบแบทช์ โดยมีพีเอชที่เหมาะสมสำหรับการดูดซับที่พีเอช 4-10 โดยมีจลนพลศาสตร์การดูดซับเป็นไปตามแบบจำลองอันดับหนึ่งเทียม (pseudo-first-order) มีรูปแบบการดูดซับเป็นไอโซเทอมการดูดซับแบบฟรุนดิช และมีค่าความจุการดูดซับสูงสุดที่ได้จากการทดลองมากกว่า 94.5 มิลลิกรัมต่อกรัม เมื่อนำไปศึกษาการดูดซับพาราควอตในระบบคอลัมน์ พบว่าประสิทธิภาพของการดูดซับพาราควอตลดลง เมื่ออัตราการไหลของสารละลายเพิ่มขึ้น เมื่อทำการศึกษาผลของความเข้มข้นของตัวชะ พบว่า กรดไฮโดรคลอริกและกรดไนทริกสามารถชะพาราควอตออกจากตัวดูดซับได้ แต่ผิวของตัวดูดซับถูกทำลาย ในขณะที่โซเดียมคลอไรด์สามารถชะพาราควอตออกจากตัวดูดซับได้โดยไม่ทำลายผิวของตัวดูดซับ นอกจากนี้ กากตะกอนสารส้ม-กรดฮิวมิก-เม็ดแอลจิเนตประยุกต์ใช้ในการทดสอบกับน้ำตัวอย่างจริงจากพื้นที่การเกษตรที่จังหวัดสุพรรณบุรี ลพบุรี และฉะเชิงเทรา พบว่าตัวดูดซับสามารถกำจัดพาราควอตออกจากน้ำตัวอย่างจริงได้

ภาควิชา เคมี ลายมือชื่อนิสิต ....

สาขาวิชา เคมี ลายมือชื่อ อ.ที่ปรึกษาหลัก ....

ปีการศึกษา 2560

5772109723 : MAJOR CHEMISTRY

KEYWORDS: ADSORPTION, PARAQUAT REMOVAL, HUMIC ACIDS, ALUM SLUDGE, ALGINATE BEAD

MUNLIKA SUKSAI: ADSORPTION OF PARAQUAT HERBICIDE IN WATER USING HUMIC ACIDS SUPPORTED ON SLUDGE FROM TAP WATER PRODUCTION ENTRAPPED IN ALGINATE BEADS. ADVISOR: ASSOC. PROF. APICHAT IMYIM, Ph.D., 66 pp.

Adsorption of paraquat in water using humic acids supported on sludge from tap water production or alum sludge entrapped in alginate beads has been studied. The adsorbent was characterized by Fourier transform infrared spectroscopy showing that it composes of humic acids, alum sludge and alginate in beads. Afterwards, the type and amount of adsorbents were studied including bare alginate beads, humic acids-alginate beads, alum sludge-alginate beads, alum sludge-humic acids-alginate beads-1 and alum sludge-humic acids-alginate beads-2. These adsorbents were subjected to the paraquat adsorption study in aqueous solutions. The results showed that all adsorbents can adsorb paraquat, especially the alum sludge-humic acids-alginate beads that can adsorb paraquat with the maximum adsorption percentage of 93.6%. After that, the adsorption efficiency of the alum sludge-humic acids-alginate beads was investigated in batch system. The optimal pH of adsorption was 4-10. The adsorption kinetics was fitted to the pseudo-first order kinetic model. The adsorption behavior of paraquat obeyed the Freundlich adsorption isotherm. The maximum adsorption amount from experiment was more than 94.5 mg/g. In column study, the efficiency of paraquat absorption decreased with the increasing flow rate of the solution. The result of the effect of eluent concentration showed that hydrochloric acid and nitric acid can elute the paraquat from the adsorbent but it can also destroy the adsorbent surface. Meanwhile, sodium chloride can elute paraquat from the adsorbent without destroying the adsorbent surface. In addition, the alum sludge-humic acids-alginate beads were applied to the real water samples collected from agricultural areas at Suphan Buri, Lopburi and Chachoengsao provinces. The adsorbent has a potential to remove paraquat from real water samples.

Department: Chemistry
Field of Study: Chemistry
Academic Year: 2017

Student's Signature ....
Advisor's Signature ....

ACKNOWLEDGEMENTS

I would like to express my gratitude to everyone who made the completion of this thesis possible. First of all, I am actually grateful to my thesis advisor, Associate Professor Dr. Apichat Imyim for his professional, valuable guidance, kindness, understanding and proofreading throughout this research. Moreover, I am also grateful to my committees: Associate Professor Dr. Vudhichai Parasuk, Associate Professor Dr. Pakorn Varanusupakul and Assistant Professor Dr. Woravith Chansuvarn for their valuable suggestion, useful guidance and comments for this thesis improvement.

This research cannot be completed without kindness, helpfulness and support from many people. Firstly, I am kindly grateful to Assistant Professor Dr. Fuangfa Unob for her suggestion, helpfulness and encouragement. Next, I would like to thank all of many people in Environmental Analysis Research Unit (EARU) for their grate support and encouragement especially to Miss Pimpimon Anekthirakun for her suggestion and helps. Furthermore, I would like to heartfelt thank my friends for their friendship, suggestion and kind support.

And indispensable, I am deeply grateful to my family for their love, care, endless supporting, understanding and especially for the encouragement throughout my life.

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LIST OF ABBREVIATION

g	Gram
mg	Milligrams
M	Molar
mg/L	Milligram per liter
mg/g	Milligram per gram
L/mg	Liter per milligram
min	Minutes
L/min	Liter per minutes
mL	Milliliters
nm	Nanometers
mol	mole
cm	Centimeters
w/v	Weight by volume
%	Percent
˚C	Degree Celsius

CHAPTER I

INTRODUCTION

1.1 Statement of problem

Paraquat herbicide is one of the most widely used to restrict weeds from growing in agriculture in several countries, especially Thailand. Paraquat is very fast-acting and non-selective contact herbicides, killing green plant tissue of grasses and weeds. Due to its high water solubility, it can easily spread into environment, particularly natural water resources such as surface water and ground-water. The water pollution problems affect on water resource and aquatic animals. Moreover, drinking water can also be contaminated by paraquat due to insufficient water treatment. High levels of paraquat can be accumulated in the human body via consuming, breathing and skin contact. In addition, the long-term effects can cause Parkinson’s disease, lung effects, and death [1-7].

In Thailand, paraquat is the top ten imported herbicide from 2007 to 2013 which is the most intensive used herbicide with 13,823,092 kg in 2013 [8]. Previous studies have shown that the contamination of paraquat in water is a serious problem. Paraquat contamination in surface water and ground water were found about 9.3-87.0 μg/L and 1.5-18.91 μg/L, respectively [9-12]. Consequently, the Pollution Control Department, Ministry of Natural Resources and Environment (PCD) of Thailand has set a limit of paraquat in water at 0.5 mg/L [13]. Thereby, the removal of paraquat is very important.

Traditional techniques for paraquat removal in water include UV treatment, chemical oxidation process, and sorption onto solid substances [14-21]. However, the limitation of some techniques is high cost, low selectivity and low efficiency. Thus, the adsorption technique is interesting due to rapidness, high removal efficiency and high selectivity.

Adsorption is one of the most common techniques used for decontaminating paraquat from water. The selection of appropriate adsorbents includes high surface area, high porosity and high selectivity which are important factors for adsorption process. Different types of adsorbents were used to remove paraquat from water such as zeolite [22, 23], spent diatomaceous earth [24], activated carbon [25, 26], bentonite [27], clay mineral [28, 29], montmorilonite [30], pipe deposits [31], humic acids [32, 33], and alginate beads [34-36]. Some adsorbents have high cost and complex preparation processes. Accordingly, humic acids and alginate beads can be used for paraquat removal because they are naturally available, easy to prepare, highly efficient, and environmentally friendly. Moreover, the sludge from tap water production process can be used as an absorbent material to improve the adsorption efficiency. It acts also as a solid support for humic acids to reduce the solubility of humic acids in water. Consequently, this work focused on using a low-cost, high surface area and eco-friendly adsorbent for the removal of paraquat from water. Therefore, humic acids supported on sludge from tap water production entrapped in alginate beads were used as adsorbents for a high performance of paraquat removal.

1.2 Objective and scope of the research

This research aimed to (1) prepare humic acids supported on sludge from tap water production entrapped in alginate beads for adsorption of paraquat herbicide in water and (2) study optimum conditions for adsorption of paraquat herbicide in water by using the prepared adsorbents.

The scope of this research firstly associated the preparation of adsorbent including humic acids supported on sludge from tap water production entrapped in alginate beads and the characterization of this adsorbent. Then, the parameters that influence paraquat adsorption efficiency including pH, adsorption kinetics and adsorption isotherms were evaluated to obtain the optimum conditions for the adsorption of paraquat in a batch method. Thereafter, effect of flow rate, breakthrough curve, and concentrations of eluent were investigated to find out the optimum conditions using a column system. Finally, the prepared adsorbent was applied to real water samples from agricultural areas in Thailand.

1.3 Benefits of this research

The humic acids supported on sludge from tap water production entrapped in alginate bead sorbent was achieved for the adsorption of paraquat herbicide in water.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Paraquat herbicide

Paraquat (1,1'-dimethyl-4,4'-bipyridinium dichloride) is a type of herbicide in bipyridinium group that is well known in the common trade name as Gramoxone. It is a biquaternary ammonium compound whose chemical structure is shown in Figure 2.1 which exhibits cationic properties on its structure [37].

Figure 2.1 Chemical structure of paraquat.

Paraquat is a non-selective compound that destroys the photosynthesis process of plants, by interfering with the exchange of electrons in this process and by inhibiting the reduction of NAPD to NADPH. This blockage results in the formation of free radicals that react with unsaturated lipids in the membrane. Subsequently, the organelle of the plant is destroyed causing to cell death [38]. Thus, it is used to control broad-leaf and narrow-leaf weeds in cultivated areas such as paddy field, cornfields, orchards, vegetable plots and banana plantations [39-41].

Paraquat is one of the main herbicides use on the agricultural areas that can be contaminated in water resource from spraying. Thus, paraquat from this processing is the major problem to environment and human health. Previous researches have shown that paraquat harms the organs of the exposed body such as eyes, nose, mouth, and skin. Until it is harmful to the lungs, heart, kidneys, and other organs [42-44]. Humans and animals often receive paraquat through direct skin contact, inhalation and ingestion. Direct contact with paraquat can cause skin irritation and burns, while paraquat inhalation causes fatal pulmonary disease. Moreover, paraquat ingestion causes burning in the mouth and throat, gastrointestinal irritation, abdominal pain, nausea, vomiting, diarrhea and death when swallowed in high doses [45-48]. Since paraquat can generate superoxide anions that can lead to induce reactive oxygen species (ROS) or free radicals. However, too much ROS cause oxidative stress that can lead to destroy the lipid membrane and results in cell death [49-52]. In addition, there are also studies in animals that confirmed the toxicity of paraquat which have shown that paraquat poisoning cause severe injury of lungs, kidneys and heart [53-56]. For this reason, the decontamination of paraquat is necessary. Adsorption technique is widely used because it is an efficient way for paraquat decontamination.

2.2 Adsorption technique

Adsorption is the process involved in adsorbing the substance (adsorbate) on the surface of the solid substrate (adsorbent) or within the adsorbent pore and without altering the structure of the adsorbent. The bond between the molecules or ions of the adsorbate and the adsorbent surface is an important factor in the classification of adsorption. The adsorption process is divided into two types; physical adsorption and chemical adsorption.

2.2.1 Physical adsorption or physisorption

Physical adsorption [57, 58] is the adsorption of adsorbate on the surface of the adsorbent by physical forces such as van der Waals force and electrostatic interaction. The mechanism is fast and reversible process. The adsorbate molecules can accumulate on the adsorbent surface forming multiple layers (multilayer adsorption). The number of layers is increased by the higher concentration of analyte in the solution.

2.2.2 Chemical adsorption or chemisorption

Chemical adsorption [59] is the adsorption of the adsorbate and the adsorbent via chemical reaction. The chemical bond occurs between electrons of analyte and the functional group on the adsorbent surface. Thus, this adsorption is irreversible. The adsorbate molecules can contact directly with the adsorbent surface and form a single-layer (monolayer adsorption).

2.2.3 Adsorption mechanisms

Adsorption mechanism is a mass transfer from the gas or liquid to the porous adsorbent. This process consists of three steps including;

I. External diffusion: the adsorbate molecules in the solution will transfer to the surface of the adsorbent.

II. Intraparticle diffusion: the adsorbate molecules at the external adsorbent surface diffuse into the pores of adsorbent.

III. Adsorption: the adsorbates are adsorbed on the adsorbent surface via physical and chemical force. The adsorption efficiency depends on the size and surface area of adsorbent, nature of adsorbate, temperature, contact time, pH of solution, and initial concentration of solution.

2.3 Adsorption kinetics

The rate of adsorption is investigated by the adsorption kinetics, which describes the adsorbates adsorbed onto the surface of adsorbent. The most widely used models of adsorption kinetics are pseudo-first and pseudo-second order kinetic models [31, 60-64].

2.3.1 Pseudo-first order kinetic model

The pseudo-first order equation is a model used to indicate the adsorption rate. The adsorption capacity can be calculated from this Equation 2.1 [65, 66]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{2.1}$$

Where q_t is the adsorption capacity of adsorbent at any time (mg/g)

q_e is the adsorption capacity of adsorbent at equilibrium (mg/g)

k_1 is the pseudo-first order rate constant (min^{-1})

When integrating the equation 2.1 with boundary condition $q_t = 0$ to $q_t = q_t$ and $t = 0$ to $t = t$ following Equation 2.2 and 2.3;

$$\ln\left(\frac{q_e}{(q_e - q_t)}\right) = k_1 t \tag{2.2}$$

$$q_t = q_e(1 - e^{-k_1 t}) \tag{2.3}$$

The linear equation can be written as Equation 2.4;

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{2.4}$$

The relation between $\log(q_e - q_t)$ and t is linear regression. The pseudo-first order rate constant (k_1) is obtained from the slope, while the adsorption capacity (q_e) can be calculated from the intercept of the linear regression.

2.3.1 Pseudo-second order kinetic model

The pseudo-second order equation is demonstrated by Equation 2.5 [29, 67, 68];

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{2.5}$$

Where q_t is the adsorption capacity of adsorbent at any time (mg/g)

q_e is the adsorption capacity of adsorbent at equilibrium (mg/g)

k_2 is the pseudo-second order rate constant (g mg^{-1} min^{-1})

When integrating the equation 2.5 with boundary condition $q_t = 0$ to $q_t = q_t$ and $t = 0$ to $t = t$ as expressed in Equation 2.6 and 2.7. The linear equation can be written as Equation 2.8;

$$q_t = \frac{q_e^2 k_2 t}{(1+q_e k t)} \tag{2.6}$$

$$q_t = \frac{t}{\left(\frac{1}{k_2 q_e^2}+\frac{t}{q_e}\right)} \tag{2.7}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{2.8}$$

The relationship between $\frac{t}{q_t}$ and t is a linear regression. The slope equals $\frac{1}{q_e}$ that can calculate the adsorption capacity (q_e) and intercept can find the pseudo-second order rate constant (k_2). This model can calculate the initial adsorption rate (h) when the value of $\frac{q_t}{t}$ approach to zero from Equation 2.9. Thus, the equation 2.8 can be rearranged as an initial adsorption rate form in Equation 2.10;

$$h = k_2 q_e^2 \tag{2.9}$$

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \tag{2.10}$$

Where h is the initial adsorption rate (mg g^{-1} min^{-1})

2.4 Adsorption isotherms

The adsorption isotherm is the study of the relationship between the adsorption amount and the concentration in solution, including to Langmuir and Freundlich isotherm models.

2.4.1 Langmuir isotherm model

The Langmuir isotherm model has been proposed in 1916, which is monolayer adsorption through the exact amount of adsorbate molecule, the exact position of adsorption, one adsorbate molecule in each adsorbent molecule and non-interaction between adjacent molecules. From the study of Langmuir isotherm at equilibrium, the relation between solution adsorption and adsorbent is expressed by Equation 2.11 and 2.12 [69];

$$q_e = \frac{q_m K_L C_e}{1+K_L C_e} \tag{2.11}$$

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \tag{2.12}$$

Where C_e is the equilibrium concentration of analyte in solution (mg/L)

q_e is the adsorption amount at equilibrium (mg/g)

q_m is the maximum adsorption amount (mg/g)

K_L is the Langmuir constant related to the free energy of adsorption (L/mg)

From equation 2.12, the relationship between $\frac{C_e}{q_e}$ and C_e is given by linear regression. The value of the maximum adsorption amount (q_m) and a constant related to the free energy of adsorption (K_L) can be calculated from the slope and the intercept of linear regression, respectively.

2.4.2 Freundlich isotherm model

The Freundlich isotherm model is a model that has been developed from Langmuir isotherm model which is a multilayer adsorption. The amount of adsorbate increasingly follows the higher concentration of sample which is the relationship between the amount of adsorbate and the concentration of sample as shown in Equation 2.13 and 2.14 [70];

$$q_e = K_F C_e^{1/n} \tag{2.13}$$

$$\log q_e = \log K_F + \frac{1}{n} \log q_e \tag{2.14}$$

Where	K_F	is the Freundlich constant related to adsorption capacity of adsorbent (mg/g)
	n	is the Freundlich constant related to adsorption intensity

From Equation 2.14, the relationship between $\log q_e$ and $\log C_e$ is a linear regression. The value of Freundlich constant related to adsorption intensity (n) and Freundlich constant related to adsorption capacity of adsorbent (K_F) can be calculated from the slope and the intercept of linear regression.

2.5 Humic acids

Humic acids are organic matters that receive from the degradation of microbiological, vegetative, and by the increased production of agricultural products. They distributed in soil and natural water. Humic acids are organic macromolecules with many properties and high complexity of structure. The structure of humic acids are various functional groups including carboxylic group, phenolic group, carbonyl group and alcoholic hydroxyl group as shown in Figure 2.2. The major components are carboxylic group and phenolic group. Moreover, the extraction of humic acids can be done using sodium hydroxide solution to dissolve the humic substance [71-75]. Then, humic acids are extracted into the layer of alkaline solution. After that, the solution can be precipitated with hydrochloric acid by adjusting the pH of the solution to be less than or equal to 2. Finally, the sediment of the humic acids can be separated by using centrifugation. Functional groups on the structure of humic acids can adsorb the positively charged molecule. From this property, humic acids are interesting to be used as a paraquat adsorbent.

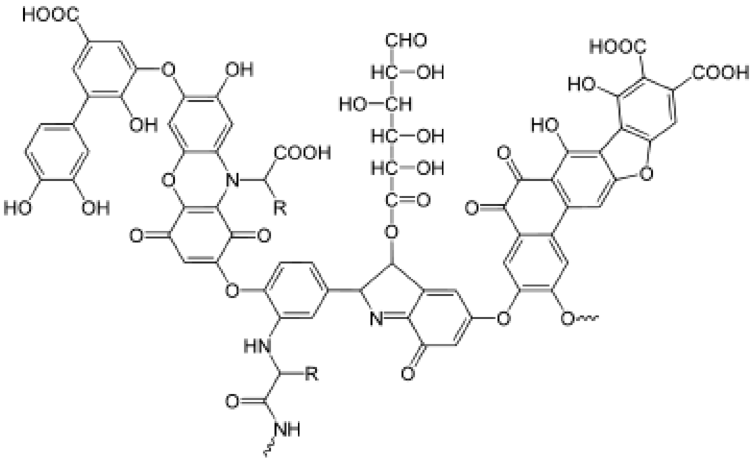

Figure 2.2 The structure of humic acids [76].

2.6 Alginate

Alginate or sodium alginate is a linear polysaccharide extracted from cell wall of brown seaweed such as *Laminaria digitata, Sargassum filipendula, Macrocystis pyrifera, Saccharina latissima, and Durvillea Antarctica* [77-81]. The alginate structure consists of β-d-mannuronic acid (M) and α-l-guluronic acid (G), so-called M-blocks and G-blocks, respectively. Some molecule of the structure is MG-blocks as shown in Figure 2.3 [82-84]. The proportion of copolymers and their structure determines the properties of alginate, such as the polymers have high G-blocks tend to be hard gel. However, the polymers have high M-blocks tend to be soft gel and have a wide gelation state. The sodium alginate can be cross-linked with calcium chloride to prepare gel structure in term of the egg-box model that presented in Figure 2.4 [85, 86]. Due to the fact that alginate can cross-link with divalent cations, it tends to be a stable hydrogel. This makes it easy to apply in the adsorption process. Therefore, alginate beads are attractive for adsorption of paraquat.

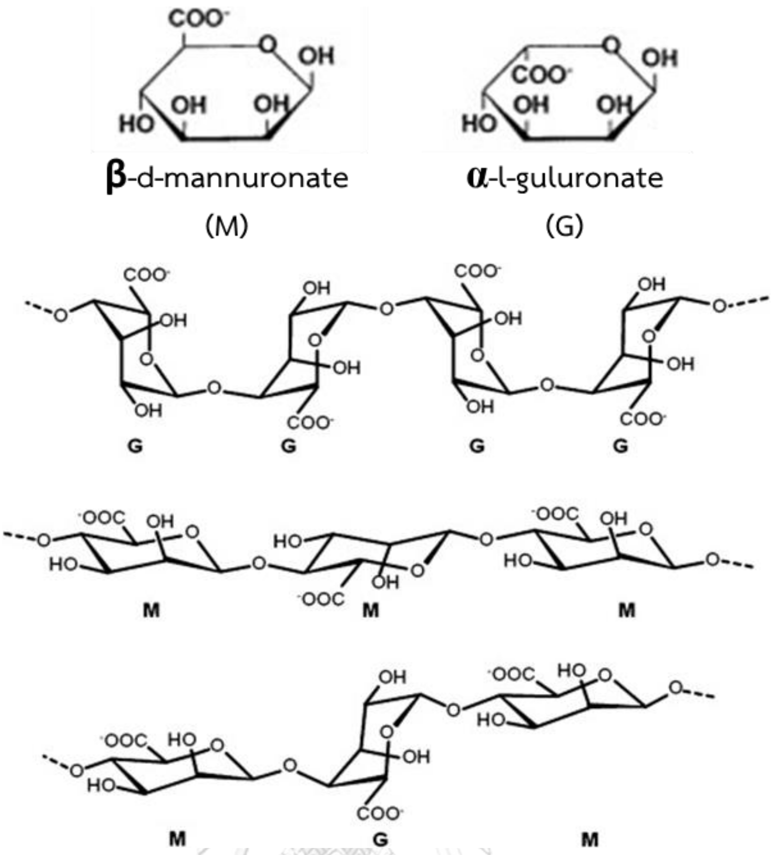

Figure 2.3 The structure of alginate [82, 83].

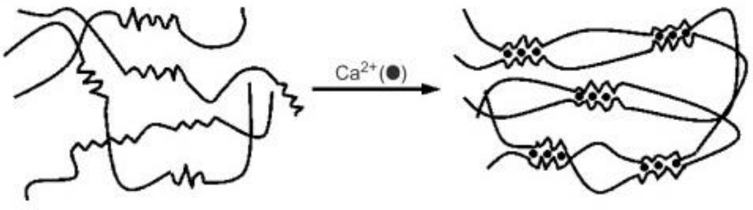

Figure 2.4 Alginate hydrogels prepared by calcium chloride cross-linking (egg-box model) [85].

2.7 Sludge from tap water production

Sludge or alum sludge is fraction of sludge products from water treatment process. In the precipitation process, the contaminants of raw water are pigments, organic, and inorganic in the tap water supply process widely used aluminium sulfate ($Al_2(SO_4)_3$•$18H_2O$), ferric chloride ($FeCl_3$•$6H_2O$), and polyaluminium chloride ($Al_2(OH)_3Cl_3$) as coagulants. When the coagulants is precipitated the contaminants in the tap water process, the sludge are accrued. The sludge is by-product resulted from the precipitation process, consists of aluminium hydroxide ($Al(OH)_3$) and ferric hydroxide ($Fe(OH)_3$). The aluminium hydroxide formation can be explained by the following chemical reaction [87-90].

$$Al_2(SO_4)_3 \cdot 18H_2O + 3Ca(OH)_2 \longrightarrow 3CaSO_4 + 2Al(OH)_3 + 18H_2O$$

And the ferric hydroxide can be described by a chemical reaction as follows;

$$Fe^{3+} + OH^- \longrightarrow Fe(OH)_3$$

Sludge is high porous and strong affinity for both cationic and anionic species. Thus, the sludge obtained from the tap water production has been utilized to provide many benefits. Most research uses sludge from tap water production as an adsorbent for the removal of phosphorus [91-94], heavy metals [95, 96], and glyphosate herbicide [97]. The sludge is interesting for low cost adsorbent of paraquat. In this research, the sludge from Metropolitan Waterworks Authority, Bangkhen, Thailand was used to be paraquat adsorbent.

Figure 2.5 Sludge from Metropolitan Waterworks Authority, Bangkhen, Thailand.

2.8 Literature review

The appropriate adsorbent materials for paraquat adsorption should be highly efficient, easy to prepare, naturally available, and environmentally friendly. Paraquat is a cationic herbicide that can be adsorbed with negatively charged surfaces of some adsorbents. Therefore, paraquat adsorbent should have negative charge on the structure. Humic acids are attractive for use as an adsorbent because there are functional groups that represent negative charges including carboxylate and phenolate. Previous researches have reported the use of humic acids as an adsorbent for paraquat removal. For example, Brigante et al. [32] investigated the effect of humic acids (HA) on paraquat adsorption by comparison between goethite adsorbent and HA-goethite adsorbent. They found that the adsorption of paraquat using HA-goethite is better than goethite because negatively charged groups of humic acids can adsorb the cationic herbicide. Iglesias et al. [33] studied the adsorption of paraquat with goethite and goethite modified with humic acids. The goethite adsorbent contains iron oxides on the structure, it did not almost adsorb paraquat at pH 4 and only slightly adsorb at pH 10 even with negative charge on the structure. While, the goethite modified with humic acids adsorbent could adsorb paraquat well at pH 4 but it also adsorbed paraquat less than bare humic acids. Because humic acids required a number of functions to bond with goethite, the number of functional groups in paraquat is decreased. Compared between goethite, humic acids, and goethite modified with humic acids, it was found that humic acids adsorbed paraquat the best, followed by goethite with humic acids and goethite could slightly adsorb paraquat.

Other adsorbent interesting for paraquat removal is alginate because inexpensive, easy way to prepare and environmentally friendly. Moreover, it can also be a gel with a good stability. There are research studies on the use of alginate beads to paraquat adsorption. Silva *et al*. [34] studied the adsorption of paraquat with an alginate/chitosan nanoparticles adsorbent. They found that paraquat was adsorbed by the nanoparticles adsorbent containing alginate/chitosan. Cocenza *et al*. [98] studied the adsorption of paraquat using three types of adsorbents as alginate, chitosan, and chitosan/alginate. They found that alginate and chitosan/alginate were good adsorbent of paraquat. In addition, alginate could also be used as an adsorbent for other herbicides for example; Moraes *et al*. [36] studied the adsorption of diquat, difenzoquat, and clomazone by using an alginate, chitosan, and chitosan/alginate adsorbents. They found that diquat and difenzoquat were well adsorbed by alginate and chitosan/alginate because the electrostatic interaction can occur between the herbicide and the adsorbent.

Furthermore, sludge from tap water production, which is by-product from tap water production process. The structure consists of aluminum and ferric hydroxides which is high porous and strong affinity for many kinds of species. So, the sludge from the production of tap water is used for maximum benefit. Previous researches have widely used sludge from tap water production as absorbent for the removal of phosphorus, heavy metals and glyphosate herbicide. Kim et al. [99] studies adsorption kinetics and adsorption isotherm of arsenite (As(III)) and arsenate (As(V)) in batch and column systems. They found that the arsenic adsorption of sludge reached equilibrium at 6-28 hours. The adsorption kinetics followed the pseudo-second-order kinetic model. The arsenic adsorption depended on porous and surface area of adsorbent. The adsorption isotherm of arsenic adsorption fitted to the Langmuir isotherm model. The adsorption capacity of As(III) and As(V) are 8.89-16.53 and 5.15-7.68 mg/g, respectively. The alum sludge preferred the adsorption of As(III) than As(V). From the results of the pH investigation, As (V) adsorbed on alum sludge decreasing with pH increased due to the fact that the sludge from tap water production could adsorb the negatively charged substances. Thus, humic acids can be immobilized on the sludge surface as well. Moreover, the sludge could also adsorb the positively charged substances. For example, Zhou et al. [95] studied the adsorption of Pb(II), Cr(III) and Cr(VI) from solution using alum sludge in a batch system. They found that the adsorption of Cr(III) > Pb(II) > Cr(VI) and adsorption kinetics followed the pseudo-second-order kinetic model. Zhou et al. [96] studies the adsorption of arsenic and selenium by alum sludge in batch method. They found that the optimal solution pH of Se(VI), Se(IV), As(V) and As(III) are 4.0, 5.0, 6.0 and 9.0, respectively. The alum sludge well adsorbed arsenic and selenium. Since the sludge from tap water production could adsorb the positively charged substances, it can adsorb paraquat as well. Thereby, the sludge from tap water production is attractive for using as a solid support for humic acids and alginate beads and used as paraquat adsorbent.

From the literature review, researchers are interested in preparing the adsorbent by using sludge from tap water production as a solid support to humic acids. The electrostatic interaction can occur between the negative charge on the structure of humic acids and the positive charge on the structure of paraquat. It can be a good adsorbent for paraquat. Moreover, alginate beads have been used to help the adsorbent to achieve good stability and ease of use. The preparation of humic acids supported on sludge from tap water production entrapped in alginate beads was done and the paraquat absorption conditions were optimized. It also reduces pollution in the environment caused by paraquat contaminated in water.

CHAPTER III

EXPERIMENTAL

3.1 Analytical instruments

All instruments used in this research are shown in Table 3.1.

Table 3.1 List of instruments

Instruments	Model, Manufacturer
UV-visible spectrophotometer	Agilent Hewlett Packard 8453
Fourier transform infrared spectrometer	Nicolet 6700
pH meter	Mettler Toledo
Stirrer	MS101, GEM
Oven	MEMMERT
Micropipette	BRAND
Analytical balance	SI-234, Denver Instrument Company
Overhead shaker	VELP scientifica ROTEX 6.8
Peristaltic pump	ISMATEC
Sonicator	Ultrasonic Steri-Cleaner
Vacuum pump	Buchi, V-700
Manifold	Supleco

The UV-visible spectrophotometer was used to determine the concentration of paraquat in solution. The operation condition for determination of paraquat is measured at wavelength 258 nm.

3.2 Chemicals

All chemicals in this work were used without further purification. They were listed in Table 3.2. Milli Q water (Millipore) was used for the preparation of analytical standards.

Table 3.2 List of chemicals

Chemicals	**Supplier**
Paraquat dichloride	Sigma-Aldrich
Sodium alginate	Union Chemical 1986, Thailand
Calcium chloride	Sigma-Aldrich
Humic acids (HA) sodium salt	Sigma-Aldrich
Hydrochloric acid 37%	Merck
Nitric acid 65%	Merck
Sodium hydroxide	Merck
Sodium chloride	Fisher Chemical

3.3 Preparation of solutions

3.3.1 Paraquat solution

Paraquat stock solution (10 mg/L) was prepared by dissolving 10.00 mg in Milli Q water. Then, Milli Q water was used to adjust the final volume in a 1000 mL volumetric flask. The stock solution was stored in a glass bottle.

3.3.2 Hydrochloric acid solutions

Hydrochloric acid solutions (0.01, 0.05, 0.1 and 1.0 mol/L) were prepared by diluting the concentrated hydrochloric acid (37%) with Milli Q water.

3.3.3 Nitric acid solutions

Nitric acid solutions (0.01, 0.05 and 0.1 mol/L) were prepared by diluting the concentrated nitric acid (65%) with Milli Q water.

3.3.4 Sodium hydroxide solutions

Sodium hydroxide solutions (0.1 and 1.0 mol/L) were prepared by dissolving an approximately amount of sodium hydroxide in Milli Q water.

3.3.5 Sodium chloride solutions

Sodium chloride solutions (0.1, 0.5 and 1.0 mol/L) were prepared by dissolving an approximately amount of sodium chloride in Milli Q water.

3.4 Preparation of sludge

The sludge from tap water production or alum sludge was supplied by Metropolitan Waterworks Authority (Bangkok, Thailand). The alum sludge was dried in an oven at 105 ˚C for 12 hours. Then dried alum sludge was crushed with a mortar. The particle size was collected using a 72-150 mesh sieve, resulting in a particle size of lower than 106 microns. After that, it was stored in a desiccator.

3.5 Preparation of adsorbent

The humic acids supported on sludge from tap water production entrapped in alginate beads or alum sludge-humic acids-alginate (AS-HA-AG) beads were prepared according to the reference method [100]. Firstly, 1% (w/v) sodium alginate was dissolved in Milli Q water under stirring for 2 hours. After that, alum sludge and humic acids with 1% (w/v) each were added to the sodium alginate solution. The solution was then stirred for 24 hours until the mixture solution was homogeneous. The homogeneous solution was dropped by the aid of a peristaltic pump into 1% (w/v) calcium chloride solution using a needle (0.8 mm diameter) to obtain small beads. The beads were washed several times with Milli Q water, and then allowed to dry in an oven for 24 hours at 45 °C. Finally, the adsorbent was kept in a desiccator.

3.6 Characterization of adsorbent

The functional groups of the humic acids supported on sludge from tap water production entrapped in alginate beads were identified with Attenuated Total Reflectance Fourier Transform Infrared Spectrometer (ATR-FTIR). The wavenumber range of 600 to 4000 cm-1. The spectra were measured using OMNIC program. The identification of the adsorbent was investigated and the structure of AS-HA-AG beads sorbent was compared with the structure of each material.

3.7 Optimization of adsorbent

3.7.1 Type of adsorbent

Four types of adsorbents including bare alginate beads (AG), humic acids-alginate beads (HA-AG), alum sludge-alginate beads (AS-AG), and alum sludge-humic acids-alginate (AS-HA-AG) beads were prepared. The three adsorbents were prepared with the same method as AS-HA-AG beads. After preparing the sodium alginate solution (1% w/v) was mixed with humic acids for HA-AG beads, alum sludge for AS-AG beads, and alum sludge and humic acids for AS-HA-AG beads with 1% (w/v) each. Then the homogeneous solution was used to fabricate beads with 1% (w/v) calcium chloride solution by using a needle (0.8 mm diameter) and a peristaltic pump. The beads were washed with Milli Q water and dried in an oven at 45 ˚C for 24 hours. Finally, the adsorbents were stored in a desiccator.

3.7.2 Amount of adsorbent

The adsorbents were prepared with the same method as AS-HA-AG beads. After preparing the sodium alginate solution, alum sludge and humic acids were then added to the solution by varying 1% and 2% (w/v) each. After that, the homogeneous solution was subjected to form small beads with 1% (w/v) calcium chloride solution by using a needle (0.8 mm diameter) and a peristaltic pump. The beads were washed several times with Milli Q water and dried in an oven for 24 hours at 45 ˚C. Finally, the adsorbent was kept in a desiccator.

3.7.3 Adsorption test

The adsorbents for paraquat adsorption including AG, HA-AG, AS-AG, AS-HA-AG-1 (1% (w/v) alum sludge and humic acids) and AS-HA-AG-2 (2% (w/v) alum sludge and humic acids) beads were studied. A 10.00 mL of 10 mg/L paraquat solution at pH 5 was pipetted into a test tube containing 0.01 g of each adsorbent and shaken for 24 hours at room temperature. Then, the solution was filtrated (0.45 µm nylon syringe filter membrane) and stored in a test tube. The paraquat concentration was determined by the UV-Visible spectrophotometer to calculate the adsorption efficiency and adsorption amount according to Equations 3.1 and 3.2, respectively.

$$Adsorption\ efficiency\ (\%) = \frac{C_i - C_e}{C_i} \times 100 \tag{3.1}$$

$$q = \frac{(C_i - C_e)v}{m} \tag{3.2}$$

Where C_i is the initial concentration of paraquat in aqueous solution (mg/L)

C_e is the equilibrium concentration of paraquat in aqueous solution (mg/L)

q is the adsorption capacity or adsorption amount (mg/g)

v is the volume of paraquat solution (mL)

m is the mass of the adsorbent (g)

3.8 Batch study

3.8.1 Effect of pH

The effect of pH was firstly studied by varied the pH values of paraquat solution. The pH of 10 mg/L paraquat solution was adjusted to a desired pH value at 1-10 by using either 1 mol/L HCl or 1 mol/L NaOH solution. Then, 10.00 mL of paraquat was pipetted into a test tube containing 0.01 g of AS-HA-AG beads and shaken for 24 hours at room temperature. After that, the solution was filtrated and kept in a test tube. The concentration of paraquat was determined by the UV-Visible spectrophotometer.

3.8.2 Adsorption kinetics

The effect of adsorption time of paraquat adsorption was investigated by varying the contact times in the range of 15 minutes to 24 hours. The pH of 10 mg/L paraquat solution was kept constant at pH 5. Ten milliliters of paraquat solution was pipetted into a test tube containing 0.01 g of AS-HA-AG beads and shaken at room temperature. Then, the solution was filtrated and stored in a test tube. The concentration of paraquat was determined by the UV-Visible spectrophotometer.

3.8.3 Adsorption isotherms

The adsorption isotherms were studied by varied the initial paraquat concentration of 10 to 500 mg/L. The pH of 10 mg/L paraquat solution was kept constant at pH 5. Ten milliliters of paraquat solution was pipetted into a test tube containing 0.01 g of AS-HA-AG beads. The mixture was shaken at room temperature. Then, the solution was filtrated and kept in a test tube. The concentration of paraquat was determined by the UV-Visible spectrophotometer. The results were fitted with Langmuir or Freundlich adsorption isotherm models to find the adsorption behavior of paraquat on AS-HA-AG beads.

3.9 Column study

In this experiment, the homemade cylinder column was used to study the efficiency of paraquat removal. The first pack column process, the cotton ball was inserted into the bottom of the column to prevent the loss of the adsorbent. Then the column was packed with the AS-HA-AG beads adsorbent at the height of 2 cm (2.35 g adsorbent). The homemade cylinder column used a 10 mL of disposable syringe (NIPRO) to study the optimum conditions in the column system as presented in Figure 3.1.

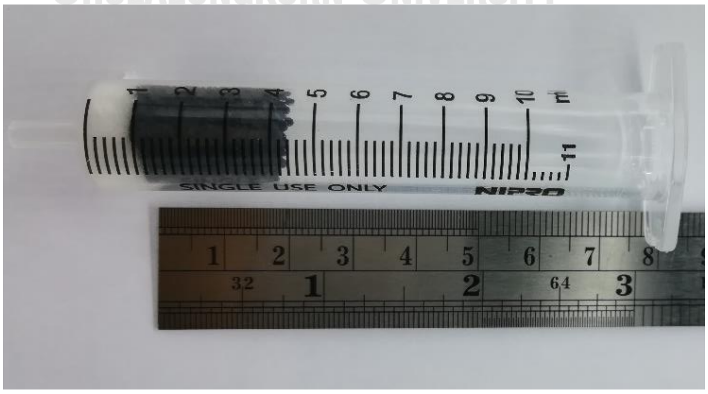

Figure 3.1 Photograph of the homemade cylinder column.

3.9.1 Effect of flow rate

The effect of flow rate of the paraquat solution was investigated by varying the flow rates at 0.5, 1, 2, 3 and 4 mL/min. The column was pre-calibrated with Milli Q water. After that, 50 mL of 10 mg/L paraquat solution (pH 5) was passed through the column that be controlled by using a manifold connected to a vacuum pump. Then, the filtrate solution was collected and the amount of paraquat was determined by the UV-Visible spectrophotometer.

3.9.2 Effect of eluent concentration

The effect of eluent concentration was investigated by using different eluent types and concentrations. The different eluents including HCl (0.01, 0.05 and 0.1 mol/L), HNO3 (0.01, 0.05 and 0.1 mol/L), and NaCl (0.1, 0.5 and 1.0 mol/L) were used. The optimal flow rate of paraquat solution was 3 mL/min. Fifty milliliters of 10 mg/L paraquat solution (pH 5) was passed through the column. After that, paraquat was eluted by passing the eluent solution through the column. The paraquat concentration was measured by the UV-Visible spectrophotometer.

3.9.3 Breakthrough curve

The column efficiency was determined by passing the paraquat solution continuously into the column containing the adsorbent. Each 10 mL of 1000 mg/L paraquat solution was added onto the adsorbent. Then, 10, 20, 30, 40 and each 50 mL of the paraquat solution was stored and determined the paraquat concentration using the UV-Visible spectrophotometer. The graph was plotted by the ratio of the remaining paraquat solution and the initial paraquat concentration (C_i/C_0) against the volume of the paraquat solution entering the adsorption process as defined for the breakthrough curve.

3.9.4 Regeneration and reusability of the column

Regeneration and reusability of the column were investigated. Sodium chloride was used as eluent for the column regeneration. Step 1, 50 mL of 10 mg/L paraquat solution (pH 5) was added into the column. Step 2, 50 mL of 1.0 mol/L sodium chloride was passed through the column under flow rate at 3 mL/min. After that, step 1 and step 2 were repeated again until the column could not be reusable. The remaining paraquat concentration was determined by the UV-Visible spectrophotometer.

3.10 Application in real water samples

Real water samples were collected from different agricultural areas including Suphan Buri, Lopburi, and Chachoengsao Province in Thailand. The removal of paraquat in real water samples were studied in the column system. Firstly, the real water samples were filtered to remove the sediment. After that, the filtrate water was spiked with paraquat in a level of 10 mg/L. The pH of spiked and non-spiked water samples were adjusted to pH 5. Then, 50 mL of water sample was passed through the column containing the adsorbent layer height at 2 cm. The flow rate of water sample was 3 mL/min. Finally, the remaining concentration of paraquat was analyzed by the UV-Visible spectrophotometer.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterization of adsorbent

In this research, the sludge from tap water production received from Metropolitan Waterworks Authority (Bangkok, Thailand). The sludge was dried in an oven at 105 °C for 12 hours. Then crushed with mortar and sieved with 72-150 mesh sieve, which resulted in a particle size of lower than 106 microns. The sludge was light brown powder. After that, the sludge was used to prepare an adsorbent that mixed with humic acids and sodium alginate. After mixing all three components, the mixture solution was dropped into calcium chloride solution. The adsorbent was small black beads containing the humic acids supported on sludge from tap water production entrapped in alginate beads, so-called alum sludge-humic acids-alginate (AS-HA-AG) beads adsorbent. The picture of the AS-HA-AG beads adsorbent was shown in Figure 4.1. The average size of beads is about 1 mm.

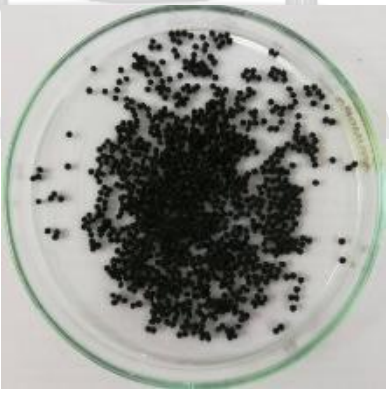

Figure 4.1 The picture of AS-HA-AG bead adsorbent.

The AS-HA-AG bead adsorbent was characterized by using an ATR-FTIR spectrometer. The spectra of sludge from tap water production, humic acids, sodium alginate, and AS-HA-AG bead adsorbent were shown in Figure 4.2 (a), (b), (c) and (d), respectively. These FTIR spectra were represented the characteristics of functional groups on the adsorbent.

The spectrum of AS-HA-AG in Figure 4.2 (d) was suggested that the adsorbent containing the sludge from tap water production, humic acids, and sodium alginate. The spectrum peak at 3696 cm^{-1} showed the C-H stretching like the spectra of alum sludge in Figure 4.2 (a). That was the sludge contained organic matters as component. Meanwhile, the spectrum represented broad peak of O-H groups at 3346 cm^{-1} similar to the spectra of humic acids and alginate in Figure 4.2 (b) and (c), respectively. Then the spectrum showed C-H stretching of aliphatic hydrocarbon groups at 2919 and 2850 cm^{-1} same as the spectra of humic acids in Figure 4.2 (b). The peak at 1592 and 1413 cm^{-1} showed the C=C stretching in aromatic ring on the structure similar to the peak of humic acids. Finally, the spectrum represented the Si-O-Si stretching band of silica on the structure at 1004 cm^{-1} same as the alum sludge spectrum. Thereby, the combination of alum sludge, humic acids and alginate can give a new adsorbent.

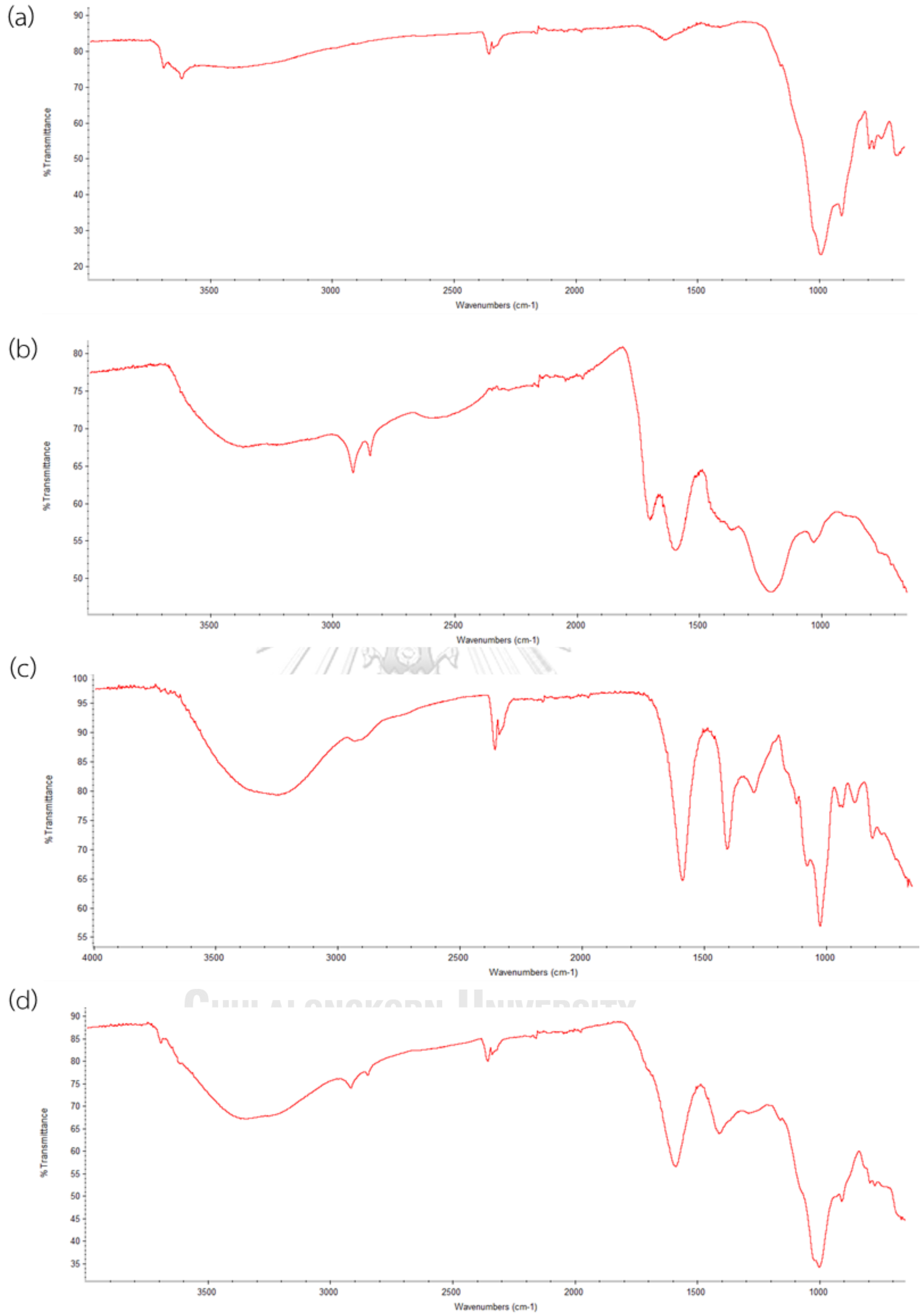

Figure 4.2 FTIR spectra of (a) sludge from tap water production, (b) humic acids, (c) sodium alginate, and (d) AS-HA-AG bead adsorbent.

4.2 Optimization of adsorbents

4.2.1 Type of adsorbents

In this experiment, four adsorbents were prepared by using different materials including alum sludge, humic acids and sodium alginate. The different adsorbents in bead type were formed in calcium chloride. The bare alginate bead adsorbent was white as shown in Figure 4.3 (a). The humic acids-alginate bead adsorbent was black as presented in Figure 4.3 (b). Meanwhile, Figure 4.3 (c) showed brown of the alum sludge-alginate bead adsorbent and Figure 4.3 (d) showed black beads of the alum sludge-humic acids-alginate bead adsorbent. After that, the adsorbents were used to test the efficiency of paraquat adsorption in solutions.

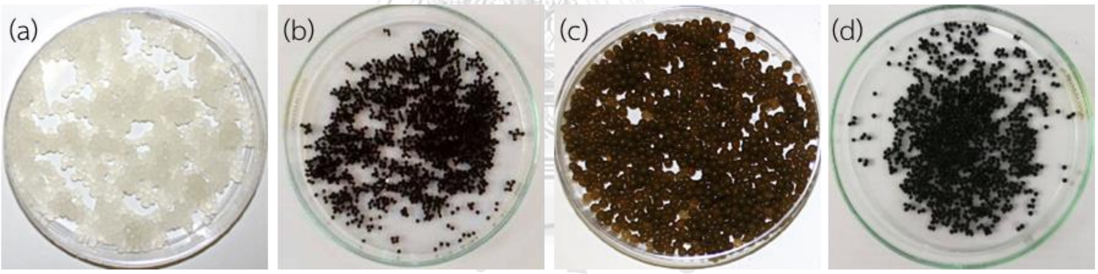

Figure 4.3 The pictures of (a) bare alginate beads, (b) humic acids-alginate beads, (c) alum sludge-alginate beads and (d) alum sludge-humic acids-alginate beads.

4.2.2 Amount of adsorbent

The adsorbent preparation of this experiment was done by changing the amount of alum sludge and humic acids. The amount of alginate was remained 1% (w/v), while the amount of sludge and humic acids were changed from 1% to 2% (w/v). The results showed that the two adsorbents with different compositions of AS-HA-AG-1 (1% (w/v) of AS and HA) and AS-HA-AG-2 (2% (w/v) of AS and HA) bead adsorbents were small black beads. After that, the adsorbents were used to evaluate the efficiency of paraquat adsorption in solutions.

4.2.3 Adsorption test

The adsorption of paraquat was tested by using AG, HA-AG, AS-AG, AS-HA-AG-1 and AS-HA-AG-2 bead adsorbents. The adsorption efficiency and adsorption capacity were calculated by Equations 4.1 and 4.2, respectively.

$$Adsorption\ efficiency\ (\%) = \frac{C_i - C_e}{C_i} \times 100 \quad (4.1)$$

$$Adsorption\ capacity\ (q) = \frac{(C_i - C_e)v}{m} \quad (4.2)$$

Where C_i is the initial concentration of paraquat in aqueous solution (mg/L)

C_e is the equilibrium concentration of paraquat in aqueous solution (mg/L)

q is the adsorption capacity or adsorption amount (mg/g)

v is the volume of paraquat solution (mL)

m is the mass of the adsorbent (g)

The results showed that all adsorbents could adsorb paraquat in solutions. The adsorption efficiency and adsorption capacity were presented in Figure 4.4. The adsorption efficiency of AG, HA-AG, AS-AG, AS-HA-AG-1 and AS-HA-AG-2 beads were 67.4, 75.1, 50.3, 93.6 and 91.6%, respectively. The adsorption capacities were 6.7, 7.5, 5.0, 9.3 and 9.1 mg/g for AG, HA-AG, AS-AG, AS-HA-AG-1 and AS-HA-AG-2 beads, respectively. The AS-HA-AG beads provided the highest adsorption efficiency and adsorption capacity. When increasing the amount of alum sludge and humic acids, the paraquat adsorption was insignificantly slightly decreased. This result reveals that increasing the amount of additives did not significantly different effect on the adsorption efficiency.

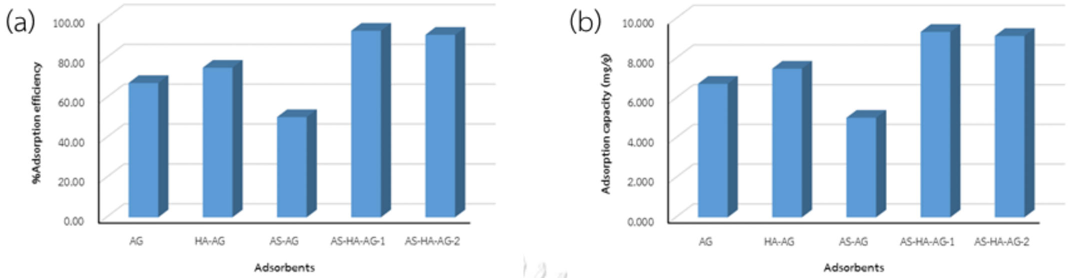

Figure 4.4 (a) Adsorption efficiency and (b) adsorption amount of paraquat by the five adsorbents.

In this research, the AS-HA-AG beads were used to be the adsorbent of paraquat due to the fact that the adsorbent contains humic acids and alum sludge that were encapsulated within the alginate beads. Humic acids play an important role in binding with paraquat in solution because of the functional groups include carboxylic and phenolic groups in the structure that can represent negatively charged functional groups. The electrostatic interaction occurred between the negatively charged humic acids and the positively charged paraquat structure as presented in Figure 4.5. Meanwhile, the alum sludge can bind with the negative charge that can adsorb humic acids as well. Moreover, the alum sludge might be also help to increase paraquat adsorption. In addition, alginate can adsorb paraquat as well. The combination of alum sludge, humic acids, and alginate shows a good potential to be a new adsorbent which was effective in paraquat removal.

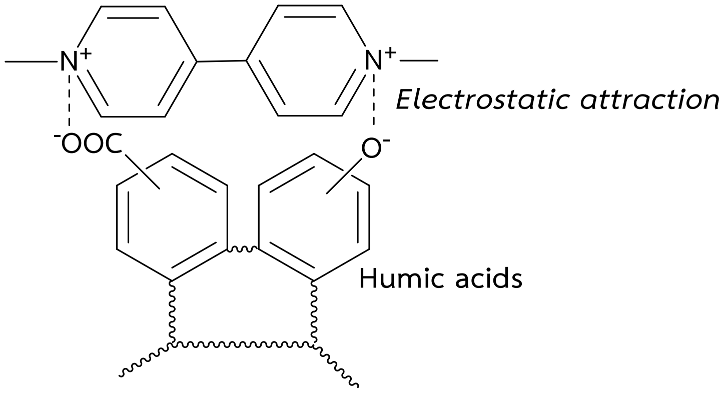

Figure 4.5 Electrostatic interactions between paraquat and humic acids.

4.3 Batch study

4.3.1 Effect of pH

The effect of pH was studied with different pH values from 1 to 10. The experiment was carried out at 10 mL of 10 mg/L paraquat solution. The adsorbent was 0.01 g of AS-HA-AG beads. The adsorbent was shaken in paraquat solution for 24 hours, after that the paraquat amount was measured by the UV-Visible spectrophotometer. The adsorption efficiency of paraquat was calculated according to Equation (4.1). The result was shown in Figure 4.6 that was presented the paraquat adsorption by AS-HA-AG beads at different pH values. The AS-HA-AG beads can adsorb paraquat in highly acidic conditions (pH 1-3) less than in slightly acidic conditions (pH 5-6). In highly acidic conditions, carboxylic and phenolic groups on humic acids structure cannot be negatively charged, resulting in less paraquat adsorption. However, the paraquat adsorption efficiency increased with increasing pH. The highest adsorption efficiency of paraquat was 95.5% at pH 5. In basic conditions (pH 8-10), the paraquat adsorption efficiency was slightly reduced. The optimal pH of paraquat adsorption was thus at pH 4-10 but in this experiment the pH 5 was chosen for further experiments due to the closeness of the pH of water from agricultural areas and surface water.

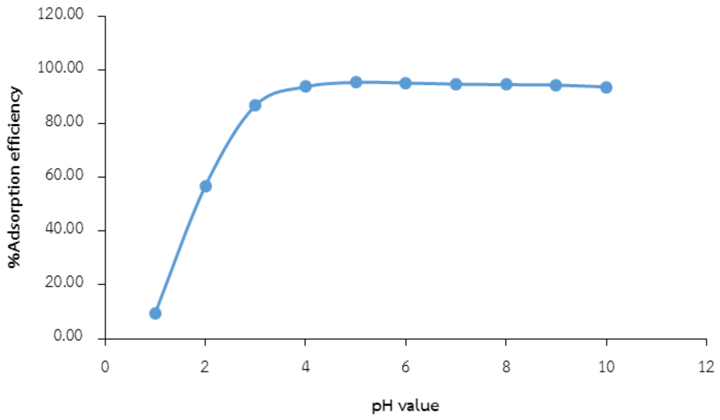

Figure 4.6 Effect of pH on the adsorption of paraquat by the AS-HA-AG beads.

4.3.2 Effect of adsorption time

The effect of adsorption time was investigated. The adsorption time was studied at 15, 30, 45, 60, 75, 90, 105, 120, 180, 240, 480, 720, 960, 1,080 and 1,440 minutes. The initial concentration of paraquat was 10 mg/L at pH 5. Then, 0.01 g of AS-HA-AG beads was shaken in 10 mL of paraquat solution at room temperature. The paraquat amount was analyzed by the UV-Visible spectrophotometer. The adsorption efficiency of paraquat was shown in Figure 4.7. The AS-HA-AG beads adsorbed more paraquat when contact time increased. At initial time, paraquat was adsorbed rapidly by AS-HA-AG beads. The equilibrium time of paraquat adsorption was 180 minutes. After that, the adsorption rate was studied by using adsorption kinetics.

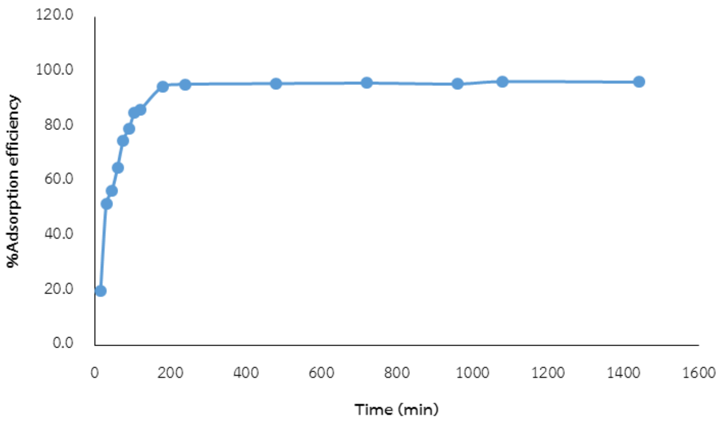

Figure 4.7 Effect of adsorption time for adsorption of paraquat by the AS-HA-AG beads.

4.3.3 Adsorption kinetics

The adsorption rate was studied by the adsorption kinetics. The results were fitted to linear equations of the pseudo-first and pseudo-second order kinetic models according to Equation (4.3) and (4.4), respectively.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{4.3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4.4}$$

$$h = k_2 q_e^2 \tag{4.5}$$

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \tag{4.6}$$

Where	q_t	is the adsorption capacity of adsorbent at any time (mg/g)
	q_e	is the adsorption capacity of adsorbent at equilibrium (mg/g)
	k_1	is the pseudo-first order rate constant (min^{-1})

k_2 is the pseudo-second order rate constant (g mg^{-1} min^{-1})

h is the initial adsorption rate (mg g^{-1} min^{-1})

The parameters of the pseudo-first and pseudo-second order kinetic models for adsorption of paraquat were presented in Table 4.1 and 4.2, respectively. The results of pseudo-first and pseudo-second order kinetic plots for paraquat adsorption were shown in Figure 4.8 and 4.9, respectively.

Table 4.1 Parameters of the Pseudo-first order kinetic for adsorption of paraquat.

Paraquat solution	Equation	R^2	k_1 (min^{-1})	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)
Paraquat	y = -0.0089x + 0.9677	0.9840	0.0205	9.45	9.28

Table 4.2 Parameters of the Pseudo-second order kinetic for adsorption of paraquat.

Paraquat solution	Equation	R^2	k_2 (min^{-1})	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)
Paraquat	y = 0.0708x + 5.0029	0.9201	0.0010	9.45	14.12

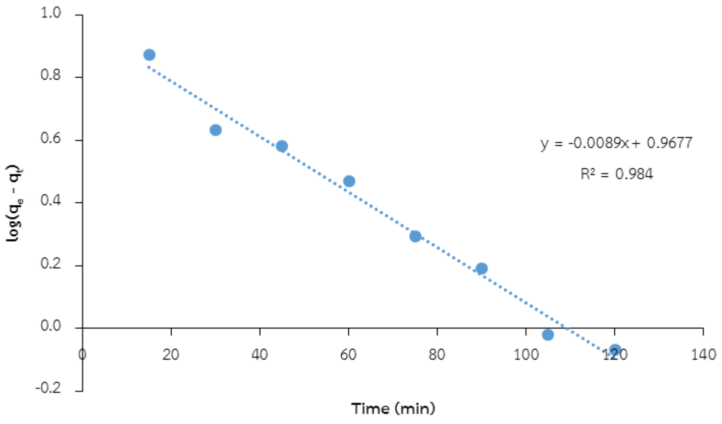

Figure 4.8 Pseudo-first order kinetic plot of paraquat adsorption.

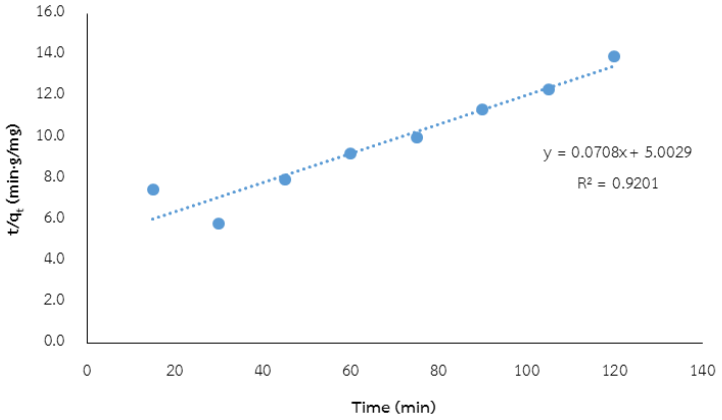

Figure 4.9 Pseudo-second order kinetic plot of paraquat adsorption.

From Figure 4.8 and 4.9, both graphs showed the linear plot of pseudo-first and pseudo-second order kinetics of paraquat adsorption by AS-HA-AG beads, it was found that the paraquat adsorption was close to the pseudo-first order kinetics. Moreover, the results obtained from Table 4.1 and 4.2 showed that the adsorption of paraquat by AS-HA-AG beads was fitted to the pseudo-first order kinetics. The correlation coefficient (R^2) of the pseudo-first and pseudo-second order kinetics were 0.9840 and 0.9201, respectively. The pseudo-first order rate constants (k_1) that calculated from the slope of the graph was 0.0205 min^{-1}. The adsorption capacity of adsorbent at equilibrium from the calculation ($q_{e,cal}$) of pseudo-first order kinetics was 9.28 mg/g which is close to the experiment result ($q_{e,exp}$) that was 9.45 mg/g.

The adsorption based on the pseudo-first order reaction showed that the rate of adsorption depends on the initial concentration of paraquat. The amount of adsorption increased when increasing the initial concentration of paraquat.

4.3.4 Adsorption isotherms

The adsorption isotherm is a study of adsorption behavior of adsorbents. In this experiment, the adsorption isotherm was investigated by varying the initial concentration of paraquat. The initial concentration was studied at 10, 20, 40, 60, 80, 100, 150, 200, 250, 300, 400 and 500 mg/L. The pH of paraquat solution was kept constant at pH 5. Then, 0.01 g of AS-HA-AG beads was shaken in 10 mL of paraquat solution for 24 hours. The paraquat amount was analyzed by the UV-Visible spectrophotometer. The results were fitted with the Langmuir or the Freundlich adsorption isotherm models as expressed by Equations (4.7) and (4.8), respectively.

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \tag{4.7}$$

$$\log q_e = \log K_F + \frac{1}{n} \log q_e \tag{4.8}$$

Where	C_e	is the equilibrium concentration of paraquat in solution (mg/L)
	q_e	is the adsorption amount at equilibrium (mg/g)
	q_m	is the maximum adsorption amount (mg/g)
	K_L	is the Langmuir constant related to the free energy of adsorption (L/mg)
	K_F	is the Freundlich constant related to adsorption capacity of adsorbent (mg/g)
	n	is the Freundlich constant related to adsorption intensity

The adsorption isotherm which is the relationship between the remaining paraquat concentration and the adsorption amount of paraquat was shown in Figure 4.10. When increasing the concentration of the paraquat solution, the amount of paraquat that adsorbed on the adsorbent surface increased until the adsorbent could not adsorb paraquat. This adsorption is monolayer adsorption so-called "Langmuir adsorption isotherm". The maximum adsorption amount (q_m) can be obtained from the calculation by Equation (4.7). The linear plot of the Langmuir adsorption isotherm was presented in Figure 4.11. The parameters of the Langmuir isotherm for paraquat adsorption were shown in Table 4.3. Meanwhile, the adsorption of paraquat on the adsorbent surface can be increased with higher concentration of the paraquat solution. This adsorption is Freundlich adsorption isotherm which is multilayer adsorption. The linear plot of the Freundlich isotherm was illustrated in Figure 4.12. Parameters of the Freundlich isotherm for paraquat adsorption were presented in Table 4.4.

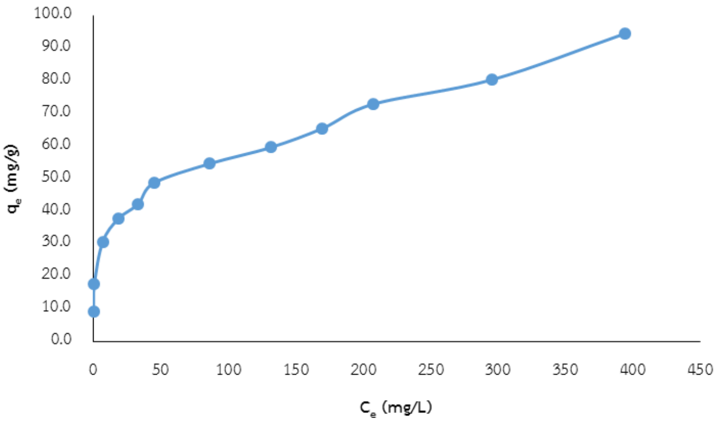

Figure 4.10 The relation between paraquat concentration at equilibrium and the adsorption amount for paraquat.

Table 4.3 Parameters of the Langmuir isotherm for adsorption of paraquat.

Paraquat solution	Equation	R^2	$q_{m,exp}$ (mg/g)	$q_{m,cal}$ (mg/g)	K_L (L/mg)
Paraquat	y = 0.0110x + 0.3623	0.9585	94.5	90.9	0.0304

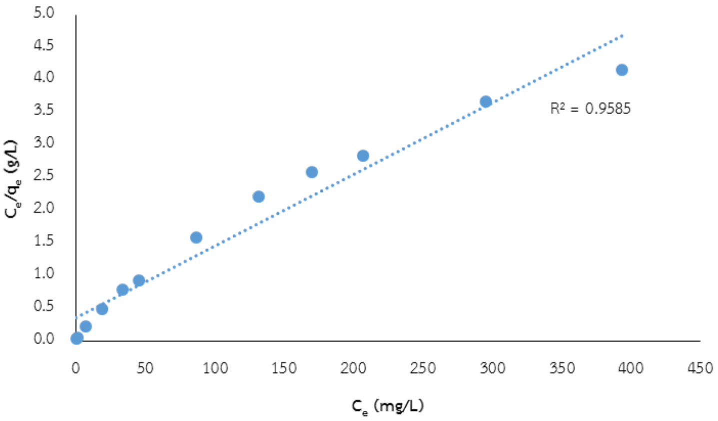

Figure 4.11 Langmuir isotherm plot of paraquat.

Table 4.4 Parameters of the Freundlich isotherm for adsorption of paraquat.

Paraquat solution	Equation	R^2	K_F (mg/g)	n
Paraquat	y = 0.2962x + 1.1814	0.9796	15.2	3.376

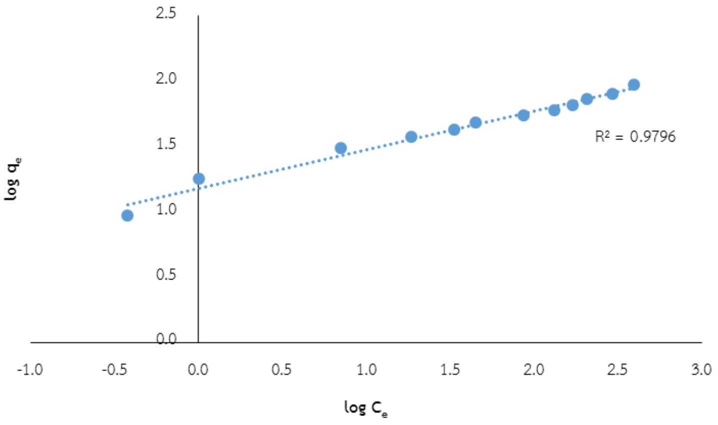

Figure 4.12 Freundlich isotherm plot of paraquat.

From Figure 4.11 and 4.12, both graphs showed the linear plot of the Langmiur and the Freundlich isotherm of paraquat adsorption by AS-HA-AG beads, it was found that the paraquat adsorption isotherm was close to the Langmuir isotherm at lower concentration. Meanwhile, the adsorption isotherm of paraquat obeyed Freundlich adsorption isotherm at higher concentration. Furthermore, the results from Table 4.3 and 4.4 showed that the adsorption behavior was best fitted to the Freundlich isotherm. The correlation coefficient (R^2) of the Freundlich isotherm was 0.9796 that close to 1. The adsorption of paraquat by AS-HA-AG beads was multilayer adsorption due to that the component of the adsorbent have many active sites such as carboxylic and phenolic groups on humic acids surface. Moreover, alum sludge and alginate can also adsorb paraquat as well. The adsorption of paraquat on AS-HA-AG bead surface can increased with higher paraquat concentrations. In addition, the maximum adsorption amount from the experiment ($q_{m,exp}$) was more than 94.5 mg/g. The adsorption amount of paraquat by various adsorbents from the literature was compared to the obtained result of this study as showed in Table 4.5. It can be seen obviously that the prerpared adsorbent showed much higher adsorption efficiency than the others.

Table 4.5 Adsorption amount of some adsorbent for paraquat adsorption.

Type of adsorbent	Adsorption amount (mg/g) of paraquat	References
Alum sludge-humic acids-alginate beads	94.5 (pH 5)	This research
Humic acids-goethite adsorbent	2.29 (pH 4.5) 2.95 (pH 6.0)	[32]
Alginate/chitosan nanoparticles	2.03 (pH 7.4)	[34]
Chitosan/alginate membrane	8.17 (pH 6.5)	[98]

4.4 Column study

In order to simplify the application of the adsorbent, the paraquat adsorption was carried out in a column system. The AS-HA-AG beads were packed into a homemade cylinder column at a layer height of 2 cm (2.35 g adsorbent). The paraquat solutions was passed through the column by using a manifold connected to a vacuum pump as presented in Figure 4.13.

Figure 4.13 Photograph of column system for paraquat removal.

4.4.1 Effect of flow rate

The effect of flow rate of the paraquat solution was firstly investigated in the column system. The effect of flow rate was studied at 0.5, 1, 2, 3 and 4 mL/min. Fifty milliliters of 10 mg/L paraquat solution at pH 5 was passed through the homemade cylinder column. The filtrate solution was kept and the paraquat amount was analyzed by the UV-Visible spectrophotometer.

The results were illustrated in Table 4.6 and Figure 4.14. From the results, the percent removal of paraquat was 83-91% at any flow rate. The paraquat removal reduced when the flow rate increased because the paraquat solution was passed the column with high velocity, reducing the contact time with the adsorbent. The adsorption of paraquat on the surface of AS-HA-AG was not completed. The optimum flow rate for the column adsorption was 3 mL/min and the maximum paraquat removal was 91.3%.

Table 4.6 Effect of flow rate of paraquat adsorption by AS-HA-AG beads.

Flow rate (mL/min)	Adsorption amount (mg/g)	%paraquat removal
0.5	0.17±0.02	87.07±0.80
1	0.17±0.01	86.52±0.67
2	0.18±0.02	88.82±0.83
3	0.18±0.01	91.27±0.68
4	0.16±0.03	83.40±1.33

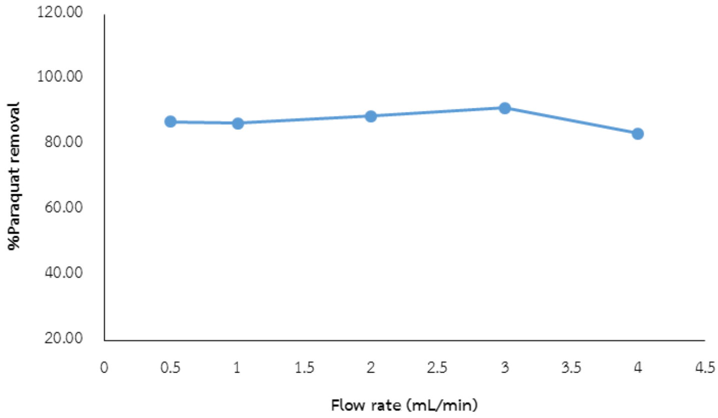

Figure 4.14 The relation between the flow rate and the percent removal of paraquat.

4.4.2 Effect of eluent concentration

In this experiment, hydrochloric acid and nitric acid were used to elute paraquat. The concentration of the eluent was studied at 0.01, 0.05 and 0.1 mol/L. 50 mL of 10 mg/L paraquat solution was passed through the column under the flow rate 3 mL/min. Five milliliters of eluent at any concentration was passed through the column. The remaining concentration of paraquat was collected and determined by the UV-Visible spectrophotometer. The results were presented in Table 4.7 and 4.8 and Figure 4.15.

From the results, the percent elution of paraquat increased with increasing concentration of eluent. However, the use of acids as eluent of paraquat elution can cause some releasing of humic acids that was related to higher percent elution than removal of paraquat. Since the functional group on the surface of the adsorbent was destroyed by H+ of acid eluent. The eluent without H+ was interested to use as an eluent of paraquat elution that was sodium chloride. Then, sodium chloride was used to the eluent for paraquat elution.

Table 4.7 Amount of paraquat adsorption and elution using HCl and HNO_3.

Eluents	Adsorption amount (mg/g)	Elution amount (mg/g)
0.01 mol/L HCl	0.16±0.03	0.033±0.026
0.05 mol/L HCl	0.16±0.01	0.082±0.022
0.1 mol/L HCl	0.17±0.04	0.14±0.02
0.01 mol/L HNO_3	0.16±0.04	0.044±0.014
0.05 mol/L HNO_3	0.16±0.04	0.13±0.06
0.1 mol/L HNO_3	0.16±0.03	0.16±0.09

Table 4.8 Percent of paraquat removal and elution using HCl and HNO_3.

Eluents	%Paraquat removal	%Paraquat elution
0.01 mol/L HCl	80.21±0.66	20.96±1.32
0.05 mol/L HCl	80.61±0.67	51.71±1.58
0.1 mol/L HCl	81.31±0.06	82.61±1.23
0.01 mol/L HNO_3	80.77±0.09	28.29±0.98
0.05 mol/L HNO_3	80.43±0.07	79.31±1.36
0.1 mol/L HNO_3	80.03±0.67	96.71±1.24

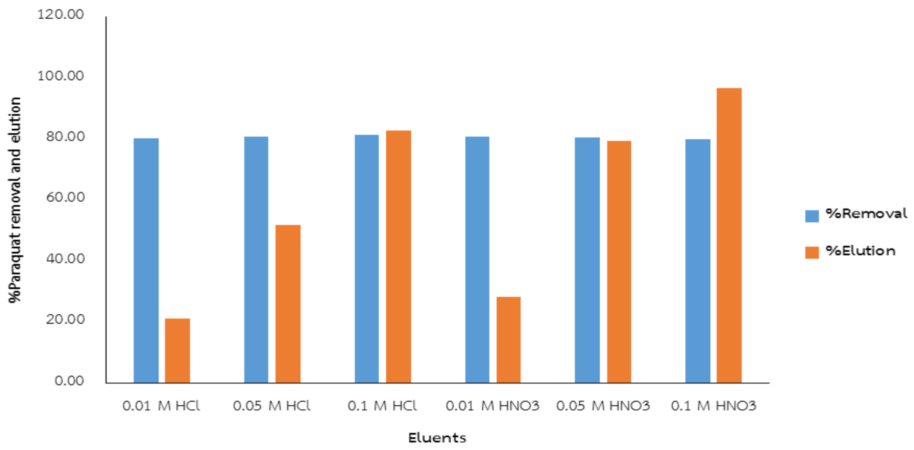

Figure 4.15 The relation between eluent concentration and the percent removal and percent elution of paraquat.

The concentration of sodium chloride was studied at 0.1, 0.5, and 1.0 mol/L. The volume of sodium chloride was studied at 10 mL (0.1, 0.5 and 1.0 mol/L) and 50 mL (1.0 mol/L). The same experiment as the acid eluent method was carried out. The elution amount of paraquat was considered.

The results of sodium chloride eluent were shown in Table 4.9 and 4.10 and Figure 4.16. When increasing the concentration of sodium chloride, the elution amount of paraquat increased. The higher volume of 1.0 mol/L sodium chloride showed the highest elution amount. The percent elution of paraquat was 68% by using 50 mL of 1.0 mol/L sodium chloride. Moreover, sodium chloride cannot damage the surface of the adsorbent and cannot release humic acids. Thereby, sodium chloride is preferably used as an eluent of paraquat elution rather than the acid.

Table 4.9 Amount of paraquat adsorption and elution using NaCl.

Eluents	Adsorption amount (mg/g)	Elution amount (mg/g)
0.1 mol/L NaCl (10 mL)	0.17±0.01	0.011±0.041
0.5 mol/L NaCl (10 mL)	0.17±0.01	0.011±0.018
1.0 mol/L NaCl (10 mL)	0.16±0.04	0.021±0.011
1.0 mol/L NaCl (50 mL)	0.16±0.04	0.11±0.04

Table 4.10 Percent of paraquat removal and elution using NaCl.

Eluents	%Paraquat removal	%Paraquat elution
0.1 mol/L NaCl (10 mL)	79.82±0.70	66.78±1.66
0.5 mol/L NaCl (10 mL)	79.40±0.69	64.44±0.10
1.0 mol/L NaCl (10 mL)	80.08±0.09	64.65±0.36
1.0 mol/L NaCl (50 mL)	80.08±0.09	67.98±0.30

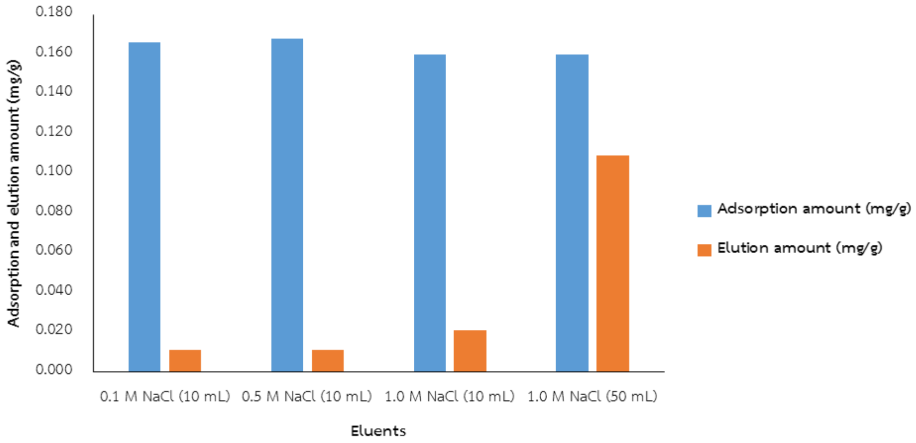

Figure 4.16 The relation between eluent concentrations and the adsorption and elution amount of paraquat.

4.4.3 Breakthrough curve

The breakthrough curve was investigated to study the adsorption capacity in the column system. The initial concentration of paraquat was 1000 mg/L at pH 5. Each 10 mL of paraquat solution was added into the column continuously. The remaining solution was collected at each 10 mL in the first 50 mL experiments and collected each 50 mL until 750 mL. The remaining paraquat concentration was determined by the UV-Visible spectrophotometer.

Breakthrough curve was plotted between C_i/C_0 and the volume of paraquat solution as represented in Figure 4.17. Where, C_0 is the initial paraquat concentration and C_i is the remaining paraquat in solution. When the paraquat solution was added into the column, the paraquat molecules can adsorb on the adsorbent surface. Adding paraquat solution continuously was increased the adsorption of paraquat until it closes to equilibrium. After that, the adsorption efficiency was gradually decreased with increasing volume of solution. Then, the remaining concentration increased. The ratio of C_i/C_0 was very low at the first step of adsorption and increased until about 0.99 at 750 mL of paraquat solution that the column completely adsorbed paraquat. The breakthrough point was 0.16 (the ratio of C_i/C_0 at 40 mL of paraquat solution). The maximum adsorption of paraquat obtained from the breakthrough curve was 416 mg/g.

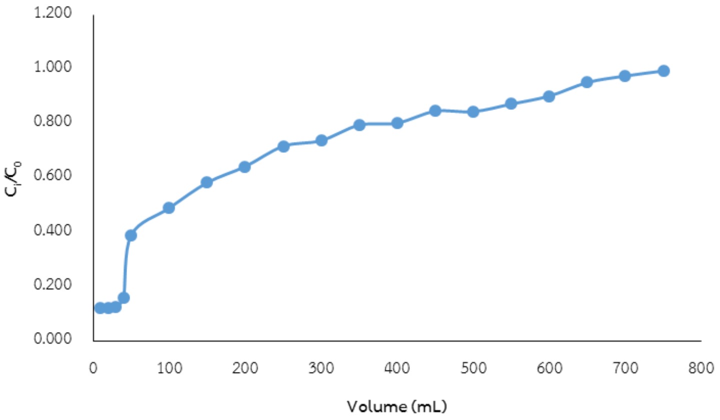

Figure 4.17 Breakthrough curve of paraquat adsorption on column system.

4.4.4 Regeneration and reusability of the column

Regeneration and reusability of the column were studied. The column was regenerated using sodium chloride solution (1.0 mol/L). After paraquat on the adsorbent was eluted, the paraquat solution was added onto the adsorbent again until the column could not be used. Then, the determination of remaining paraquat concentration by the UV-Visible spectrophotometer was performed. The results of regeneration and reusability of the column were presented in Table 4.10 and 4.11 and Figure 4.18, respectively.

From the results, the performance of the column decreased with a second reuse and eventually became unusable. The column was regenerated with high concentration of sodium chloride that caused the swelling of alginate beads and they eventually burst resulting that the alum sludge and humic acids were released from the adsorbent beads. Therefore, the column could be reused twice.

Table 4.11 Amount of paraquat adsorption and elution for column regeneration and reusability.

Times	Adsorption amount (mg/g)	Elution amount (mg/g)
1	0.16±0.02	0.11±0.02
2	0.13±0.03	0.10±0.06

Table 4.12 Percent of paraquat removal and elution for the study of column regeneration and reusability.

Times	%Paraquat removal	%Paraquat elution
1	81.77±1.37	69.14±1.89
2	67.08±1.23	72.97±0.98

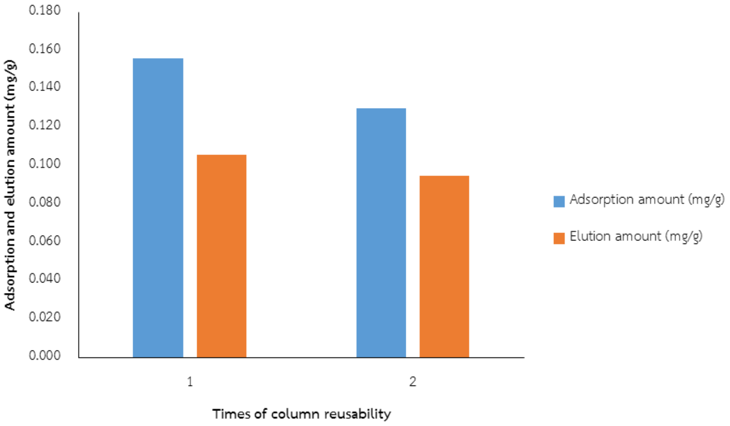

Figure 4.18 The relation between cycles of column reusability and the adsorption and elution amount of paraquat.

4.5 Application in real water samples

The real water samples form Suphan Buri, Lopburi and Chachoengsao in Thailand were studied for adsorption amount and percent removal of paraquat using column system. The homemade cylinder column was packed the AS-HA-AG beads in a column at a height of 2 cm (2.35 g adsorbent). The real water samples were filtrated and spiked with 10 mg/L paraquat solution. Then, 50 mL of non-spiked and spiked samples were passed through the column under a flow rate 3 mL/min. The concentration of filtrated samples was determined by the UV-Visible spectrophotometer.

As UV-Visible spectrophotometry was used for the determination of paraquat in this study, the concentrations of paraquat might not be actual concentration of paraquat due to the non-selectivity of the measurement. These concentrations could be represented paraquat and other UV-Vis absorbing substances at the measure wavelength of 258 nm. Thus, paraquat was added in the samples obtaining spiked samples in order to study the adsorption performance of the adsorbent toward paraquat.

The results of paraquat removal in real water samples were shown in Table 4.13. From the results, the removal percentages of paraquat of non-spiked water samples were 20.4, 33.8 and 28.8 for Suphan Buri, Lopburi and Chachoengsao samples, respectively. While, the percent removal of paraquat in spiked water samples at Suphan Buri, Lopburi and Chachoengsao samples were 57.1, 63.0 and 55.9, respectively. This is only a preliminary result of column study for paraquat removal from real water samples. The adsorption efficiency could be improved by modifying column parameters such as bed height. The result indicates that the AS-HA-AG beads have a potential to remove paraquat from real water samples.

Table 4.13 The result of paraquat removal in water sample.

Water samples	Adsorption amount (mg/g)	%Paraquat removal
Suphan Buri		
- Non-spiked	0.018±0.012	20.4±0.5
- Spiked	0.15±0.01	57.1±1.1
Lopuri		
- Non-spiked	0.016±0.025	33.8±1.5
- Spiked	0.13±0.02	63.0±1.1
Chachoengsao		
- Non-spiked	0.026±0.013	28.8±0.7
Spiked	0.15±0.01	55.9±1.1

CHAPTER V

CONCLUSION

5.1 Conclusion

The humic acids supported on sludge from tap water production (alum sludge) entrapped in alginate beads were prepared by dissolving the 1% (w/v) of sodium alginate solution in Milli Q water. Then, 1% (w/v) of humic acids and alum sludge were added into the sodium alginate solution. After that, the heterogeneous solution was dropped into calcium chloride solution to form small beads by using a needle (0.08 mm diameter) and a peristaltic pump. The small black beads were washed with Milli Q water and were dried. The characteristics of the adsorbent were identified by attenuated total reflectance Fourier transform infrared spectrometer (ATR-FTIR). The spectra of AS-HA-AG suggested that the adsorbent containing the alum sludge, humic acids, and sodium alginate. The optimization of adsorbent was investigated by studying the type of adsorbent including bare alginate beads (AG), humic acids-alginate beads (HA-AG), alum sludge-alginate beads (AS-AG), and alum sludge-humic acids-alginate (AS-HA-AG) beads and the amount of adsorbent i.e. AS-HA-AG-1 (1% (w/v) alum sludge and humic acids) and AS-HA-AG-2 (2% (w/v) alum sludge and humic acids) beads. Five adsorbents were studied paraquat adsorption test. The results showed that all adsorbents can adsorb paraquat in solutions. The batch adsorption capacity was 6.7, 7.5, 5.0, 9.3 and 9.1 mg/g for AG, HA-AG, AS-AG, AS-HA-AG-1 and AS-HA-AG-2 beads, respectively. The adsorption efficiency of AG, HA-AG, AS-AG, AS-HA-AG-1 and AS-HA-AG-2 beads were 67.4, 75.1, 50.3, 93.6 and 91.6%, respectively. The AS-HA-AG beads presented the highest adsorption efficiency and were used as the adsorbent for paraquat adsorption.

The optimum conditions for the adsorption of paraquat in a batch method were investigated. Firstly, the effect of pH was studied by varying the pH value from 1 to 10. The optimal pH of paraquat adsorption was pH 5. Then, the effect of adsorption time was investigated by studying the contact time from 15 minutes to 24 hours. The equilibrium time of paraquat adsorption was 180 minutes. After that, the adsorption rate was studied by fitting to linear equations of the pseudo-first and pseudo-second order adsorption kinetic models. The adsorption of paraquat by AS-HA-AG beads was fitted to the pseudo-first order kinetics (R^2 = 0.9840) rather than pseudo-second order kinetics (R^2 = 0.9201). The adsorption capacity at equilibrium from pseudo-first order kinetics ($q_{e,cal}$) was 9.28 mg/g which close to the experiment result ($q_{e,exp}$) that was 9.45 mg/g. The rate of adsorption depends on the initial concentration of paraquat. The adsorption behavior was studied by varying the initial concentration of paraquat in range 10-500 mg/L. The adsorption behavior fitted to the Freundlich adsorption isotherm (R^2 = 0.9796) that was multilayer adsorption. Because of three componants of AS-HA-AG beads can adsorb paraquat in solutions. Moreover, the maximum adsorption amount from experiment ($q_{m,exp}$) was more than 94.5 mg/g.

In column system, the homemade cylinder column was packed by AS-HA-AG beads adsorbent (height of 2 cm) that was used to study the efficiency of paraquat removal. The paraquat solution was passed through the column by using a manifold connected to a vacuum pump. The effect of flow rate was firstly studied at 0.5, 1, 2, 3 and 4 mL/min. The optimum flow rate for column adsorption was 3 mL/min and the maximum paraquat removal was 91.3%. Then, the effect of eluent concentration was investigated by using different eluent types and concentrations including hydrochloric acid (0.01, 0.05 and 0.1 mol/L), nitric acid (0.01, 0.05 and 0.1 mol/L), and sodium chloride (0.1, 0.5 and 1.0 mol/L). The acid eluent (5 mL) can elute the paraquat from adsorbent but it can also destroy the adsorbent surface. Meanwhile, the sodium chloride was eluted the paraquat amount from adsorbent that cannot destroy the adsorbent surface. The percent elution of paraquat was 68% by using 50 mL of 1.0 mol/L sodium chloride. After that, the adsorption capacity was studied to investigate the breakthrough curve. The maximum adsorption of paraquat obtained from the breakthrough curve was 416 mg/g.

In addition, the real water samples from agricultural areas at Suphan Buri, Lopburi and Chachoengsao in Thailand were studied. The adsorption amount and percent removal of paraquat using column system were evaluated. The non-spiked water samples at Suphan Buri, Lopburi and Chachoengsao showed the paraquat removal of 0.018, 0.016 and 0.026 mg/g, respectively. While, the paraquat removal in spiked water samples were 0.15, 0.13 and 0.15 mg/g for Suphan Buri, Lopburi and Chachoengsao samples, respectively. The results demonstrated that the AS-HA-AG bead adsorbent can remove paraquat from real water samples.

5.2 Suggestion for the future work

- Interferences for paraquat adsorption by AS-HA-AG beads shall be further investigated.

- The AS-HA-AG beads should be used as adsorbent for removal other pollutants in water.

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APPENDIX

VITA

Miss Munlika Suksai was born on September 26th, 1991 in Nakhon Si Thammarat, Thailand. She graduated with Bachelor of Science in Chemistry from Chulalongkorn University in 2014. Afterwards, she continued her academic education with Master degree of Science in Analytical Chemistry at the Department of Chemistry, Faculty of Science, Chulalongkorn University and became a member of Environmental Analysis Research Unit (EARU). She completed her Master degree of Science in Analytical Chemistry in 2017. Her present address in 100 Moo 2, Pak Phun Sub-district, Mueang District, Nakhon Si Thammarat, 80000. Contact number is 092-438-9308. E-mail: munlika.s@hotmail.com.