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**ชื่อโครงการ** Removal phosphorus from aqueous solution by acid modified orange peels/alginate adsorbent beads

**ชื่อนิสิต** Miss Phakhwan Sukarin

**ภาควิชา** Environmental Science

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orange peels/alginate adsorbent beads

ชื่อนิสิต Miss Phakhwan Sukarin เลขประจำตัว 6033334823

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คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

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Removal phosphorus from aqueous solution by acid modified orange peels/alginate  
adsorbent beads

Phakhwan Sukarin

A Senior Project in Partial Fulfillment of the Requirements for  
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Senior Project Title	Removal phosphorus from aqueous solution by acid modified orange peels/alginate adsorbent beads
Name	Miss Phakhwan Sukarin
Student ID	6033334823
Project Advisor	Associate Professor Dr. Roongkan Nuisin
Department	Environmental Science
Academic year	2020

---

Accepted by Department of Environmental Science, Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirement for the Bachelor's Degree



..... Head of Department of Environmental Science  
(Assistant Professor Dr. Pasicha Chaikaew)

#### PROJECT COMMITTEE



.....  
(Dr. Supawin Watcharamul)

Chairman



.....  
(Assistant Professor Dr. Sermpong Sairiam)

Committee



.....  
(Associate Professor Dr. Roongkan Nuisin)

Project Advisor

หัวข้อโครงการ	การกำจัดฟอสฟอรัสจากสารละลายโดยเม็ดดูดซับเปลือกส้มตัดแปรด้วยกรด/แอลจิเนต
ชื่อ	นางสาวพาขวัญ สุกรินทร์
รหัสประจำตัวนิสิต	6033334823
อาจารย์ที่ปรึกษา	รองศาสตราจารย์ ดร.รุ่งกานต์ นุ้ยสินธุ์
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### บทคัดย่อ

ศึกษาตัวดูดซับของเหลือชีวภาพจากผงเปลือกส้มในการกำจัดฟอสฟอรัส เตรียมผงเปลือกส้ม เม็ดแอลจิเนต และเม็ดปิดผงเปลือกส้มตัดแปรด้วยกรดอะซิติก/แอลจิเนต (Alg-Acid@Or-P) ได้เม็ดปิด Alg-Acid@Or-P ทรงกลม สีเหลือง ขนาดของเม็ดปิดแห้งอยู่ช่วง 1.6 ถึง 1.8 มิลลิเมตร มีการกระจายขนาดที่แคบ วัดค่าประจุเป็นศูนย์ของเม็ดปิด Alg-Acid@Or-P ได้ 6.5 ศึกษาผลของปริมาณตัวดูดซับและความเข้มข้นเริ่มต้นของฟอสฟอรัส ในกระบวนการกำจัดด้วยการทดลองแบบกะ ปริมาณตัวดูดซับแต่ละชนิดที่เหมาะสม 2 กรัม ได้ค่าร้อยละการกำจัดฟอสฟอรัสสูงสุด ลำดับของร้อยละการกำจัดฟอสฟอรัส คือ ผงเปลือกส้มมากกว่าเม็ดปิดแอลจิเนตและมากกว่าเม็ดปิด Alg-Acid@Or-P ค่าความจุของการดูดซับสูงสุดมีค่า 269.75 มิลลิกรัมต่อกรัม เมื่อใช้ตัวดูดซับผงเปลือกส้ม 2 กรัม ในฟอสฟอรัสความเข้มข้นเริ่มต้น 15 มิลลิกรัมต่อลิตร เวลาสัมผัส 3 ชั่วโมง เม็ดปิด Alg-Acid@Or-P วัดค่าความจุของการดูดซับได้ต่ำสุด คือ 8.25 มิลลิกรัมต่อกรัม อาจเกิดจากผลของการเปลี่ยนแปลงประจุที่ผิวของเม็ดปิดผงเปลือกส้มตัดแปรด้วยกรดอะซิติก/แอลจิเนต ไอโซเทอมของการดูดซับไม่ได้ทำการศึกษาเนื่องจากสถานการณ์การระบาดของโรคโควิด-19 และการปิดห้องปฏิบัติการ

**คำสำคัญ:** แอลจิเนต; เม็ดปิด; เปลือกส้ม; การดูดซับฟอสฟอรัส

Senior Project Title	Removal phosphorus from aqueous solution by acid modified orange peels/alginate adsorbent beads
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Advisor	Associate Professor Dr. Roongkan Nuisin
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### ABSTRACT

The bio-based adsorbent from orange peels powder was investigated for phosphorus removal. The orange peel powder (Or-P), alginate (Alg), and acid modified orange peel/alginate beads (Alg-Acid@Or-P) was prepared. The spherical shape with yellow in color of Alg-Acid@Or-P beads were obtained. The dry beads in size range of 1.6 to 1.8 mm with narrow size distribution was prepared. The point of zero charge of 6.5 for Acid@Or-P bead was measured. The effects of adsorbent dosage, and initial concentration of phosphorus on the removal process were investigated in batch experiment. The optimum dosage of 2 g of each adsorbent, the highest percent removal of phosphorus was revealed. The percent phosphorus removal as follows; Or-P > Alg > Alg-Acid@Or-P was calculated. The highest adsorption capacity ( $q_e$ ) of 269.75 mg/g was observed for an adsorbent dose of 2 g Or-P for an initial concentration of 15 mgP/L at contact time 3 h. Alg-Acid@Or-P was measured the low  $q_e$  at 8.25 mg/g. The effect of surface charge on modified orange peel/alginate beads may concerns. The adsorption isotherms were not conducted due to the COVID-19 pandemic situation with the laboratory closure.

**Keywords:** alginate; bead; orange peels; phosphorus adsorption

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## ABBREVIATIONS AND SYMBOLS

Alg	alginate
Alg-Acid@Or-P	acid modified orange peel/alginate beads
$C_f$	remain concentration of adsorbate
$C_0$	concentration of adsorbate at initial
$C_e$	concentration of adsorbate at equilibrium
$^{\circ}\text{C}$	degree Celcius
g	gram
G	guluronate
h	hour
$K_F$	Freundlich constants
$K_L$	Langmuir constants
$K_1$	rate constant of pseudo-first order
$K_2$	rate constant of pseudo-second-order
mg/L	milligram per litre
mg P/L	milligram phosphate per litre
mg/g	milligram per gram

M	mannuronate
Or-P	orange peels powder
P	phosphorus
$q_e$	adsorption capacity at equilibrium
$q_m$	maximum adsorption capacity
$q_t$	adsorption capacity at design time
rpm	revolutions per minute
TP	total phosphorus
V	volume
w/v	weight per volume
W	weight

## CHAPTER 1

### INTRODUCTION

#### 1.1 Background and significant problems

Phosphorus is a necessary nutrient for the growth of organisms acting as producers in water sources such as algae, phytoplankton, and plant. The rapid increase of phosphorus in an ecological system, mainly from agricultural activities, industrial and household wastewater discharge, leads to a significant environmental problem. Eutrophication (algal bloom), or over enrichment with nutrients, is an environmental issue of concern for wetlands, streams, rivers, lakes, and reservoirs worldwide, which is cause of fish death and loss of aquatic species (Smith, 2009). According to Environmental Protection Agency (EPA), the maximum permissible level and the stringent discharge limit of phosphate ions are 0.1 mg/L and less than 0.05 mg/L, respectively (Liu & Zhang, 2015). In Thailand, Ministry of Natural Resource and Environment set the standard for sewage control from municipal wastewater treatment system that the total phosphorus (TP) must not exceed 2 mg-P/L. In general, most of phosphorus found in water are in the form orthophosphate ( $\text{PO}_4^{3-}$ ,  $\text{HPO}_4^{2-}$ ,  $\text{H}_2\text{-PO}_4^-$ ).

The sustainable and environmentally friendly technologies for removal phosphorus before releasing into water source were developed. Phosphorus removal methods from wastewater are physico-chemical processes e.g. chemical precipitation, membrane technology, adsorption process, ion exchange resin, and biological treatment (Liu & Zhang, 2015). The chemical precipitation can remove more than 96% of phosphorus from swine wastewater (Huang *et al.*, 2017). Polysulfone matrix as membrane adsorbent can adsorb

phosphorus on its 0.071 mg-P/L (Furuya *et al.*, 2017). The methods that mentioned above for phosphate removal had many limitations, such as high cost, instability, sophistication in operation as secondary-pollution. Adsorption is a surface process that leads to transfer of a molecule from a fluid bulk to solid surface. These phenomena can occur because of physical forces or by chemical bonds. In most of the cases, adsorption process is described at the equilibrium by means of some equations that quantify the amount of substance attached on the surface given the concentration in the fluid. It is a surface process, that is, only the surface of the adsorbent is involved, and adsorbate does not diffuse into the structure of the adsorbent (in this case indeed the process is called absorption). Usually it is reversible (the reverse process is called desorption); then it is responsible not only for a subtraction of substances but also for release them. The reverse process, that is, the drop of a molecule from a solid surface, is called desorption (Artioli, 2008). The adsorption method was considered to be the most promising technique due to simplicity and flexibility of design, ease of operation and cost-effectiveness, and suitable for low total phosphorus concentration (Liu & Zhang, 2015).

The orange peels waste obtained from orange juice production is one of the agro-industrial residues. The orange peel waste often processed into cattle feed, molasses extracted for flavonoids and D-limonene (Nair *et al.*, 2018). Orange peel waste are low cost, easy to find, a nontoxic, biodegradation and water solubility. The orange peels consisted of cellulose so it has qualification as biosorption. However, the bare orange peels have low efficiency of adsorption due to its disintegration properties. To improve the efficiency of adsorption, the bare orange peels were entrapped in the polymer. Alginate is a general term

for a family of polysaccharides produced by seaweed, brown algae, and bacteria. It is a heteropolysaccharide made from two randomly arranged uronic acid and sugar molecules. Alginates are natural polymers consisting of linear copolymers of  $\beta$ -(1-4) linked d-mannuronic acid and  $\beta$ -(1-4)-linked l-guluronic acid units (Alihosseini, 2016).

The aim of this study is preparing the adsorbent bead from orange peels entrapped in calcium alginate by precipitation technique. The acid modified orange peel/alginate beads were used for phosphorus removal in aqueous solution. The adsorption efficiency was evaluated by parameter as follows; adsorbent dosage and initial phosphorus concentration under batch experiment.

### **1.2 Research objectives**

- 1) To prepare the adsorbent bead from orange peels entrapped in calcium alginate by precipitation technique
- 2) To modify orange peel/alginate beads for phosphorus removal in aqueous solution
- 3) To evaluate the adsorption efficiency by variation of parameter e.g. adsorbent dosage and initial phosphate concentration

### **1.3 Research outcomes**

- 1) Acid modified orange peel/alginate beads can be formed by precipitation technique.
- 2) The optimum conditions to removal phosphorus can be obtained.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Problem of phosphorus in environment

Phosphorus (P) is an important nutrient in water source. In freshwater ecosystems, it is commonly the limiting nutrient controlling primary productivity, and determining the total biomass of algal organisms. Although phosphorus is loaded to river systems by natural decaying of rocks and soils in the catchment but the dominant source of phosphorus is human activities such as agriculture. Phosphorus is a main component of fertilizers and mostly reaches rivers via surface runoff during major rainfall. Phosphorus can discharge to water source from domestic and agriculture waste effluent (Yuan *et al.*, 2021). Large amount of phosphorus contaminate in water source lead to environmental problem called eutrophication and it affect to many aquatic life, decrease biodiversity and as well as changes in the ecosystem (Smith, 2009). Phosphorus in natural sources and wastewater is in phosphate form in which classified into 3 types:

- 1.) Orthophosphate is a dissolved phosphate and provides  $\text{PO}_4^{3-}$ ,  $\text{HPO}_4^{2-}$ ,  $\text{H}_2\text{-PO}_4^-$
- 2.) Polyphosphate is phosphate-containing substances in many groups of molecules such as  $\text{Na}_3(\text{PO}_4)_6$ ,  $\text{Na}_5\text{P}_3\text{O}_{10}$ ,  $\text{Na}_4\text{P}_2\text{O}_7$ . These substances are dehydrated phosphate so hydrolyzed to orthophosphate, and
- 3.) Organic phosphate is various organic substances phosphate such as nucleic acid, phospholipids and sugar phosphate.



## 2.2 Adsorption

Adsorption is a surface process that leads to transfer of a molecule from a fluid bulk to solid surface. This can occur because of physical forces or by chemical bonds. Usually it is reversible (the reverse process is called desorption); then it is responsible not only for a subtraction of substances but also for release. In most of the cases, this process is described at the equilibrium by means of some equations that quantify the amount of substance attached on the surface given the concentration in the fluid. These equations are called isotherms (the most famous are the Langmuir and the Freundlich equations) because of the dependence of their parameters on the temperature, which is one of the most important environmental factors affecting adsorption (Artioli, 2008).

Adsorption is the process when a molecule, or ion, called adsorbate present in a gaseous or liquid bulk sticks on the surface of a solid, rarely a liquid, called adsorbent. It is a surface process, that is, only the surface of the adsorbent is involved, and adsorbate does not diffuse into the structure of the adsorbent (in this case indeed the process is called absorption). The reverse process, that is, the drop of a molecule from a solid surface, is called desorption (Artioli, 2008)

### 2.2.1 Adsorption isotherm

The Langmuir model is one of the best known, theoretically understood, and widely applied models. Developed by Langmuir in 1916 originally, it was a theoretical equilibrium isotherm relating to the amount of gas adsorbed per unit mass of the adsorbent. It is based on a uniform, monolayer, and finite adsorption

site. The Langmuir adsorption isotherm assumes that there is no interaction among molecules adsorbed on the neighboring adsorption sites (Bhandari & Ranade, 2014).

Langmuir:

$$q_e = q_m \frac{K_L C_e}{1 + K_L C_e} \quad \dots (2.1)$$

where  $q_e$  (mg/g) is the adsorption capacity at equilibrium,

$q_m$  (mg/g) is a maximum adsorption capacity,

$K_L$  is the Langmuir constants,

$C_e$  is equilibrium concentration in solution phase (mol/m<sup>3</sup>)

The Freundlich equation is an empirical equation based on adsorption on heterogeneous sites. It is also one of the most common two-parameter isotherms applied for wastewater treatment. It assumes that stronger binding sites are occupied first, and the strength of adsorption decreases with the degree of occupation (Bhandari & Ranade, 2014).

Freundlich:

$$q_e = K_F C_e^{\frac{1}{n}} \quad \dots (2.2)$$

where  $q_e$  (mg/g) is the adsorption capacity at equilibrium,

$K_F$  is Freundlich constants,

$1/n$  is the heterogeneity factor,

$C_e$  is equilibrium concentration in solution phase ( $\text{mol/m}^3$ ).

### 2.2.2 Adsorption kinetics

Adsorption kinetics is the measure of the adsorption uptake with respect to time at a constant pressure or concentration and is employed to measure the diffusion of adsorbate in the pores (Saha & Grappe, 2017). The adsorption kinetic models, such as the pseudo-first-order model (Eq. 2.3) and the pseudo-second-order model (Eq. 2.4).

$$q_t = q_e (1 - e^{-K_1 t}) \quad \dots (2.3)$$

$$q_t = \frac{K_2 q_e^2 t}{1 + K_2 q_e t} \quad \dots (2.4)$$

where,  $q_e$  (mg/g) and  $q_t$  (mg/g) are amount of P adsorption at equilibrium and at design time, respectively.

$K_1$  (1/h) and  $K_2$  (g/mg h) are rate constants respectively of pseudo-first-order and pseudo-second-order kinetics models.

### 2.3 Orange peels and their composition

Annual production of the citrus fruit is about more than 115 million tones (Aichour & Zaghouane-Boudiaf, 2020). It makes this kind of fruit very abundant in the world. A loss of citrus peels explains almost 50% of the wet mass of the fruit (Aichour & Zaghouane-Boudiaf, 2020). Also, orange peels are biologically and environmentally

friendly and it is suitable for preparation of low-cost adsorbents. Orange peels rich of cellulose which resulted to orange peels has qualification as biosorption. Cellulose is a linear polymer of  $\beta$ -1,4-linked glucose residues and is the major component of plant cell walls (Figure 2.1). Cellulose is planar, water-insoluble, and difficult to hydrolyze (Holtzapfle, 2003). It has hydroxyl group that reactivity with phosphate.

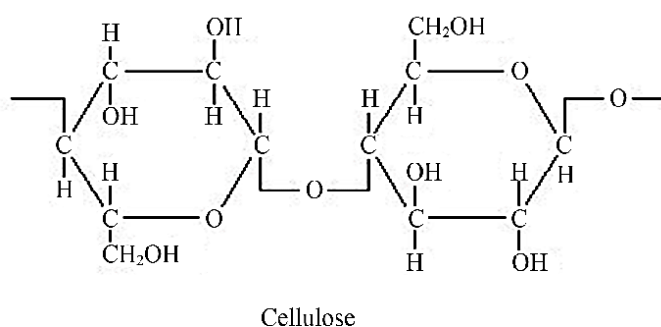
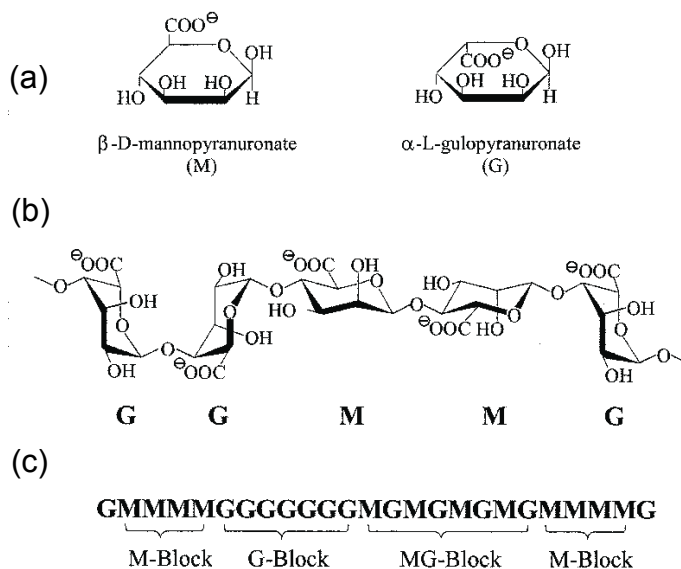


Figure 2.1 Structure of cellulose (Richards *et al.*, 2012)

## 2.4 Alginate

Alginates are natural polymers consisting of linear copolymers of  $\beta$ -(1-4) linked d-mannuronic acid and  $\beta$ -(1-4)-linked l-guluronic acid units (Alihosseini, 2016). Alginate is a general term for a family of polysaccharides produced by seaweed, brown algae, and bacteria. It is a heteropolysaccharide made from two randomly arranged uronic acid and sugar molecules. Alginate is now known to be a whole family of linear copolymers containing blocks of (1,4)-linked  $\beta$ -D-mannuronate (M) and  $\alpha$ -L-guluronate (G) residues. The blocks are composed of consecutive G residues (GGGGGG), consecutive M residues (MMMMMM), and alternating M and G residues (GMGMGM) (Figure 2.2.). Generally, alginates with more G blocks have stiffer chains in comparison with alginates that have

more M-blocks, which suggest a more flexible structure with more swelling capacity. The two uronic acids can bind to metal ions, such as sodium and calcium (Fincher, 1999).



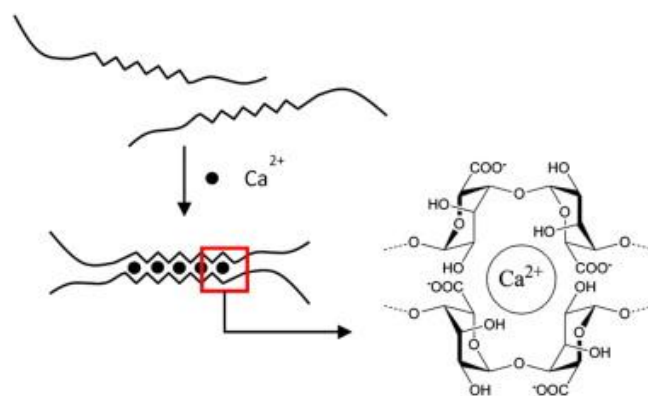
**Figure 2.2** Alginate structural (a) alginate monomers (M versus G); (b) the macromolecular conformation of the alginate polymer; (c) chain sequences (Davis *et al.*, 2003)

## 2.5 Orange peels/alginate encapsulation technique

### 2.5.1 Formation of alginate beads

Alginate beads can be prepared through chemical and/or physical crosslinking of the polymer chains. The properties of the alginate bead are dependent on the type of crosslinking, cross-linking density, and molecular weight and composition of the alginate. The most common method for the formation of alginate gels is by ionic cross-linking with cations such as  $\text{CaCl}_2$ . The

gelation of alginate occurs by an exchange of sodium ions from the guluronic acid (G) blocks with cations, and the stacking of these G blocks to form a characteristic “egg-box” structure (Figure 2.3). Gels prepared from alginates with a high G content tend to form stronger, stiffer, more brittle and more porous gels. M content results in gels which are more elastic and weaker (Paques *et al.*, 2014).



**Figure 2.3** Formation of an alginate gel by calcium cations (Paques *et al.*, 2014)

### 2.5.2 Formation of alginate beads with other materials

Citrus particles and Ca-alginate has been as adsorbent for removal Se (IV) (Dev *et al.*, 2020). The Ca-alginate@citrus bead was made by adding crushed citrus peels to 2% (w/v), sodium alginate solution at 0.02% (w/v) and stirred continuously to form a uniform mixture. The mixture formed the composite beads by drop into 3% (w/v) CaCl<sub>2</sub> solution followed by incubation at 25 °C for 1 h. The composite beads of Ca-alginate@citrus were dried by filtering it from the solution and incubating at 37 °C for 48 h.

Zinc oxide nanoparticles (nano-ZnO) are attractive as fertilizer materials but high concentrations may negatively affect the environment. To reduce their dispersion in the environment we entrapped in biodegradable polymer beads consisting of alginate and polyvinyl alcohol (PVA) (Knijnenburg *et al.*, 2021). To prepare bead, sodium alginate dissolved in DI water, added nano-ZnO and PVA and continuous stirring to form a homogeneous milky suspension. The suspension was then manually dropped using a syringe into  $\text{Ca}^{2+}$  solution. When dried, the pure dried alginate beads can be described as small and hard, whereas the PVA-containing beads were more elastic. The dry beads containing PVA were significantly and progressively larger than the PVA-free beads so the dimensions depending on the material which entrapped in calcium alginate. After immersion in tap water for 24 h, calcium alginate significantly increased in size upon swelling.

## CHAPTER 3

### MATERIALS AND METHODS

#### 3.1 Materials and equipment

##### 3.1.1 Chemicals and Materials

- 1) Orange peels from Sai Nam Phueng orange, Thailand
- 2) Sodium alginate ( $C_6H_7O_6$ )<sub>n</sub>, AR grade, Carlo Erba, Italy
- 3) Acetic acid glacial ( $CH_3COOH$ ), AR grade, QRëC, New Zealand
- 4) Calcium chloride ( $CaCl_2$ ), AR grade, Carlo Erba, Italy
- 5) Sulphuric acid ( $H_2SO_4$ ), AR grade, QRëC, New Zealand
- 6) Sodium hydroxide (NaOH), AR grade, Carlo Erba, Italy
- 7) Sodium chloride (NaCl), AR grade, Carlo Erba, Italy
- 8) Ammonium molybdate tetrahydrate ( $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ ), AR grade, Macron Fine, Chemicals, Thailand
- 9) L-Ascorbic acid ( $C_6H_8O_6$ ), AR grade, Unilab, Thailand
- 10) Deionized water (DI)

##### 3.1.2 Equipment

- 1) Sieve size 500 micrometer, Endecotts Ltd, England
- 2) Hotplate Stirrer, C-MAG HS7, Kittisit Enterprise Co., Ltd., Thailand



- 3) Reciprocal shaker, Gerhardt, Scientific Promotion Co., Ltd., Germany
- 4) 4 decimal place analytical balance, Mettler Toledo, Thailand
- 5) 2 decimal place analytical balance, Toledo, Thailand
- 6) Spectrophotometer, Spectro SC, Thailand
- 7) Syringe (volume 3 ml., Nipro company, Thailand)
- 8) Oven, Model 700, Memmert, Germany
- 9) pH meter, Denver Instrument, USA.

## 3.2 Methodology

In this study, the adsorbent bead from orange peels entrapped in calcium alginate was prepared by precipitation technique. The orange peel/alginate beads were subsequently used for phosphorus removal in aqueous solution.

### 3.2.1 Adsorbent preparation

Orange peels powder (Or-P) from fresh orange peels were oven dried for 24 h. The dried orange peels were grounded with blender. The orange peel powder was sieved using 500 micrometer sieve-screen, and kept in zip-lock bag at room temperature for further use.

Acid modified orange peels powder (Acid@Or-P) was prepared by acetic acid treatment. The fifty grams of untreated-Or-P were added into 0.6 M of 500 ml acetic acid. The mixture was continuously stirred for 1 h. The Acid@Or-P was

rinsed by DI water for eliminated surplus acetic acid. Acid@Or-P slurry was dried by oven for 24 h.

### **3.2.2 Alginate beads (Alg)**

Sodium alginate 2% (w/v) was dissolved in deionized water and continuous stirring until the homogeneous solution obtained. Alginate droplet was dropped using syringe. The alginate beads were crosslinked in 1.5 %w/v of CaCl<sub>2</sub> solution. The alginate beads (Alg) was soaked in the CaCl<sub>2</sub> solution for 1 h. After separate Alg beads out of CaCl<sub>2</sub> solution, the Alg beads was rinsed twice by DI water for removal the surplus CaCl<sub>2</sub>. The wet Alg beads was dried in an oven at 60°C for 24 h.

### **3.2.3 The orange peel/alginate beads (Alg-Acid@Or-P)**

Sodium alginate 2% (w/v) was dissolved in deionized water and continuous stirring until the solution will be homogeneous. Fifty grams of Acid@Or-P were added into sodium alginate solutions and continuous stirring until the mixture will be homogeneous again. The Alg-Acid@Or-P mixture was dropped into 1.5% (w/v) of CaCl<sub>2</sub> using the needle to for forming Alg-Acid@Or-P beads. The Alg-Acid@Or-P beads was soaked in the CaCl<sub>2</sub> for 1 h. The Alg-Acid@Or-P beads was taken off and rinsed by DI water twice for removal the surplus CaCl<sub>2</sub>. The Alg-Acid@Or-P beads was dried in an oven at 60°C for 24 h.

### 3.2.4 Adsorption study

The batch experiment was performed for all adsorption study of phosphate removal. The effect of adsorbent dosage on phosphate removal was investigated. The different amount of adsorbent 0, 1, 1.5, 2 g was used. Each amount of adsorbent was added into 5, 10, 15 mg/L phosphate solution 50 mL and shook with 120 rpm for 3 h. Determination of the remaining concentration of phosphate was performed by ascorbic acid method. Percent removal and adsorption capacity were calculated by Eq. (3.1) (3.2) respectively;

$$\% \text{ Removal} = \frac{C_0 - C_f}{C_0} \times 100 \quad \dots(3.1)$$

where,  $C_0$  is initial concentration of phosphate.

$C_f$  is remain concentration of phosphate.

$$q_e \text{ (mg/g)} = \frac{C_0 - C_f}{M} \times V \quad \dots(3.2)$$

where,  $C_0$  is initial concentration of phosphate.

$C_f$  is remain concentration of phosphate.

$V$  (L) is volume of phosphate solution.

$M$  (gram) is mass of adsorbent

## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1 Orange fruit characteristics

Physical and chemical characteristics of an orange (Som Sai Nam Phueng on Thai) was investigated. The whole orange weighing approximately one kilogram (n=9), were used. Table 4.1 shows that one orange fruit was consisted of weight, pulp and peels of 103.2, 84.2, 18.2 g, respectively. The average volume of orange, pulp and peels was 107.0, 82.6, and 19.9 cm<sup>3</sup>, respectively.

**Table 4.1** Orange fruit characteristics

Characteristics	Properties	
	Weight (g) $\pm$ SD	Volume (cm <sup>3</sup> ) $\pm$ SD
Whole orange	103.2 $\pm$ 8.43	107.0 $\pm$ 9.07
Orange pulp	84.2 $\pm$ 9.06	83.0 $\pm$ 7.23
Orange peels	18.2 $\pm$ 1.37	20.0 $\pm$ 1.75

#### 4.2 Characterization of adsorbent

Orange powder was sieved (sieve size = 500  $\mu$ m) and pretreated with 0.6 M acetic acid. It was found that the orange peel color turn from orange appearance to dark yellow (Figure 4.1). Figure 4.2(a) shows the optical micrographs of spherical shape of wet alginate bead. The wet alginate bead in size range from 3.8 to 4.0 mm was measured (n = 100).

The average alginate bead size of 3.9 mm. The alginate bead color in opaque white was observed. Figure 4.2(b) shows the dry alginate bead, the average diameter of dried alginate bead was obviously smaller than the wet bead. The wet and dry Alg-Acid@Or-P had yellow beads as shown as Figure 4.3. The average wet beads size of approximately 4.2 mm was measured (Figure 4.3a). The dry beads in size range of 1.6 to 1.8 mm was measured (Figure 4.3b). In general, the wet beads size was found larger than the dry bead. The histogram of bead size distribution was shown in Figure 4.4, the narrow size distribution patterns of both wet and dry bead were observed.



**Figure 4.1** Optical micrographs of Acid@Or-P powder (sieve size = 500  $\mu\text{m}$ )

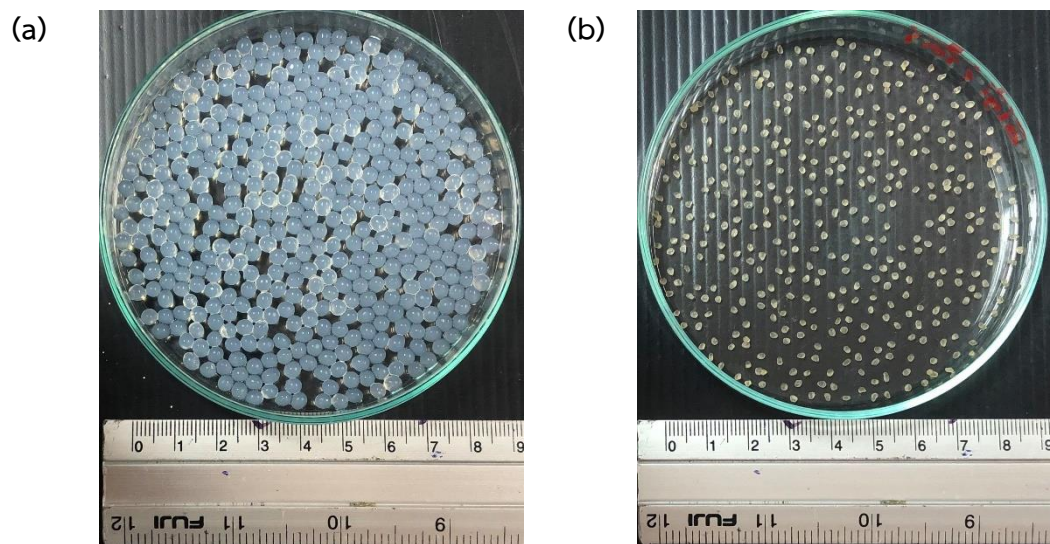


Figure 4.2 Optical micrographs of alginate bead (a) wet (b) dry beads

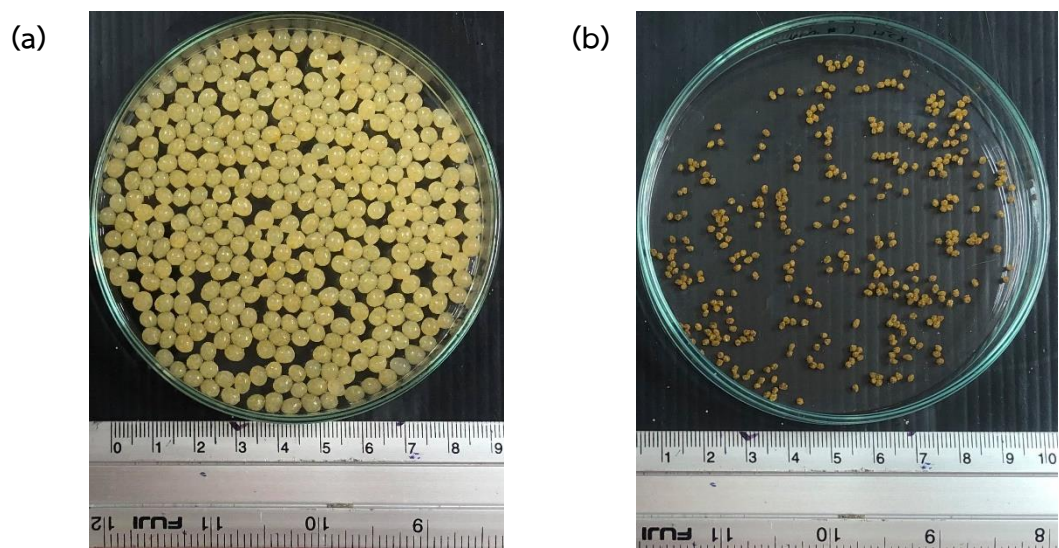


Figure 4.3 Optical micrographs of Alg-Acid@Or-P beads (a) wet (b) dry beads

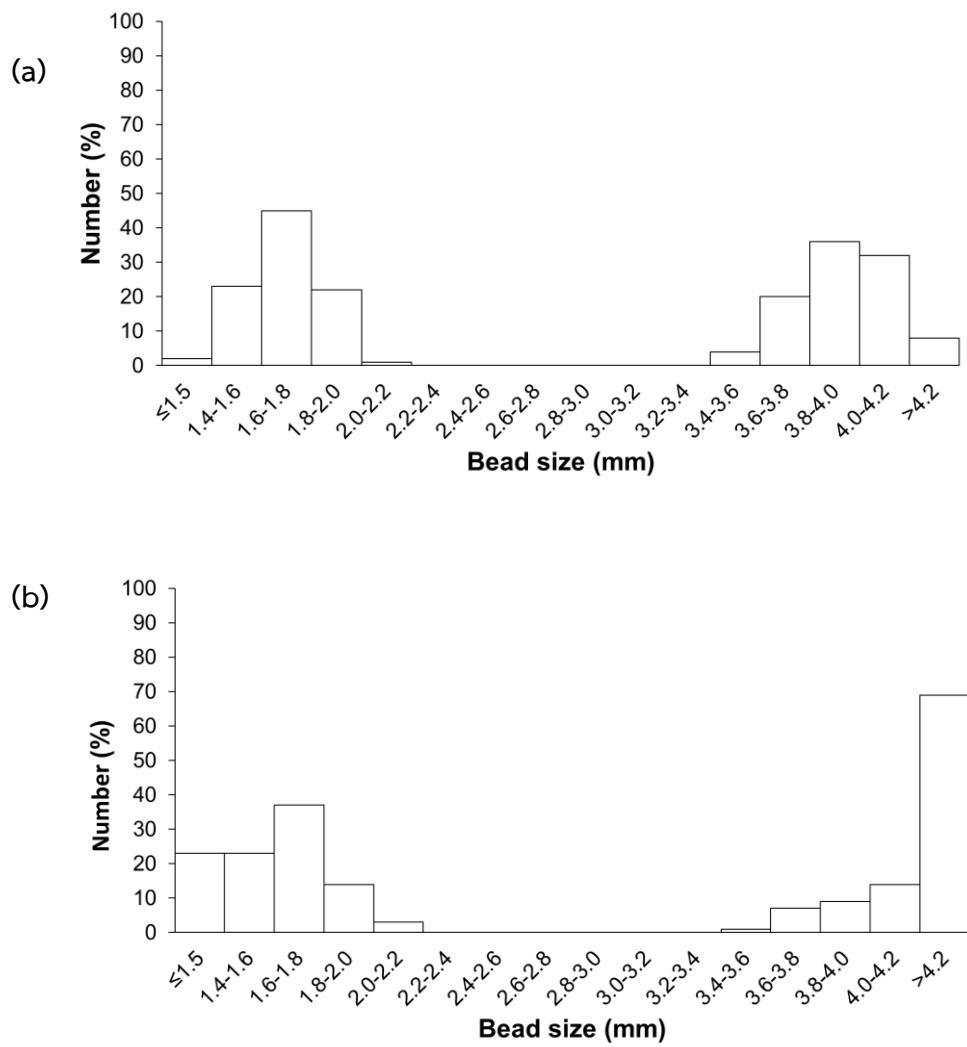


Figure 4.4 Histogram of bead size distribution of adsorbent (a) wet and dry Alg (b)

wet and dry Alg-Acid@Or-P

### 4.3 Point of Zero Charge ( $pH_{pzc}$ )

Point of Zero Charge ( $pH_{pzc}$ ) is generally described as the total pH on surface adsorbent at which the net charge of total particle surface is equal to zero. That means initial pH and final pH are equal. If  $pH < pH_{pzc}$  charge on surface adsorbent was more than zero but  $pH > pH_{pzc}$  charge on surface adsorbent was less than zero. Figure 4.5 shows the  $pH_{pzc}$  of Or-P at 5.5 was obtained. Besides, the  $pH_{pzc}$  of Alg, and Acid@Or-P was 6.5, and 4.5, respectively. Figure 4.6 and Figure 4.7. Pretreatment Or-P by acetic acid may affect to the surface properties of Acid@Or-P. Then, the values of  $pH_{pzc}$  of Acid@Or-P were measured lower than Or-P. However, adsorption phosphate experiment should fix at pH lower than 7 for efficacy of phosphate adsorption. Phosphate ion had negatively charged, so the suitable surface adsorbent should have positively charged.

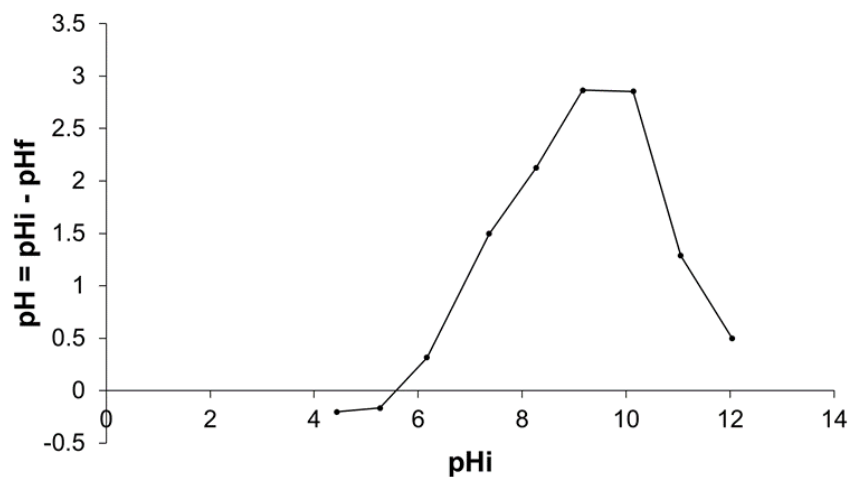


Figure 4.5 Point of Zero Charge of Or-P



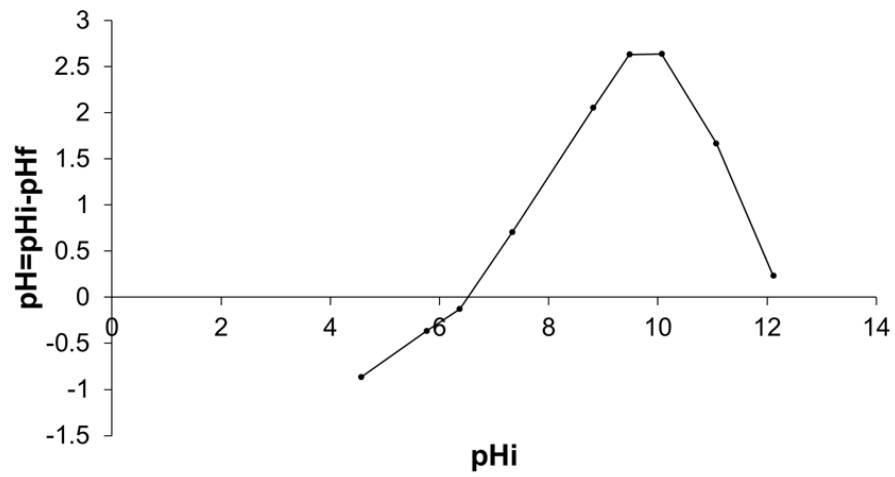


Figure 4.6 Point of Zero Charge of Alginate (Alg)

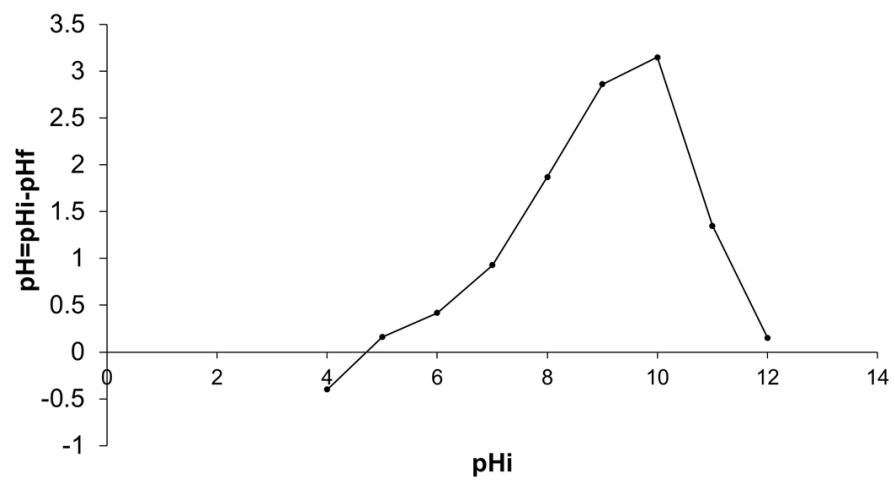


Figure 4.7 Point of Zero Charge of Alg-Acid@Or-P

## 4.4 Adsorption study

### 4.4.1 Effect of adsorbent type on phosphate removal

The percent removal of phosphate in solution for three different type of adsorbent namely orange peel (Or-P), alginate (Alg), and acid modified orange peel/alginate bead (Alg-Acid@Or-P) was studied. Figure 4.8(a) shows the removal of phosphate by various amount of Or-P dosage. It was found that the highest percent removal when two grams of Or-P at 15 mg/L of initial phosphate concentration applied. The high amount of adsorbent dosage may affect to surface area to adsorb phosphate. Figure 4.8(b) shows percent removal of each Alg bead dosage with different initial phosphate concentration. It was found that the two grams of Alg with initial phosphate concentration at 5 mg/L given the better percent removal. Since, the higher amount of dose affects to surface area to adsorb phosphate. Figure 4.8(c) show percent removal of each Alg-Acid@Or-P dose with different initial phosphate concentration. It was found that the two grams of Alg-Acid@Or-P with initial phosphate concentration at 5 mg/L, the better percent removal of phosphate. An increasing adsorbent dosage was provided the high surface area to adsorb phosphate ion.

Moreover, the different phosphate binding force are depending on surface charged of each adsorbent. The presence of  $H^+$  ions on the Or-P surface promote which may cause the surface to be positively charge and hence increase interaction with phosphate. On the other hand, the charge on surface of Alg and

Alg-Acid@Or-P may be negatively charge from  $\text{COO}^-$  so reduce interaction with negative charge of phosphate.

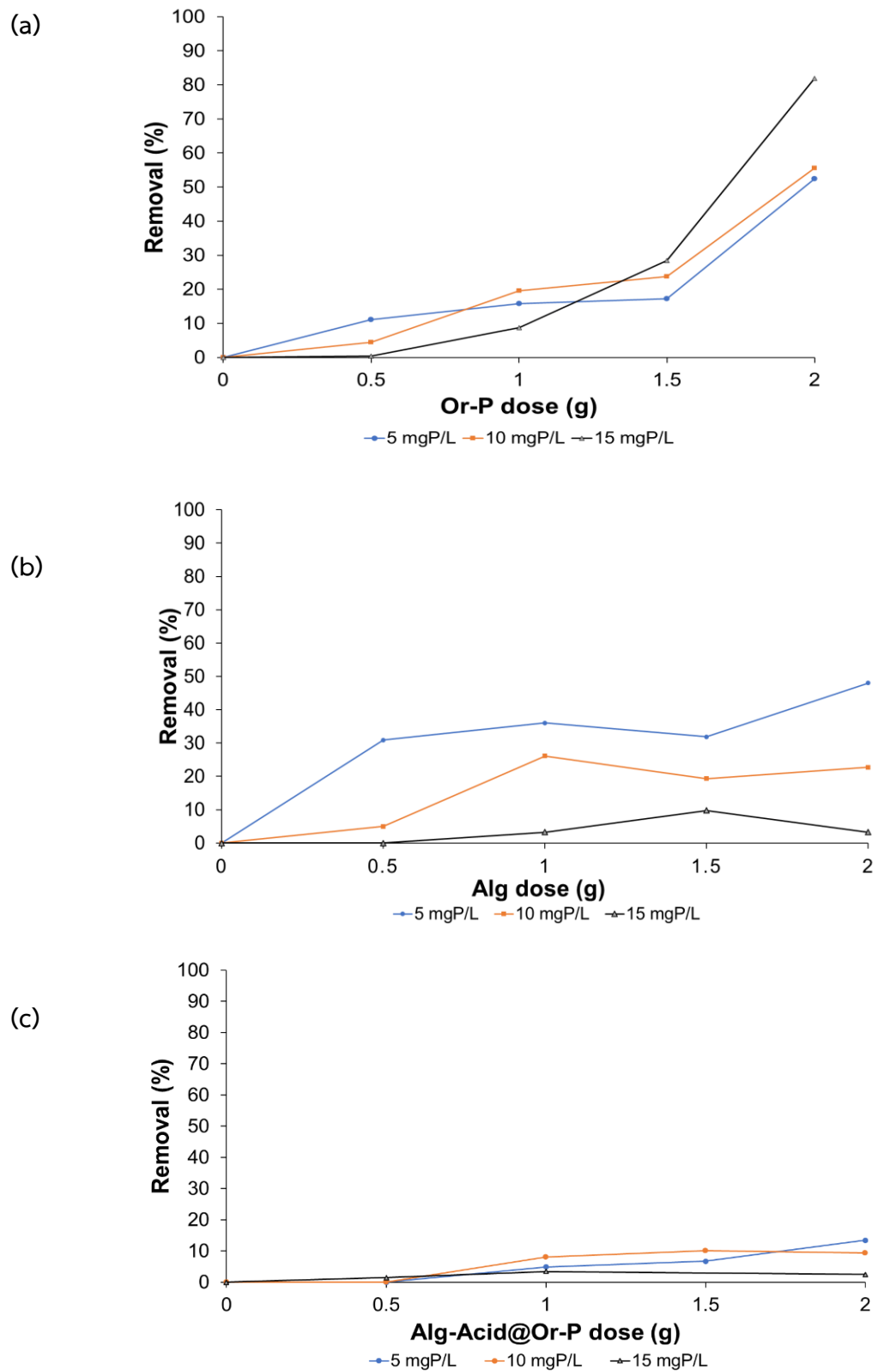


Figure 4.8 Effect of various adsorbent types and dosage on phosphate removal a) Or-P,

b) alginate bead, and c) Alg-Acid@Or-P at contact time 3 h

#### 4.4.2 Effect of initial phosphate concentration

Phosphate adsorption capacity ( $q_e$ ) on various type of adsorbent namely Or-P, Alg, and Alg-Acid@Or-P (2 g each) was investigated (Figure 4.9). It was found that an increasing of phosphate concentration from 5 mg/L to 15 mg/L enhanced the adsorption capacity of Or-P. The highest adsorption capacity (269.75 mg/g) was observed at a high initial concentration of phosphate due to the higher phosphate mass transfer at the surface of this adsorbent (Dev *et al.*, 2020). On the other hand, an increasing of phosphate concentration to 15 mg/L did not result in a significant increase of phosphate adsorption capacity for Alg and Alg-Acid@Or-P. In contrast, the adsorption capacity was decreased to 11.25 mg/g and 8.25 mg/g, respectively. The adsorption capacity of phosphate by Alg and Alg-Acid@Or-P was found lower than Or-P throughout every initial phosphate concentration studied. The result shows that the entrapment of acid modified Or-P in alginate polymer (Alg-Acid@Or-P), the adsorption capacity was decreased.

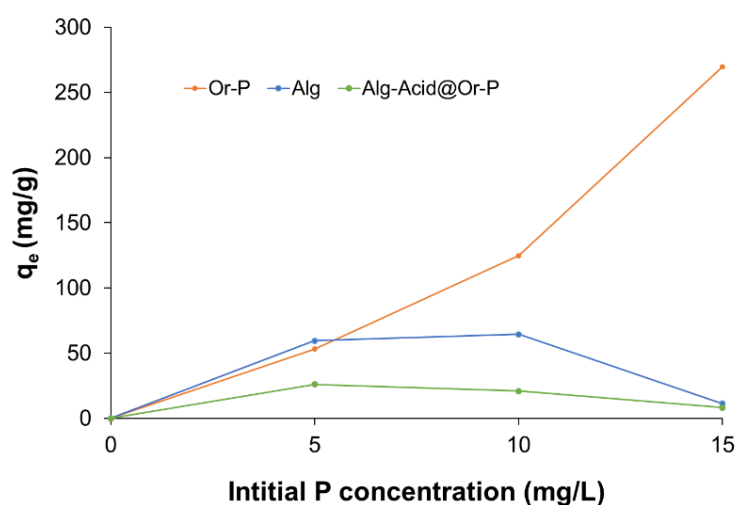


Figure 4.9 Effect of initial phosphate concentration on different types of adsorbent

#### 4.4.3 Effect of adsorbent dosage on phosphate removal

The effect of adsorbent dose on phosphate adsorption was investigated (Figure 4.10). The different surface properties of an Or-P, Alg, and Alg-Acid@Or-P beads, the different pattern of phosphate adsorption was observed. The adsorption capacity of 193 mg/g at 0.5 g of Alg bead was obtained. An increasing of Alg bead dosage, the adsorption capacity decreased. While the adsorption capacity by Alg-Acid@Or-P was found lower than Or-P throughout all dosage applied. The result shows that the entrapment of acid modified Or-P in alginate polymer (Alg-Acid@Or-P), the adsorption capacity was decreased.

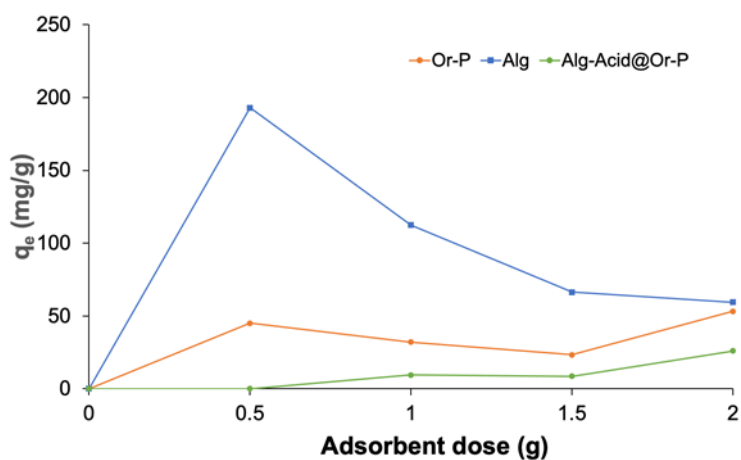


Figure 4.10 Effect of Adsorbent dose at fixed initial phosphate concentration (5 mg/L)

## CHAPTER 5

### CONCLUSION

#### 5.1 Conclusion

In this work, orange peels powder (Or-P) was pretreated by acetic acid and subsequently encapsulated in alginate (Alg-Acid@Or-P). After pretreated orange peel powder with acetic acid, it was found that the orange peel color turn from orange appearance to dark yellow. The spherical shape with narrow bead size distribution of Alg-Acid@Or-P beads was fabricated. The average wet bead diameter was found larger than the dry bead. The Alg-Acid@Or-P bead was used as adsorbent to removal phosphorus in aqueous solution. The batch experiment for phosphorus removal was performed. The percent phosphate removal each absorbent type to each initial phosphate concentration was followed; Or-P > Alg > Alg-Acid@Or-P bead, respectively. The highest adsorption capacity ( $q_e$ ) of 269.75 mg/g was measured when 2 g Or-P at initial concentration of 15 mgP/L at contact time 3 h. The low  $q_e$  at 8.25 mg/g was examined when an Alg-Acid@Or-P bead used. The low adsorption capacity may cause by the surface charge on modified orange peel/alginate beads. As the acid modified on orange peel powder, the positive charge may enhance and obstruct the binding ability of phosphate on the surface.

#### 5.2 Suggestion

The adsorption isotherms should carry out under the parameter e.g. contact time, pH and temperature.

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## BIOGRAPHY



**Name:** Phakhwan Sukarin

**Education:** Department of Environmental Science, Faculty of Science,  
Chulalongkorn University

**Academic year:** 2020

**Postal Address:** 555/10 Moo 25 The more village Tumbon Sila Amphur Muang  
KhonKaen 40000

**E-mail:** [phakhwansukarin@gmail.com](mailto:phakhwansukarin@gmail.com)

**Mobile:** 083-2849392