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ชื่อนิสิต	Miss Nuttaporn Chotvichasirikul
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คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

การเตรียมเม็ดบีดเปลือกส้มที่ถูกดัดแปร/แอลจิเนตสำหรับกำจัดฟอสฟอรัส

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คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2563

Preparation of modified orange peel/alginate beads for phosphorus removal

Nuttaporn Chotvichasirikul

A Senior Project Submitted in Partial Fulfillment of the Requirements for the

Bachelor's Degree of Science Program in Environmental Science

Department of Environmental Science

Faculty of Science, Chulalongkorn University

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Project title	Preparation of modified orange peel/alginate beads for phosphorus removal
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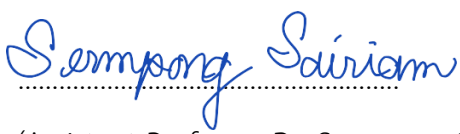

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บทคัดย่อ

การศึกษานี้ ใช้ตัวดูดซับจากธรรมชาติ คือ แอลจิเนต เปลือกส้ม และเปลือกส้มดัดแปรผสมกับแอลจิเนต มาทดสอบการกำจัดฟอสฟอรัสในน้ำ เม็ดบีดเปลือกส้มดัดแปรผสมกับแอลจิเนตเตรียมด้วยวิธีการการตกตะกอน โดยหยดสารละลายผงเปลือกส้มดัดแปรและแอลจิเนตให้เกิดการเชื่อมขวางในสารละลายแคลเซียมคลอไรด์ได้เม็ดบีด ทำการศึกษาผลของปริมาณตัวดูดซับ และความเข้มข้นเริ่มต้นของสารละลายฟอสฟอรัสในการทดลองแบบกะภายใต้การควบคุมความเป็นกรด-ด่าง และเวลาการทดลอง 3 ชั่วโมง จะได้เม็ดบีดเปลือกส้มดัดแปรผสมกับแอลจิเนตที่มีประสิทธิภาพในการกำจัดฟอสฟอรัส เมื่อเปรียบเทียบความจุของการดูดซับกับเม็ดบีดแอลจิเนตและผงเปลือกส้ม พบว่าเม็ดบีดเปลือกส้มดัดแปรผสมกับแอลจิเนตมีประสิทธิภาพในการกำจัดฟอสฟอรัสสูงกว่าเม็ดบีดแอลจิเนตและผงเปลือกส้ม ค่าความจุในการดูดซับสูงสุด คือ 653 มิลลิกรัมต่อกรัมที่ปริมาณตัวดูดซับ 0.5 กรัม นอกจากนี้ปริมาณเม็ดบีดเปลือกส้มดัดแปรผสมกับแอลจิเนตหนึ่งกรัมและความเข้มข้นเริ่มต้นของฟอสฟอรัส 10 มิลลิกรัมต่อลิตร สามารถกำจัดฟอสฟอรัสได้มากกว่าร้อยละ 99.4 อย่างไรก็ตามไอโซเทอมของการดูดซับไม่ได้ทำการศึกษาเนื่องจากสถานการณ์การระบาดของโรคโควิด-19 และการปิดห้องปฏิบัติการ

คำสำคัญ: แอลจิเนต; เม็ดบีด; การดูดซับ; เปลือกส้ม; ฟอสฟอรัส

Title	Preparation of modified orange peel/alginate beads for phosphorus removal
By	Miss Nuttaporn Chotvichasirikul
Student ID	6033318823
Project advisor	Associate Professor Dr. Roongkan Nuisin
Department	Environmental Science
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Abstract

In this study, natural adsorbents such as alginate, orange peel and modified orange peel/alginate were investigated for phosphorus removal from aqueous solution. Modified orange peel/alginate beads were prepared by precipitation. The modified orange peel/alginate solution droplets were crosslinked into calcium chloride solution to form granule beads. The effects of adsorbent dosage and initial phosphorus concentration have been examined in batch experiment under control pH and contact time of 3 hour. The modified orange peel/alginate bead was an effective adsorbent for phosphate removal was obtained. The adsorption capacity has been compared to that of alginate beads and orange peel powder. The highest adsorption capacity of 653 mg/g at the 0.5 g dosage of modified orange peel/alginate beads was examined. One gram adsorbents dosage at 10 mgP/L initial phosphorus concentrations, phosphorus removal more than 99.4% was determined. However, the adsorption isotherms were not conducted due to the COVID-19 pandemic situation with the laboratory closure.

Keywords: alginate; adsorption; bead; orange peel; phosphorus

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Nuttaporn Chotvichasirikul

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ABBREVIATION AND SYMBOLS

ALG	alginate bead
C_0	concentration of adsorbate at initial.
C_e	concentration of adsorbate at equilibrium.
°C	degree Celsius
g	gram
h	hour
n	number of samples
M	mass
mg/L	milligram per liter
mg/g	milligram per gram
min	minute
ml	milliliter
mm	millimeter
OPP	orange peel powder
OPAA	modified orange peel /alginate bead
q_e	equilibrium adsorption capacity on adsorbent

V	volume
W	weight
w/v	weight per volume
w/w	weight per weight

CHAPTER 1

INTRODUCTION

1.1 Background and significant problem

Phosphorus is an essential nutrient of plant, especially algae and phytoplankton that is a starting point food web. At the beginning, it stimulates phytoplankton and algae growth that increase oxygen in water. However, high concentration of phosphorus in water, can lead to environmental problems. An increasing phosphorus content in water, the population of phytoplankton and algae were increased and spread in water. The organic compounds were decomposed by microorganisms that use oxygen from water, the life in water die due to lack of oxygen to sustained life call this situation is eutrophication. Eutrophication causes destruction of water ecosystem due to lack of water resources and excessive growth of algae, which may adverse effect the economy from fishery products (Siwek *et al*., 2016; Jia *et al.,* 2020). The source of phosphorus contamination in environmental from municipal and industrial were affected to environment. The phosphate from municipal wastewater was 4 to 15 mg/L, whereas effluent from industrial such as metal coating processes was 14 to 25 mg/L (Krishnan and Haridas, 2008). The total phosphorus standard in effluent from municipal that determined by Natural Resources and Environment is 2 mg/L (Natural Resources and Environment, 2010) and the levels of phosphate equals 0.05 mg/L were allowed in enter sources to prevent the growth of algae (Jia *et al*., 2020).

Phosphorus removal methods from wastewater including biological phosphorus removal, chemical precipitation, ion exchange, membrane technology and adsorption have been studied. Among these methods, the adsorption has the advantages including highly efficient to removal low concentration phosphorus in wastewater, excellent adsorption selectivity, low cost and less toxic to the environment (Schoubben *et al*., 2010; Paques, 2015; Siwek *et al*., 2016). The adsorption process is defined as a mass transfer of adsorbate in both form of gaseous or liquid to the surface of porous soils as an adsorbent. Physical adsorption is the simplest advanced wastewater treatment method for the contaminate in wastewater is adheres on adsorption structure of an adsorbent. Biosorbents are emerging trend from agricultural waste or biopolymer in environment to separate contaminant from wastewater. The adsorbents have characteristics and properties biodegrade and environmental friendly such as activated carbon (Jung *et al.*, 2016) and biosorbent (Nguyen *et al*., 2014; Siwek *et al*., 2016).

Cellulose-based materials is biodegradable polymer which have many activated functional groups such as hydroxyl groups (Yue *et al*., 2019). Cellulose as a residue from orange peels that it is readily available from agriculture in Thailand. The most popular species of agriculture of orange is Sai Nam Phueng or Shogun. It is commonly grown, accounting for 40.7% of orange produce in the market. In addition, related research improvements be to remove toxic form wastewater and they show that chemical or physical activation increase properties of organe peels to adsorption toxic such as porosity and surface area, and increases the number of available active sites (Tomul *et al.*, 2017). It was reported for several heavy metal removal e.g. Cr (III), Pb(II), Ni(II), Se(IV)

and Cr(VI) (Dev *et al.*, 2020)and chlorophenoxyacid herbicides (Pandiarajan *et al.*, 2018). However, the pristine orange peels powder has some disadvantage. It was disintegrated, and clogged in reactor. Thus, calcium alginate is used to improve the structural stability and reuse capacity of orange peels (Dev *et al*., 2020). Alginate is a structure on brown seaweed cell walls. It has a structure that consists of α-L-guluronic acid (G) and β-D-mannuronic acid (M) residues which are linearly linked by 1,4 glycosidic linkages and the ratio of mannuronic acid and guluronic acid are vary with source that impact to physical properties soft gel or hard gel. The physicochemical properties of alginates have the functional group including carboxyl group (-COOH) and hydroxyl group (-OH) (Paques, 2015; Tomul *et al.*, 2017; Alba and Kontogiorgos 2018; Dev *et al*., 2020). The alginate / goethite composite has been used for adsorption phosphate in water such as alginate/goethite Hydrogel (Siwek, Bartkowiak, and Włodarczyk, 2019), and alginate/ iron (III) chloride capsules (Siwek *et al*., 2016).

The aim of this study, orange peel powder from orange peel waste was prepared. The orange peel powder was modified by surface activated with sodium bicarbonate. The orange peel powder/alginate bead (OPAA) was prepared by precipitation technique in calcium chloride solution. To investigate the adsorption capacity, the orange peel powder, alginate bead, and peel/alginate bead as adsorbent was performed in batch adsorption method. The effects adsorbent dosage, and contact time were investigated of various initial phosphate concentration. The adsorption and efficiency of removal phosphate from aqueous solution were evaluated.

1.2 Expected benefits

1. The developer can prepare the bio-polymer adsorbent that create business worthiness.

2. The developer can adapt a range of influences to remove phosphorus in contaminated water.

3. Able to decrease phosphorus in the water contaminated before discharge into environmental.

CHAPTER2

LITERATURE REVIEW

2.1 Phosphorus in water

The source of pollution is point sources such as discharge from industrial or wastewater pipelines and non-point source such as leaching run off from residential or agricultural areas (Peterson and Wasley, 2007).

Phosphorus in water has two main forms that is dissolved and a component of particulate. The primary dissolved form is orthophosphate. It is microbial conversion of organic to $H_2PO_4^-$ or HPO_4^{2-} that readily used by algae, phytoplankton and aquatic plants call mineralization. Particulate form can change in variety form depends on environment (Figure 2.1). However, the particulate that bound with mineral such as aluminum are not available for algae, phytoplankton and aquatic plants (Peterson and Wasley, 2007).

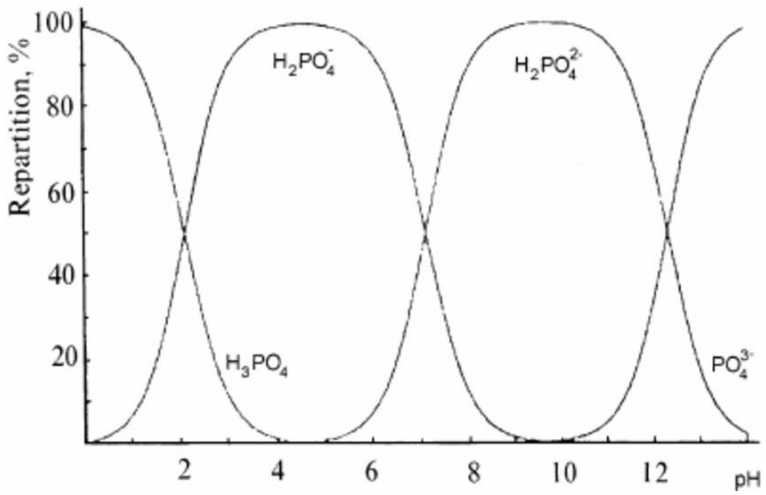

Figure 2.1 Percent repartition of various forms of orthophosphate at different pH levels (Pismenskaya *et al.*, 2001)

Phytoplankton in water will stimulate bloom when addition phosphorus of 0.02 mg/L and can cause major eutrophication (Yazdani *et al.*, 2017). When concentration of phosphorus or nutrients was increased, the growth rate of algae, phytoplankton and plants were dense bloom on surface water. Submarine plant cannot receive sufficient sunlight and oxygen in air cannon dissolve in to water that is aquatic plants may die. It will be leading to reduction habitat area and food of aquatic life. Also, death aquatic plant and algae are decomposition will reduce that dissolved oxygen level in water, which will be negatively impacts in ecosystem such as decreases survival rates of aquatic life (Gold and Sims, 2005).

2.2 Orange peel as adsorbent

The bio-waste material is an agro-industrial waste generated in orange juice factories. Natural materials containing cellulose, hemicellulose and lignin are suitable as sorbents because the composition of the substance is full of hydroxyl and carboxylic groups. Figure2.2 show the composition of sweet orange peel contains moisture (40.7%), ash (7.39%), fat (1.85%), pectin (7.0%), lignin (6.4%), crude fiber (7.8%), total sugar (14.08%), reducing sugars (10.70%) and non-reducing sugar (3.70%) (Ahmed *et al.,* 2016*).*

The lignin component has a function group that can bind molecules well. The modified biomass by chemical treatment such as NaOH, KOH, K_2CO_3, Na_2CO_3, H_2SO_4 and $Ca(OH)_2$. The chemical treatment will be increased internal surface area, decreased polymerization and cellulose crystallinity (Agbor *et al.,* 2011; Mukhtar *et al.,* 2020) but

pure orange peels can clog in reactor previous research studies entrapped by alginate (Dev *et al*., 2020). The use of orange peel as adsorbent has been investigated for heavy metals. Besides, soybean meal has been used for phosphate removal (Tomul *et al.*, 2017; Nguyen *et al*., 2014).

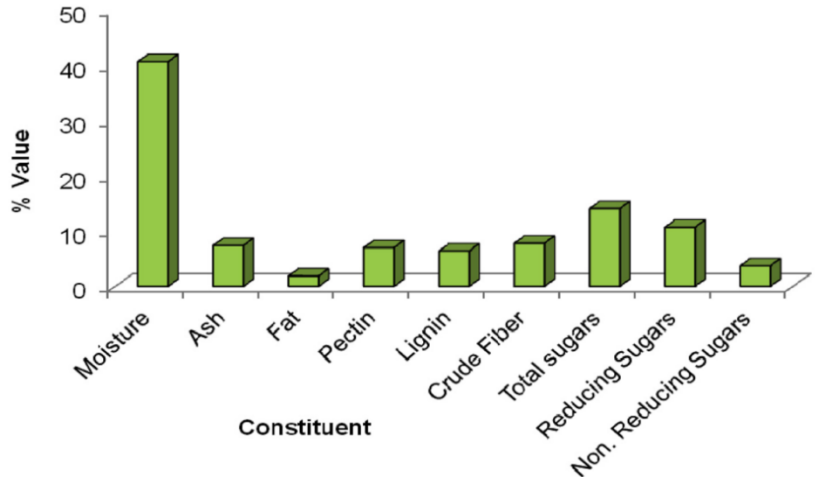

Figure 2.2 Chemical composition of orange peel

(Ahmed *et al*., 2016)

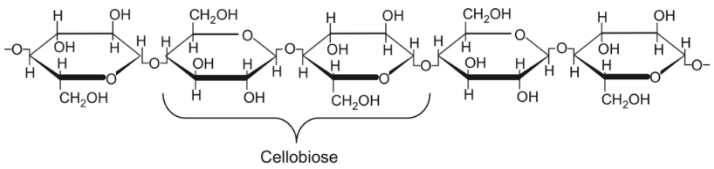

Figure 2.3 Chemical structure of cellulose

(Machmudah *et al.,* 2017)

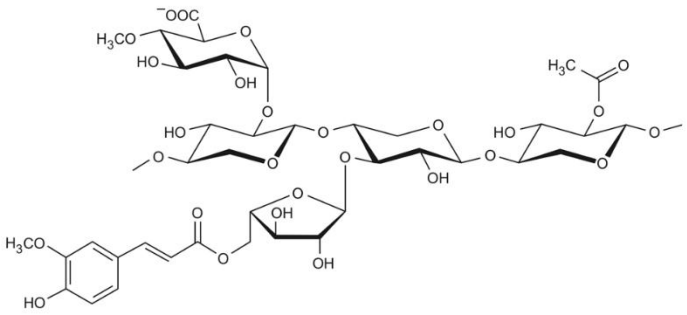

Figure 2.4 Chemical structure of hemicellulose

(Machmudah *et al.*, 2017)

2.3 Alginate

Alginate is biopolymer, anionic and hydrophilic polysaccharide that synthesized from two sources including marine plants such as brown seaweed and bacteria such as Pseudomonas species.

The structure of alginate molecule has consisted of β-D-mannuronic acid (M) and α-L-guluronic acid (G) residues linked by 1⟶4 glycosidic linkages. The most sequence of structure that common found in environment is guluronic acid (G-blocks) or mannuronic acid (M-blocks) and regions of alternating sequences (e.g., MG, MMG, GGM) (Figure 2.5), respectively (Alba and Kontogiorgos 2018). It consists of four reactive sties available for reaction including two functional groups and two bonds, that is carboxylic functional groups, hydroxyl functional groups, 1 ⟶ 4 glycosidic and internal glycolic

bonds. The functional groups on the backbone can modification to tailor other desired properties (Zia *et al.*, 2015).

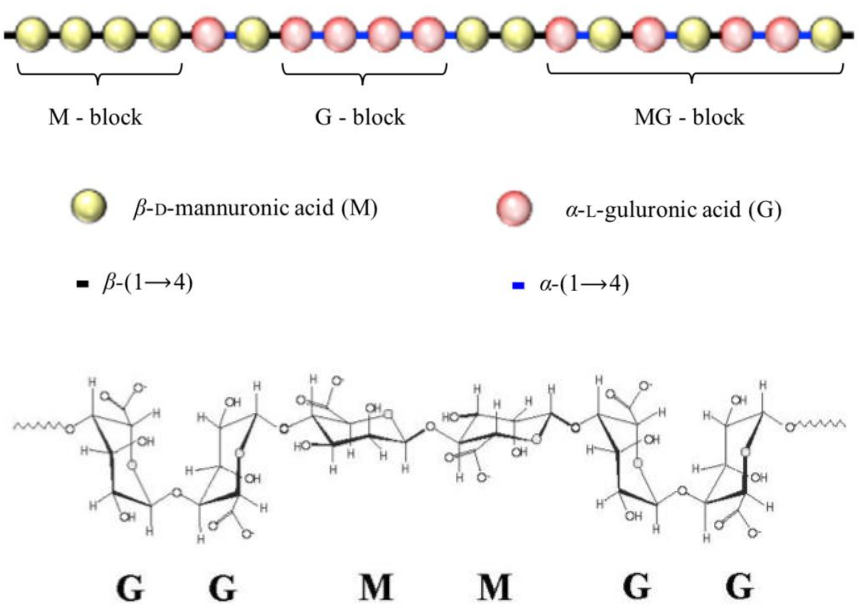

Figure 2.5 Chemical structure of alginates

(Alba and Kontogiorgos, 2018)

2.4 Orange peel/alginate bead preparation technique

Alginate beads are usually produced by external gelation, internal gelation or a combination of both techniques. External gelation can be obtained by simply dripping a sodium alginate solution in a calcium chloride solution that dripped under the influence of gravitational force or external force, sprayed by air intake through a nozzle (Schoubben *et al.*, 2010). If alginate is to be modified with a soothing agent, such as orange peel (Dev *et al.,* 2020), calcium carbonate (Zahid *et al.,* 2015) , iron(III) chloride (Siwek *et al.,* 2016). Then, the substance must be homogeneously mixed with the

alginate solution before forming bead pellets by dripping into solution of calcium chloride.

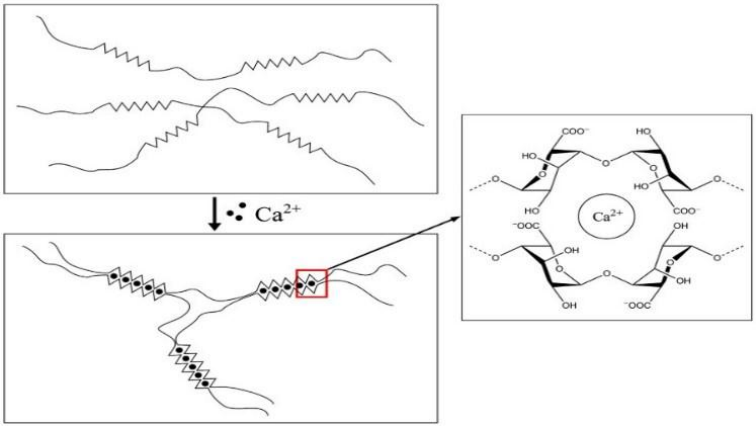

Figure 2.6 Ionic cross-linking of alginate gelation

(Paques, 2015)

2.5 Adsorption process

Adsorption is the process that molecule or ion transfer from gaseous or liquid phase to attach or get interaction on surface of solid or rarely a liquid that called adsorbent. The molecule or ion called adsorbate in this process, adsorbate does not diffuse in to adsorbent structure. Adsorption can be divided into three majors including chemical sorption, physical sorption and electrostatic sorption. The adsorption capacity at equilibrium stage between the solution, adsorbent dose and adsorbent are calculate in Eq. (2.1). The adsorption can study by using isotherm and kinetic (Vinet and Zhedanov, 2011).

$$q_e = [(C_0 - C_e) * V] / M \quad \text{.....(2.1)}$$

where q_e (mg/g) is the equilibrium adsorption capacity on adsorbent

C_0 (mg/L) is the concentration of adsorbate at initial

C_e (mg/L) is the concentration of adsorbate at equilibrium

V (ml) is solution volume

M (g) is the mass of adsorbent

2.5.1 Adsorption isotherms

The isotherms of adsorption use to evaluate the adsorption from solution that can be obtains the amount of adsorbed species. It can be represented property of adsorbent such as removal efficient. However, adsorbed can evaluate only when equilibrium. In addition, the adsorption isotherm has influencing parameter includes dosage of adsorbent and the adsorbate concentration (Vinet and Zhedanov, 2011). It has many theories, but the most used widely models are Langmuir and Freundlich.

Langmuir isotherm was used for explain monolayer adsorption that depends on concentration of adsorbate. The assumptions of Langmuir model are homogeneous surface and every site equivalent energetically, monolayer process, no lateral interaction between adsorbed molecules, limit surface site

and reversible. It will increases adsorb when increases concentration of adsorbate until it saturated. Langmuir isotherm calculate in the Eq. (2.2) and convert to linear form in Eq. (2.3).

$$q_e = [(Q_m * K_L * C_e)/(1+K_L * C_e)] \quad \text{.....(2.2)}$$

$$C_e/q_e = (C_e/Q_m) + (1/K_L * Q_m) \quad \text{.....(2.3)}$$

Where, q_e (mg/g) is the equilibrium adsorption capacity on adsorbent

C_e (mg/L) is the concentration of phosphate in solution at equilibrium

K_L (mg/g) is the constants in the Langmuir which related to adsorption capacity

Q_m is monolayer saturated adsorption capacities on adsorbent call maximum adsorption

Freundlich isotherm was used for explaining adsorbents which were heterogeneous surface, multilayer sorption and reversible. It has different binding energies adsorption site. Freundlich isotherm calculate in the Eq. (2.4) and convert to linear form in Eq. (2.5).

$$q_e = K_F * C_e^{1/n} \quad \text{.....(2.4)}$$

$$\ln q_e = (1/n) \ln C_e + \ln K_F \quad \text{.....(2.5)}$$

where, q_e (mg/g) is the equilibrium adsorption capacity on adsorbent

C_e (mg/L) is the concentration of phosphate in solution at equilibrium.

K_F (mg/g) are the constants in the Freundlich which is related to adsorption capacity

Q_m is monolayer saturated adsorption capacities on adsorbent

n is the adsorption intensity of Freundlich isotherm

2.5.2 Adsorption kinetics

Adsorption kinetics are describing the rate of retention or release solution from aqueous environment to attach on adsorbents. It can give information about adsorption pathways and probable mechanism involved. It uses to understand characteristics and identify dynamic of adsorption process. The most used widely models are pseudo first-order model and pseudo second-order (Vinet and Zhedanov, 2011; Jia *et al.*, 2020).

The pseudo first-order model is model that base on assumption includes rate of uptake solution are directly proportional to saturation concentration and solid up take with time, adsorption from electrostatic interaction with adsorbent surface and adsorbate and it is chemical sorption. This model can calculate on Eq. (2.6).

$$\text{Log } (q_e - q_t) = \log q_e - (k_1 t/2.303) \quad \text{.....(2.6)}$$

where, q_t (mg/g) is the amount of phosphate absorbed at a certain

interval

q_e (mg/g) is the amount of phosphorus at an equilibrium state

k_1 (1/min) is the adsorption rate constant of the Pseudo first order

model

The pseudo second-order model is kinetic model base on assumption include chemical sorption and this adsorption rate dependent on adsorption capability of active site not concentration of adsorbate as Eq. (2.7).

$$t/q_t = (1/q_e^2 k_2) + (1/q_e)\, t \qquad \text{..... (2.7)}$$

where, q_t (mg/g) is the amount of phosphate absorbed at a certain

interval

q_e (mg/g) is the amount of phosphate absorbed at an equilibrium state.

C_0 (mg/L), C_t(mg/L) and C_e (mg/L) are the phosphate concentration at

initial, t-time and equilibrium in solution, respectively

k_2 (g/mg·min) is the adsorption rate constant of the Pseudo second

order model

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials and Chemicals

3.1.1 Chemicals and Reagents

- Orange peels from *Citrus sinensis*, Thailand

- Sodium alginate $(C_6H_7O_6)_n$, AR grade, Carlo Erba, Italy

- Sodium bicarbonate ($NaHCO_3$), AR grade, Riedel-deHaën, Germany

- Calcium chloride ($CaCl_2$), AR grade, Carlo Erba, Italy

- Sulphuric acid (H_2SO_4), AR grade, QRëC, New Zealand

- Sodium hydroxide (NaOH), AR grade, Carlo Erba, Italy

- Sodium chloride (NaCl), AR grade, Carlo Erba, Italy

- Ammonium Molybdate ($(NH_4)_6Mo_7O_{24}\,4H_2O$), AR grade, Macron Fine Chemicals, Thailand

- L-Ascorbic acid ($C_6H_8O_6$), AR grade, Unilab, Thailand

- Distilled water

3.1.2 Materials and Equipment

- Sieve size 500 micrometer, (Endecotts Ltd., England)

- Hotplate Stirrer (model C-MAG HS7, Kittisit enterprise Co,Ltd., Thailand)

- Reciprocal shaker (Gerhardt, Scientific Promotion Co,Ltd., Germany)

- 4 Decimal Analytical balance (Mettler Toledo, Thailand)

- 2 Decimal Analytical balance (Mettler Toledo, Thailand)

- Spectrophotometer (Spectro SC, Thailand)

- Syringe diameter size 0.27 mm. (Nipro company, Thailand)

- Oven (model 700, Memmert, Germany)

- pH meter (Denver Instrument, USA.)

- Blender (SARA KIT s-9902, V Enterprise.Co,Ltd, Thailand)

3.2 Methodology

3.2.1 Orange characterization

Oranges were washed and clean up. The whole fruit, peel, and pulp of orange fruits were determined by gravimetric, volume determination, moisture content determination and bulk density.

Weight was determined on gravimetric techniques using 2 decimal analytical balance.

Volume of an orange peel was determined by displacement in water method in beaker 1000 ml then calculated volume in Eq. (3.1) and Eq. (3.2).

Final volume – Initial volume = Volume of water displaced ……(3.1)

Average volume = Volume of water displaced/Total number of fruits or peel ……..(3.2)

Moisture content was determined by electronic balance, that dried orange peels in oven at 60° C for 2 days and placed in a desiccator for 24 h. The moisture content was calculate in Eq. (3.3) and Eq. (3.4) (Olabinjo *et al*., 2017)

$$\text{Dry matter (\%)} = [(W_3 - W_0) / (W_1 - W_0)] * 100 \quad \text{……(3.3)}$$

$$\text{Moisture content (\%)} = 100 - \%DM \quad \text{……(3.4)}$$

where, W_0 is weight of empty aluminium foil

W_1 is weight of aluminium foil plus sample before drying

W_3 is weight of aluminium foil plus sample after drying

3.2.2 Adsorbent preparation

3.2.2.1 Preparation of alginate beads (ALG)

The sodium alginate 2% (w/v) was dissolved in distilled water. The alginate solution was dropped into 1.5% (w/v) calcium chloride using syringe with a diameter of 0.27 mm, then stirred for 1 h for beads hardening process. The beads were took off the solution and rinsed

with distilled water twice. The beads were dried in an oven at 60°C for 24 h.

3.2.2.2 Preparation of modified orange peel/alginate beads (OPAA)

Oranges were washed twice and peeled of the orange peel. The orange peels were then baked at 60°C for 48 h, blended by blender to transform into a powder, then sieved with sieve size of 500 micrometer.

The fifty grams of orange peels powder (OPP) that passed the sieve was treated with a solution of sodium bicarbonate. The sodium bicarbonate solution was prepared by dissolving sodium bicarbonate 10% (w/w) in 500 ml of water for 1 h. The modified orange peel powder was leached with distilled water twice and baked at 60°C for 48 h. Two grams of modified orange peel powder was mixed with 2% (w/v) sodium alginate solution stirring until homogeneous solution. The modified orange peel/alginate solution was dropped to 1.5% (w/v) calcium chloride solution stirred for 1 h to form OPAA beads. After that, the wet beads were washed with distilled water twice and baked at temperature 60°C for 24 h. (Solid and lumpy appearance of modified orange peel powder was observed after bake in oven. Then, it takes a long time to mix in sodium alginate solution until homogeneous.)

3.2.3 Effect of adsorbent dosage and initial concentration

The batch experiment for adsorption studies were performed using 125 ml erlenmeyer flask. The adsorbent dosage in range of 0 to 1.5 g of ALG, OPP and OPAA. Adsorbents were investigated at initial phosphorus concentration of 5, 10 and 15 mgP/L. The 50 ml of phosphorus stock solution was transferred to an erlenmeyer flask containing a design adsorbent and shake with 120 rpm for 3 h. After that, the solution was diluted for 25 time to check the residual phosphate in solution. The phosphorus removal efficiency was determined using ascorbic method. The adsorption amount of phosphorus on adsorbent was calculated by the plot between adsorbent dosage and phosphate removal rate as calculate from Eq. (3.6) and the adsorption capacity was calculate from Eq. (3.7) (Jung *et al*., 2016).

$$\text{Phosphate removal rate (\%)} = [(C_0 - C_e) / C_0] * 100 \quad \text{.....(3.6)}$$

$$q_e = [(C_0 - C_e) * V] / M \quad \text{.....(3.7)}$$

where, C_0 (mg/L) is the concentration of adsorbate at initial

C_e (mg/L is the concentration of adsorbate at equilibrium

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

V (ml) is solution volume

M (g) is the mass of adsorbent

CHAPTER 4

RESULTS AND DISCUSSTION

4.1 Orange characterization

The characterization of orange fruit, orange peel and orange pulp were investigate as shown in Table 4.1. The one kilogram of Sai Nam Phung orange fruit consisted of a fresh orange peel (17.6%) and orange pulp (81.6%) was calculated. The value of dry matter is 32.5% and the moisture content is 67.5%. In addition, the physical appearance of orange fruit has been changed from orange to brown due to the dehydration. The surface of the orange peel can be more clearly visible the porosity or unevenness of the orange peel.

Table 4.1 Orange characterization

Composition	Characteristics	
	Weight (g) ± SD	**Volume (cm^3) ± SD**
Whole orange	103.2 ± 8.94	107.0 ± 8.98
Orange pulp	84.2 ± 9.06	82.0 ± 7.23
orange peels	18.2 ± 1.37	19.9 ± 1.75
Dry matter (%)	17.8 ± 1.59	
Moisture content (%)	36.9 ± 1.59	

4.2 Characterization of adsorbents

Figure 4.1 shows the optical micrographs of wet alginate beads (ALG), the white color with spherical shape was observed. The dried alginate beads were found smaller in size with opaque white than that of wet beads. The average diameter of alginate beads was measured by an ImageJ program (n=100). Figure 4.2 shows diameter size of wet alginate beads in size range of 3.8 to 4.0 mm, and dried alginate beads in size range of 1.6 to 1.8 mm. The average size of dried beads is about 2.2 times smaller than wet beads. The average of diameter of wet and dry beads were 3.9 and 1.8 mm, respectively.

Figure 4.3 shows the optical micrographs of wet modified orange peel/alginate beads (OPAA). The orange color with spherical shape was observed by naked eyes. The dried OPAA beads were found smaller than wet beads. The opaque white color of dried beads was observed. The diameter of wet OPAA beads (n=100) in range of 3.1 to 4.8 mm were measured. The dry OPAA beads size range of 0.9 to 1.8 mm were observed Figure 4.4. The average size of wet and dry OPAA beads were 3.9 and 1.3 mm, respectively. The beads size of dry bead was approximately three times smaller than wet beads. The OPAA beads was subsequently used for adsorption in phosphorus solution.

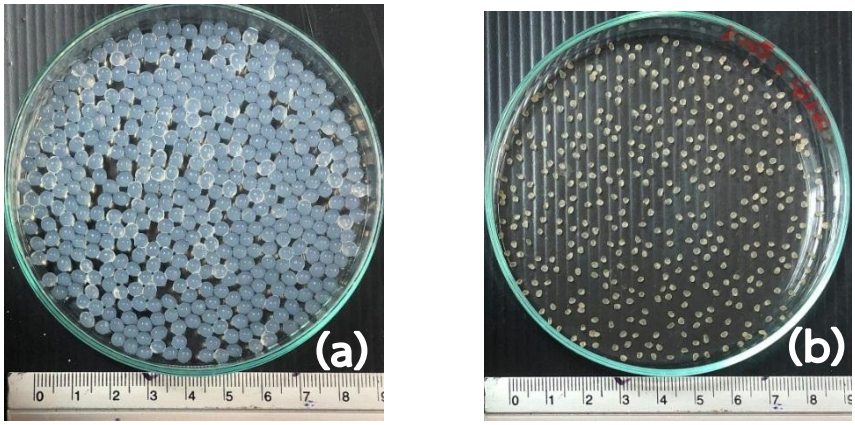

Figure 4.1 Optical photographs of alginate beads

(a) wet beads, (b) dry beads

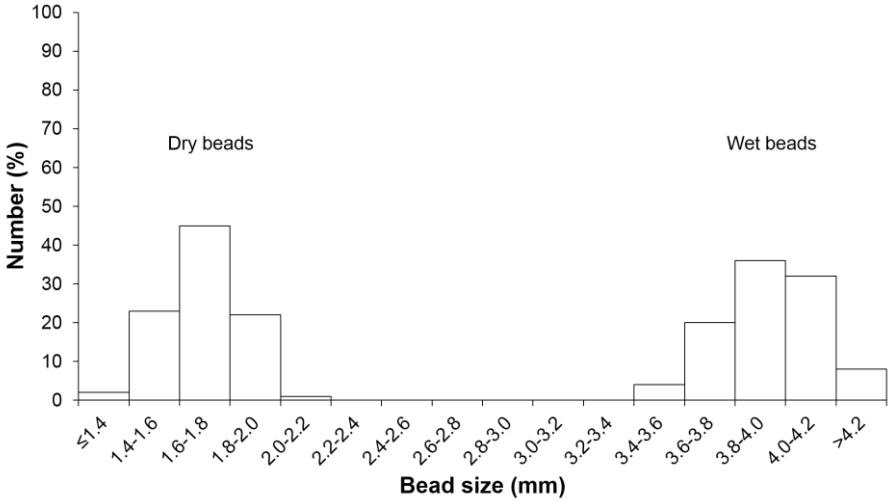

Figure 4.2 Histogram of beads size distribution of alginate

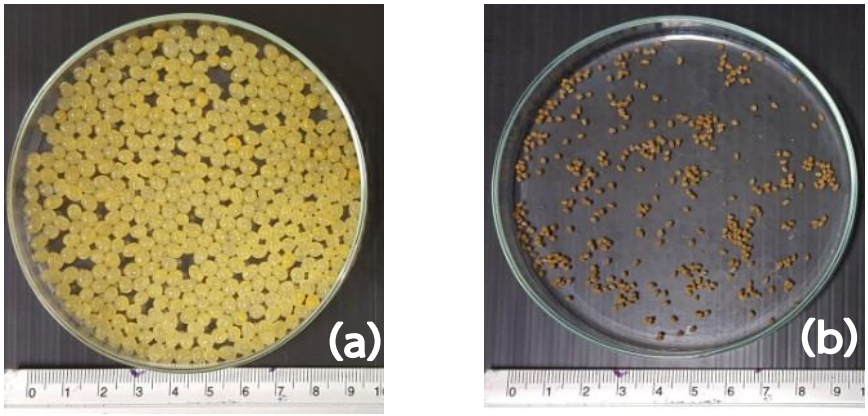

Figure 4.3 Optical photographs of modified orange peel/alginate beads

(a) wet beads, (b) dry beads

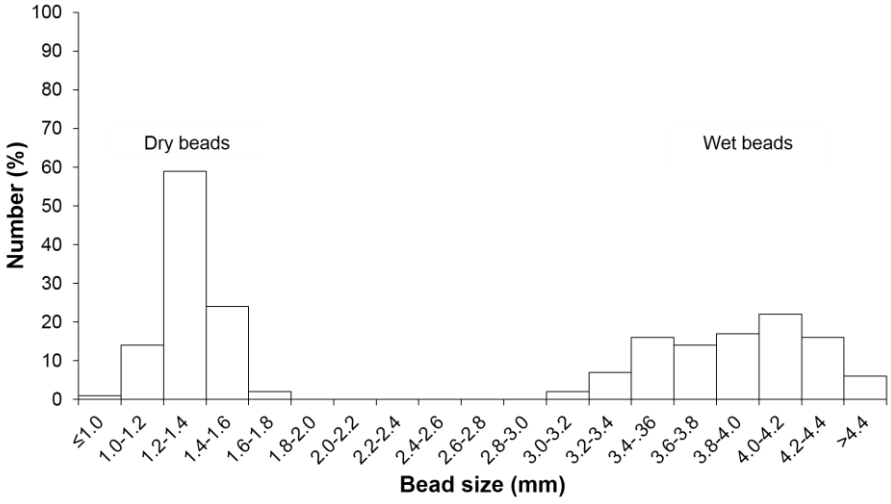

Figure 4.4 Histogram of beads size distribution of modified orange peel/alginate beads

4.3 Adsorption studies

4.3.1 Effect of adsorbent dosage on phosphorus removal

The effect of adsorption phosphorus by alginate beads (ALG), orange peel powder (OPP) and modified orange peel/alginate beads (OPAA) were investigated. The highest phosphorus removal rate of each adsorbent was 48.0%, 81.9% and 99.9%, respectively. An increasing the adsorbent dosage, the removal rate of phosphorus was increased. These can explain by the surface-active site to adsorb adsorbate. For ALG bead as adsorbent, it was found that increasing of bead dosage, the removal rate was increased. The removal was decreased when the dosage of alginate beads increasing.

The effect of adsorbent type and dosage on removal rate of phosphorus was investigated. Figure 4.5 shown the highest phosphorus removal rate was observed at an initial concentration of 5 mgP/L for all alginate dosage. An OPP as an adsorbent the greatest removal rate was obtained when the 0.5 g of OPP used. The highest removal rate (17.2%) for initial 5 mgP/L phosphorus concentration was measured (Figure 4.6). However, an increasing the adsorbent dosage, the phosphorus removal rate was increased from the 5 mgP/L to initial higher initial concentrations of 10 and 15 mgP/L, respectively. The phosphorus removal rate was increased due to the high surface area of the adsorbent. At high concentration of phosphate solution, the high amount of phosphate ions was dissolved in water. The competition between the binding site of an adsorbent and ions in solution occurs, it causes of reducing the removal

rate. Figure 4.7 shows the consequence of amount of OPAA dosage on the removal of phosphorus. It is well known with an increase in the amount of OPAA bead doses, the numbers of active sites are increased for the sorption reaction. The similar trend in percentage removal of phosphorus as a function of adsorbent dose was observed. The percentage removal of phosphorus by OPAA was observed to increase from 79.2 to 96.5% (for 5 mgP/L), 70.7 to 99.9% (for 10 mgP/L), and 44 to 99.1% (for 15 mgP/L) while increasing the adsorbent dose from 0.5 to 1.5 g. It was clearly demonstrated that the entrapment of modified orange peel powder by alginate favors the adsorption process.

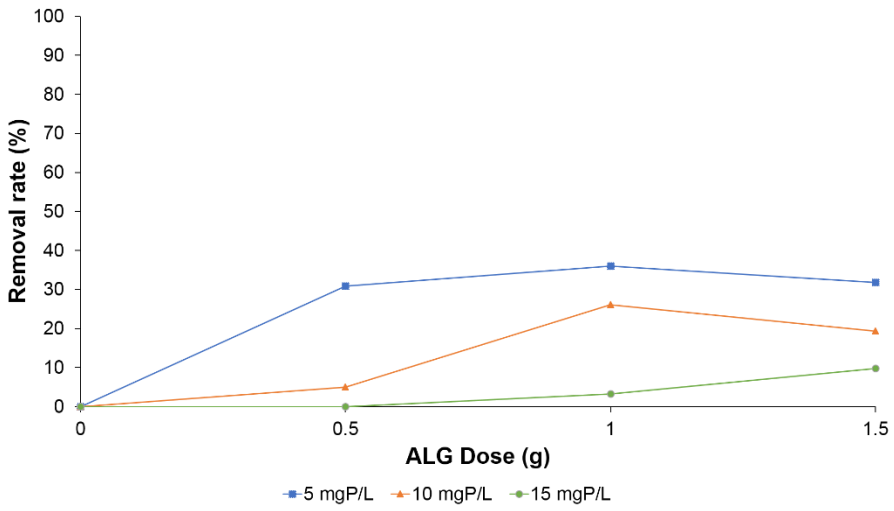

Figure 4.5 Effect of alginate beads dosage on phosphorus adsorption at contact time 3 h

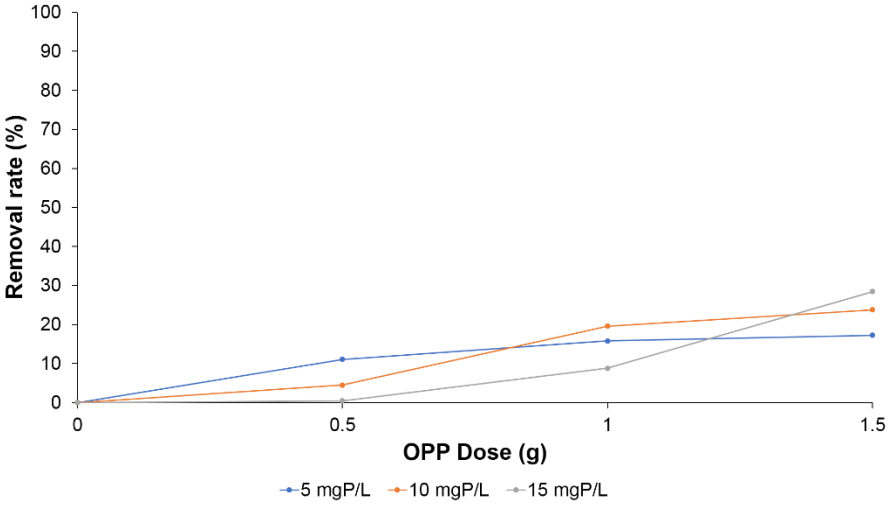

Figure 4.6 Effect of orange peel powder dosage on phosphorus adsorption at contact time 3 h

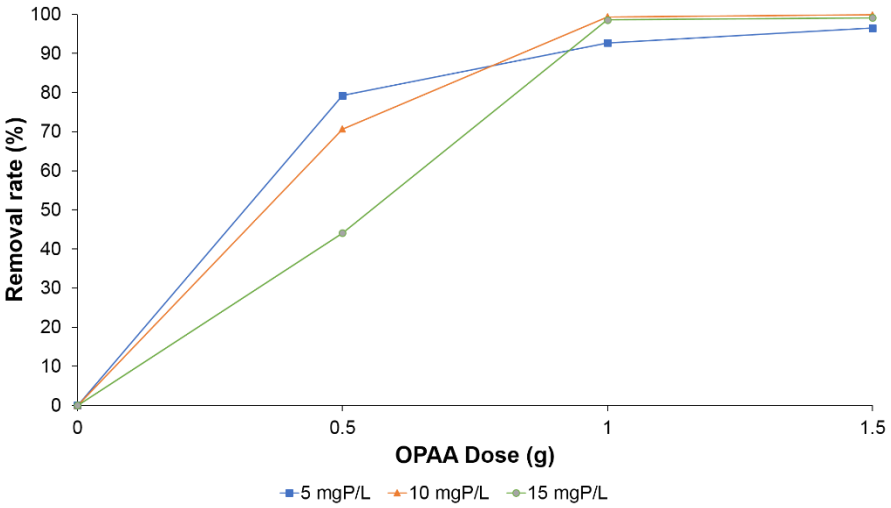

Figure 4.7 Effect of modified orange peel /alginate beads dosage on phosphorus adsorption at contact time 3 h

4.3.2 Effect of adsorbent dosage of modified orange peel /alginate beads

Figure 4.8 shown the effect of orange peel activated-alginate beads (OPAA) dosage on adsorption of 10 mgP/L of phosphorus solution, contact time 3 h. It was found that an increasing of OPAA dosage the phosphorus removal rate increased. The highest adsorption capacity of 653 mg/g, was calculated at 0.5 g of OPAA dosage. Over all, one gram adsorbent was considered as an optimum amount for further adsorption studies due to the effective on removal rate.

Figure 4.9 shown the influence of adsorbent dosage and types on phosphorus adsorption. The lowest adsorption capacity was determined when all dosage of an orange peel power (OPP) was applied. The adsorption capacity of phosphorus solution was enhanced when alginate beads was used. The highest adsorption capacity of phosphorus solution was obtained when using OPAA beads as adsorbent.

The orange peel powder consisted of hydroxy groups on cellulose structure. After modified with sodium bicarbonate, a partially carbonate ion group was activated. Besides, alginate had hydroxyl and carboxylic groups functional group that can adsorbed by ligand exchange hydroxyl group. The modified orange/alginate beads had highest adsorption capacity due to the OPP modified by sodium bicarbonate. Its broke

hemicellulose, lignin and cellulose that destroy the orange peel surface. The surface of orange peel activated was more porosity and had carbonate functional group adhere on surface. When, used OPAA extrapolated that phosphate ion were diffused into the pores, the phosphate ion was interacted to a modified orange peel surface that entrapped and alginate by anion exchange and ligand exchange. The carbonate ion was removed out from the beads. It was found that the final pH of solution after adsorption treatment process was increased from initial pH.

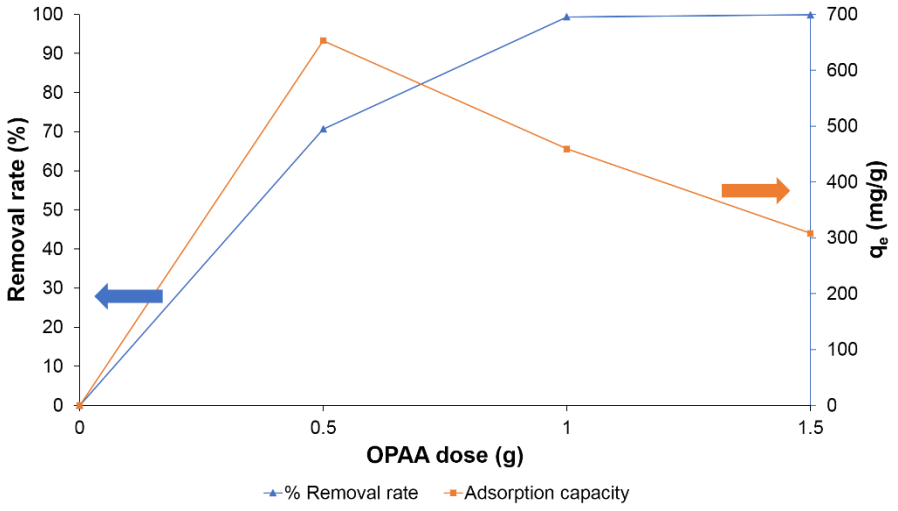

Figure 4.8 Effect of OPAA dosage on phosphorus adsorption at initial concentration 10 mgP/L at contact time 3 h

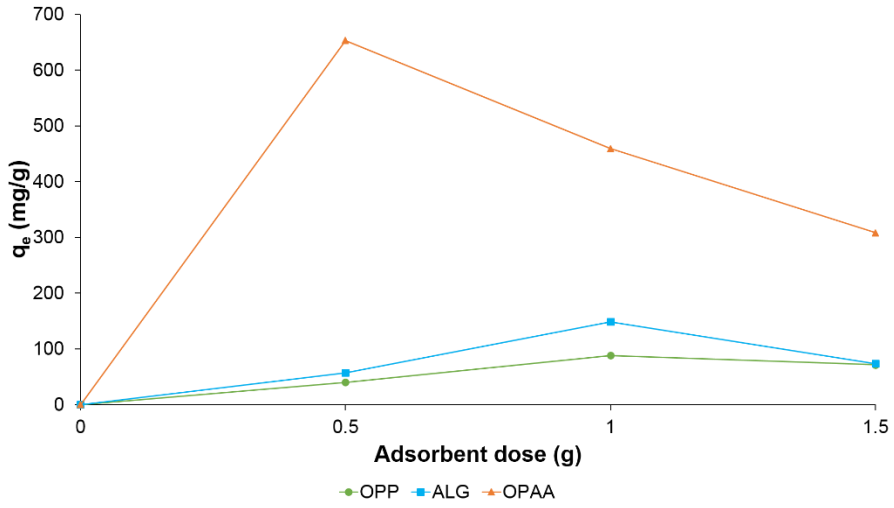

Figure 4.9 Effect of ALG, OPP and OPAA dosage on phosphorus adsorption at initial concentration 10 mgP/L at contact time 3 h

4.3.3 Effect of initial concentration of phosphorus solution

Figure 4.10 shown the effect of one gram of OPAA dosage for initial concentration 5, 10 and 15 mg/L phosphorus solution, and contact time for 3 hr. The phosphorus removal rate of 92.7%, 99.4% and 98.6% with the adsorption capacity of 158.5, 459 and 672 mg/g were measured.

The high influence of phosphorus removal by OPAA beads at all initial concentration phosphorus was found, when compare to ALG bead and orange peel powder (Figure 4.11). The lowest adsorption capacity was OPP in 5mgP/L and 10 mgP/L and ALG in 15 mgP/L that account for 32, 88 and 22.5 mg/g.

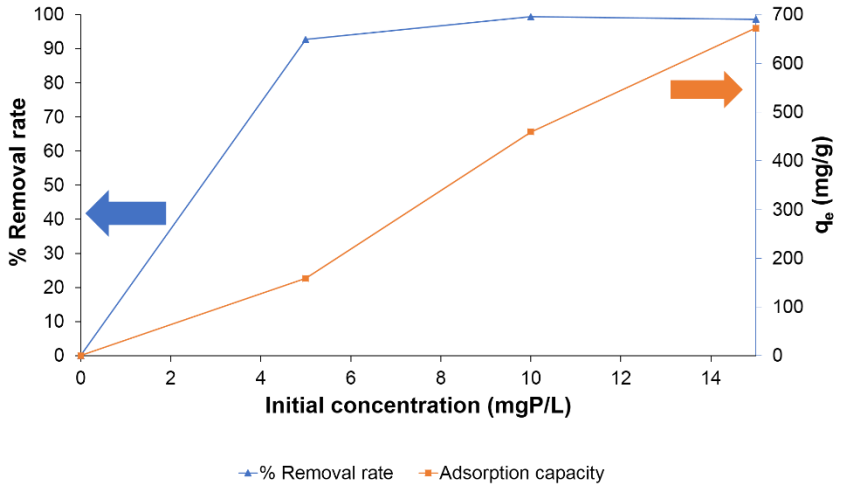

Figure 4.10 Effect of initial phosphorus on one gram of OPAA at contact time 3 h

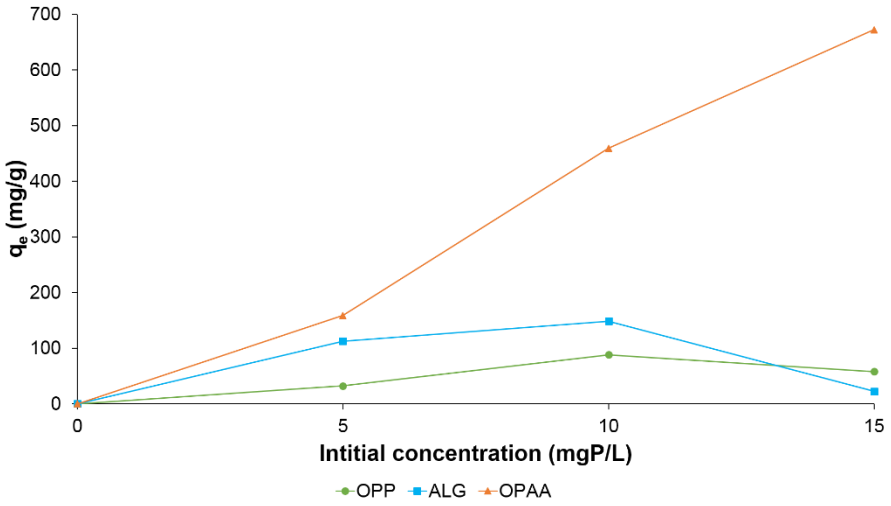

Figure 4.11 Effect of initial phosphorus removal on one gram of ALG, OPP and OPAA dosage at contact time 3 h

CHAPTER 5

CONCLUSIONS AND RECOMMENDATION

The orange peel powder (OPP), and further, it was pretreated with sodium bicarbonate was prepared. The modified orange peel powder was encapsulated in alginate beads (ALG) by simple ionic gelation method using calcium ion as crosslinking agent. The modified orange peel/alginate beads (OPAA) were suitable for phosphorus removal from aqueous solution. The OPAA had a high efficiency to removal phosphorus when compared to ALG and OPP. One gram of ALG, OPP and OPAA adsorbent dosage in 10 mgP/L phosphorus concentration, the removal rate of 26.1%, 19.6% and 99.4%, were examined**.** OPAA beads shows the high adsorption capacity to 10 mgP/L of initial concentration of phosphorus.

However, it is worth to note that the OPAA beads showed the orange color during adsorption process. The determination of phosphorus by colorimetric using ascorbic method may concerns on color appearance from phosphate solution after treatment.

REFERENCES

Agbor, V. B., Cicek, N., Sparling, R., Berlin, A., & Levin, D. B. (2011). Biomass pretreatment: Fundamentals toward application. In *Biotechnology Advances, 29*(6), Elsevier Inc: United States, pp.675–685.

Ahmed, I., Zia, M. A., Hussain, M. A., Akram, Z., Naveed, M. T., & Nowrouzi, A. (2016). Bioprocessing of citrus waste peel for induced pectinase production by Aspergillus niger; its purification and characterization. *Journal of Radiation Research and Applied Sciences*, *9*(2), 148–154.

Alba, K., & Kontogiorgos, V. (2018). Seaweed polysaccharides (agar, alginate carrageenan). In *Encyclopedia of Food Chemistry, 1*, Elsevier Inc: United States, pp. 240–250.

Dev, S., Khamkhash, A., Ghosh, T., & Aggarwal, S. (2020). Adsorptive Removal of Se(IV) by citrus peels: Effect of adsorbent entrapment in calcium alginate beads. *ACS Omega*, *5*(28), 17215–17222.

Gold, A. J., & Sims, J. T. (2005). Aquatic Eutrophication. In *Encyclopedia of Soils in the Environment*, Elsevier Inc: United States, pp. 486–494.

Jia, Z., Zeng, W., Xu, H., Li, S., & Peng, Y. (2020). Adsorption removal and reuse of phosphate from wastewater using a novel adsorbent of lanthanum-modified platanus biochar. *Process Safety and Environmental Protection*, *140*, 221–232.

Jung, K.-W., Jeong, T.-U., Kang, H.-J., & Ahn, K.-H. (2016). Characteristics of biochar derived from marine macroalgae and fabrication of granular biochar by entrapment in

calcium-alginate beads for phosphate removal from aqueous solution. *Bioresource Technology*, *211*, 108–116.

Krishnan, K. A., & Haridas, A. (2008). Removal of phosphate from aqueous solutions and sewage using natural and surface modified coir pith. *Journal of Hazardous Materials*, *152*(2), 527–535.

Machmudah, S., Wahyudiono, Kanda, H., & Goto, M. (2017). Hydrolysis of Biopolymers in Near-Critical and Subcritical Water. In *Water Extraction of Bioactive Compounds: From Plants to Drug Development*, Elsevier Inc: United States, pp. 69-107.

Mukhtar, I., Leman, Z., Zainudin, E. S., & Ishak, M. R. (2020). Effectiveness of alkali and sodium bicarbonate treatments on sugar palm fiber: mechanical, thermal, and chemical investigations. *Journal of Natural Fibers*, *17*(6), 877–889.

Nguyen, T. A. H., Ngo, H. H., Guo, W. S., Zhou, J. L., Wang, J., Liang, H., & Li, G. (2014). Phosphorus elimination from aqueous solution using 'zirconium loaded okara' as a biosorbent. *Bioresource Technology*, *170*, 30–37.

Olabinjo, O. O., Ogunlowo, A. S., Ajayi, O. O., & Olalusi, A. P. (2017). Analysis of physical and chemical composition of sweet orange (*Citrus sinensis*) peels. *International Journal of Environment, Agriculture and Biotechnology*, *2*(4), 2201–2206.

Pandiarajan, A., Kamaraj, R., Vasudevan, S., & Vasudevan, S. (2018). OPAC (orange peel activated carbon) derived from waste orange peel for the adsorption of chlorophenoxyacetic acid herbicides from water: Adsorption isotherm, kinetic

modelling and thermodynamic studies. *Bioresource Technology*, *261*, 329–341.

Paques, J. P. (2015). Alginate Nanospheres Prepared by Internal or External Gelation With Nanoparticles. In *Microencapsulation and Microspheres for Food Applications,* Academic Press:United States, pp.39–55.

Pismenskaya, N., Laktionov, E., Nikonenko, V., El Attar, A., Auclair, B., & Pourcelly, G. (2001). Dependence of composition of anion-exchange membranes and their electrical conductivity on concen-V. *Journal of Membrane Science*, *181*(2), 185–197.

Royal Government Gazette. (2010). Notification of the Ministry of Finance and the Regulation on the Regulation of the Sewerage Control of the Community Wastewater Treatment System, *Ministry of Natural Resources and Environment,* 127, 27-28.

Schoubben, A., Blasi, P., Giovagnoli, S., Rossi, C., & Ricci, M. (2010). Development of a scalable procedure for fine calcium alginate particle preparation. *Chemical Engineering Journal*, *160*(1), 363–369.

Siwek, H., Bartkowiak, A., & Włodarczyk, M. (2019). Adsorption of phosphates from aqueous solutions on alginate/goethite hydrogel composite. *Water (Switzerland)*, *11*(4), 1-13.

Tomul, D. D. F., Kendüzler, E., Arslan, Y., Kabak, B., & Demir, K. (2017). Determination of adsorption characteristics of orange peel activated with potassium carbonate

for chromium(III) removal. *Journal of the Turkish Chemical Society, Section A: Chemistry*, 1057–1070.

Vinet, L., & Zhedanov, A. (2011). Adsorption processes for the removal of contaminants from wastewater: the perspective role of nanomaterials and nanotechnology. *Journal of Physics A: Mathematical and Theoretical*, *44*(8), 1689-1699.

Yazdani, M. R., Virolainen, E., Conley, K., & Vahala, R. (2017). Chitosan-Zinc(II) complexes as a bio-sorbent for the adsorptive abatement of phosphate: Mechanism of complexation and assessment of adsorption performance. *Polymers*, *10*(1), 1–19.

Yue, X., Huang, J., Jiang, F., Lin, H., & Chen, Y. (2019). Synthesis and characterization of cellulose-based adsorbent for removal of anionic and cationic dyes. *Journal of Engineered Fibers and Fabrics*, *14,* 1-10.

Zahid, M., Saqib, N., Nadia, J., Asma, S., & Adnan, A . (2015). Adsorption studies of phosphate ions on alginate-calcium carbonate composite beads. *African Journal of Environmental Science and Technology*, *9*(3), 274–281.

Zia, K. M., Zia, F., Zuber, M., Rehman, S., & Ahmad, M. N. (2015). Alginate based polyurethanes: A review of recent advances and perspective. *International Journal of Biological Macromolecules*, 79, 377–387.

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