UNIVERSITI PUTRA MALAYSIA

ADSORPTION OF PHOSPHATE BY POLYVINYL ALCOHOL-IRON (III) – SODIUM ALGINATE HYDROGEL BEADS

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By

NORANALYZA BINTI PUTEH YAHAYA

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,
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DEDICATION

Specially dedicated this thesis to my dearest mother (Rabiah binti Ramli) and father (Puteh Yahaya bin Abdul Rashid) for their eternal love, my children (Syafiq Amirrullah, Errine Adlyne and Mohammed Yusoff Umarullah),), families and all my beloved teachers and friends for their support and encouragement.

Thank you so much, I love all of you with all of my heart

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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Chairman : **Abdul Halim Bin Abdullah, PhD**
Faculty : **Science**

Phosphate is regarded as one of important nutrient elements to support the growth of biological organisms in aquatic environment. However, the presence of excessive phosphate is often responsible for causing eutrophication problems in lakes, confined water bodies and coastal water. In this paper, Polymeric ion exchanger is very selective towards phosphate and chemically stable. Polyvinyl alcohol, (PVA) hydrogel beads with Iron ion on its cross-linking structure were prepared by chemical cross-linking in the mixed aqueous solution of saturated boric acid and $FeCl_3$. The effects of different parameters such as initial concentration, mass of adsorbent, pH, contact time and temperature have been studied to understand adsorption behavior of the adsorbent under various conditions. It was found that the increasing of the mass of $FeCl_3$ and cross-linking time, the adsorption capacity first increasing because there are large number of adsorption sites and then decreasing may be attributed to overlapping or aggregation of adsorption sites resulting in a decrease in total adsorbent surface area.

From FTIR analysis, after adsorption, the new peak at 1044.33 cm^{-1} appeared showed the bending vibration of phosphate. EDX analysis showed the surface of beads became smooth and the characteristic signal of phosphate also appeared. It showed that phosphate was adsorbed onto PVA-Iron hydrogel beads. From BET analysis, the beads exhibited a type III adsorption isotherm and are macroporous solid with a very small surface area.

To study the mechanism of adsorption process, the Lagergren pseudo-first order model, pseudo-second order kinetic model were examined. It was found that this adsorption fitted with pseudo-first order kinetic model. Furthermore, the adsorption equilibrium data fitted to the Langmuir adsorption isotherm model indicating the adsorption was the homogeneous nature of the monolayer adsorption. The optimum condition of adsorption were occurred at pH 5, initial concentration of phosphate solution was 30 ppm and the mass of adsorbent used was 2.0g at room temperature. The maximum phosphate adsorption capacity of PVA hydrogel at this condition reached at 3.86 mg/g.

Abstrak tesis yang dikemukan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Master Sains

PENJERAPAN FOSFAT OLEH HIDROGEL POLIVINIL ALKOHOL –FERUM (III) –SODIUM ALGINAT

Oleh

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April 2019

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Fosfat merupakan salah satu bahan atau unsur penting untuk membantu pertumbuhan organisma biologi di dalam persekitaran akuatik. Walaubagaimanapun, kehadiran fosfat secara berlebihan akan menyebabkan berlakunya masalah eutrifikasi di dalam tasik, kolam dan sekitaran pantai. Di dalam kajian ini, penukaran ion polimer di pilih kerana ianya merupakan kaedah yang terbaik untuk menyingkirkan fosfat dan stabil dari segi kimianya. Hidrogel polivinil alcohol (PVA) dengan silang bersama ion ferum (III) disediakan secara rangkai silang di dalam campuran larutan akuas asid borik dan ferum (III) klorida. Kesan atau faktor-faktor yang berbeza parameter seperti kepekatan awal larutan, jisim bahan penjerap, nilai pH, masa bertindakbalas dan suhu dikaji bagi memahami sifat-sifat penjerapan oleh bahan penjerap di bawah pelbagai keadaan. Di dapati dengan bertambahnya jisim $FeCl_3$ dan pertambahan masa rangkai silang, kapasiti penjerapan pada awalnya meningkat disebabkan peningkatan luas permukaan penjerapan dan kemudian berkurangan disebabkan oleh pengagregatan permukaan penjerapan yang mengurangkan jumlah luas permukaan bahan penjerap.

Keputusan analisis FTIR menunjukkan bahawa selepas penjerapan, satu puncak baru pada 1044.33 cm^{-1} muncul dan ini menunjukkan adanya lenturan getaran oleh fosfat. Analisis EDX menunjukkan permukaan bahan penjerap menjadi rata, licin dan ciri-ciri kehadiran fosfat juga ditunjukkan. Ini menunjukkan bahawa fosfat telah diserap ke dalam bahan penjerap hidrogel PVA-Fe(II)-SA. Manakala analisis BET menunjukkan bahan penjerap hidrogel PVA-Fe(III)-SA adalah isotherm penjerapan jenis III yang merupakan pepejal makroporos dan mempunyai luas permukaan yang kecil.

Bagi melihat mekanisma proses penjerapan, model kinetik Lagergren pseudo-pertama, pseudo-kedua dikaji. Proses penjerapan ini didapati lebih memenuhi kriteria model kinetik pseudo-pertama.

Proses penjerapan ini juga mematuhi model isoterma Langmuir dan seterusnya menunjukkan bahawa ianya adalah penjerapan satu lapisan dan bersifat homogen. Keadaan optimum bagi penjerapan adalah pada nilai pH 5, kepekatan awal larutan fosfat 30 ppm dan jumlah bahan penjerap yang digunakan adalah 2.0 g pada suhu bilik. Kapasiti penjerapan fosfat yang optimum oleh bahan penjerap hidrogel PVA-Fe(III)-SA adalah 3.86 mg/g.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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LIST OF ABBREVIATIONS

BET	Brunauer, Emmet and Teller Isotherm Model
FTIR	Fourier Transform Infrared Spectroscopy
FESEM	Field Emission Scanning Electron Microscopy
EDX	X-Ray Energy Dispersive Analysis System
ICP-OE	Inductively coupled plasma optical Emission Spectrometer
ATR	Attenuated Total Reflectance
PVA	Polyvinyl alcohol
NaAlg	Sodium alginate
BNR	Biological nutrient removal
CP	Chemical precipitation
RO	Reverse Osmosis
$FeCl_3$	Iron(III) chloride
NaOH	Sodium hydroxide
HCl	Hydrochloric acid
BA	Boric acid
IMS	Integrated membrane systems
BPR	Biological phosphorus removal
PAOs	Phosphorus accumulating organisms
HFO	Hydrated ferric oxide
ARHA	Adsorbent rice husk ash

CHAPTER 1

INTRODUCTION

1.1 Overview of Study

Phosphates are widely used in many industries such as food, agriculture, beverage, and detergent. The excessive use of phosphorus has resulted in a large amount of pollution and environment problems, such as severe eutrophication which contributes to aquatic species death, algal bloom, and parasite infections. Therefore, it has become a global necessity to efficiently decontaminate phosphates with minimal environmental impact. Phosphorus is widely recognized as the nutrient that regulates the production of algae in lakes and reservoirs. In the last decades, removal of phosphorus from water or wastewater has been widely investigated for the protection of relatively stagnant water bodies such as lakes as sanctuaries from eutrophication (Kumar et al., 2007).

Biological Nutrient Removal (BNR) and chemical precipitation (CP) are commonly applied techniques for the removal of phosphate from wastewater. However, they are more suitable for relatively high concentrations of phosphate and advanced treatments for phosphate removal are often needed to meet more stringent requirements. Furthermore, recovery of phosphate is difficult by these two methods. Biological phosphate removal tends to be sensitive and subject to many fluctuations, making it difficult to achieve full compliance with discharge standards (Onyel et al., 2013).

These processes essentially transfer phosphate from the liquid to the sludge phase which subsequently needs to be hauled and disposed of elsewhere. In general, CP and BNR processes are effective in reducing phosphate levels in municipal wastewater. However, these processes are sensitive to seasonal and diurnal variations in temperatures and changes in feed compositions. Complete removal of phosphate is also unattainable by CP and BNR due to thermodynamic and kinetic limitations (Bing and Lin, 2013).

Besides CP and BNR, there are several physic-chemical methods available for the treatment of wastewaters include ion exchange, reverse osmosis, electrodialysis, solvent extraction and adsorption (Nath et al., 2007). Among these, the adsorption technique is the most widely employed method for removal of phosphates due to its environmentally safe process, simple and fast operation and low cost (Nath et al., 2007).

Adsorption by activated carbon is still by far the most widely used method. Activated carbon is, however, an expensive material and the procedures for its preparation and regeneration are tedious; hence there is a continuous search for low-cost potential adsorbents. Developing new adsorbents with high adsorption capacities is of great significance for the effective adsorption and removal of phosphate from the environment.

The utilization of industrial wastes or by-product as adsorbents for phosphate removal has been widely investigated such as fly-ash based materials, bio sorbents from organic residue, blasts of furnace slag, red mud, spent alum sludge, ferric sludge, iron-rich residues as recently reviewed. The advantage of using these kinds of adsorbents for wastewater treatment is that they are cost-effective (Xie et al., 2015).

However, adsorbents in fine powder form cannot be easily recycled after use due to the difficulty in solid and liquid separation (Nillimanka, 2013).

Though granulation can overcome the separation problem, agglomeration of adsorbent particles would reduce the specific surface area and number of surface reaction sites and increase the intra-particle diffusion distance and depress the adsorptive capacity as a result (Lai et al., 2016).

Recently, polymeric ion exchanger has been employed as adsorbent in wastewater treatment. A polymeric ion exchanger is referred as a sorbent with transition metal cations immobilized appropriately onto a polymer phase and acting as anion-exchange sites with relatively high affinities towards anions with strong ligand characteristics such as phosphate (Shuibo et al., 2010).

1.2 Problem Statement

Many studies have been conducted into the phenomenon, its causes and effects (Wei et al.,2013). Such studies have indicated that the nutrients in eutrophication of freshwater systems are usually phosphorus and nitrogen and that eutrophication can be controlled by significantly reducing the phosphorus load discharged into a catchment.

Chemical precipitation method which makes use of metal salt, such as iron, aluminium, and calcium to react with phosphate in wastewater is an early and widely applied phosphorus removal technology. However the cost is high and a large amount of sludge is produced (Haas et al.,2000).

Biological treatment which conducts the wastewater disposal by biological (bacteria, mildew, and protozoa) metabolism, is widely used in the removal of organo-phosphorus chemicals in food and domestic wastewater, however, the processing cycle is too long and complicated (Long et al., 2011).

Adsorption is known to be one of the most effective removal processes for phosphate from water, even at relatively low concentration of phosphorus. Moreover, the adsorbed phosphorus may be recovered, provided that the amount adsorbed is high and a suitable desorption method is available.

1.3 Justification of study

The concept of the ion exchanger, offers an unique and powerful tool in the separation and purification of various industrial and environmental chemical. In this regard, sorbents with high capacity and affinity toward the target species have been consistently sought (Zhao and SenGupta, 2000). Polymeric ligand exchangers are considered as an effective way of meeting the desired limits in many studies aiming to remove, recover, concentrate or separate ions from aqueous solutions.

In this study, polyvinyl alcohol (PVA)-Fe(III)-sodium alginate hydrogel beads were prepared as adsorbent for the removal of phosphate in aqueous solution. PVA has attracted significant attention in wastewater treatment via polymeric ion exchange method due to its good biocompatibility, non -toxicity, high mechanical strength, and low cost. Using polymeric PVA as an adsorbent, the network structure of PVA hydrogel facilitated the phosphate adsorption. While sodium alginate is used because it is a natural water soluble salt of alginic acid. It has high bioavailability and the ability to form hydrogels is one of the main properties of alginate. The hydrogel sodium alginate can be used as a potential sorbent because its low cost, hydrophilicity, nontoxicity and biocompatibility (Safoura et al., 2018).

It was hypothesized that the phosphate adsorption capacity could be further improved if some metal ions were cross-linked into PVA structure. Hence Iron (III) ion was chosen as a cross-linker agent because it is considered to be environmentally friendly and is relatively abundant in the earth's crust.The physical properties of the polymer depending upon the degree of cross linking between the cross linkers and the polymer chain. Cross linking results in elasticity. As the degree of cross linking increases, the polymer becomes more rigid and less elastic. Once the cross-links form, the polymer's shape cannot be changed again. Crosslinked materials cannot dissolve in solvents but can absorb solvents and it can improve the adsorption capacity. Crosslinked material is called a gel after absorbing a lot of solvent (Jaya and Vivek, 2014).

1.4 Objectives of the study

This research aims to prepare an adsorbent for phosphate removal. In this work, (PVA)-Fe(III)-sodium alginate was prepared and used as an adsorbent for phosphate removal. The studies include pH studies, the dosage of adsorbent, sorption kinetics, sorption isotherms, and thermodynamics.

The specific objectives of this study are:

1. To synthesize and characterize (PVA)-Fe(III)-sodium alginate hydrogel beads
2. To evaluate the effectiveness of (PVA)-Fe(III)-sodium alginate hydrogel beads towards phosphate adsorption
3. To investigate the desorption and reusability of (PVA)-Fe(III)-sodium alginate hydrogel beads

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