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Phosphate Removal from Water Using Zirconium-Based Mesoporous Materials

Submitted by
Niti Pitakteeratham

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Engineering

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学 位 論 文 内 容 の 要 旨

DISSERTATION ABSTRACT

博士の専攻分野の名称　　博士（工学）
氏名 Niti Pitakteeratham

学 位 論 文 題 名
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Phosphate removal from water using zirconium-based mesoporous materials
(ジルコニウム系メソポーラス物質を用いた水からのリン酸塩除去)

The element phosphorus (P) is essential to all life (e.g. plants, animals and bacteria) and is a key ingredient in fertilizers to sustain high crop yields. However, the lifetime of exploitable reserves of natural ore deposits containing P is estimated to range from the next few decades to several hundreds of years, since P is intensively used in agriculture and other industries. The use of P yields large amounts of P-containing wastewater. P discharged from municipal and industrial wastewater treatment plants as sludge and water is approximately estimated to be 40,000 tons P per year in Japan. Hence, the wastewater can be considered as an alternative source of P to phosphate rock. Since the release of P-containing wastewater into water bodies leads to deterioration in water quality, such as eutrophication, P in the wastewater also has to be removed from an environmental point of view. Therefore, substantial attention has been paid to the efficient removal and recovery of P from wastewater and then recycling of P. P can be removed from both raw wastewater and P rich side-streams in wastewater treatment plants by chemical precipitation with addition of Fe, Al(III) or Ca salt, biological processes, adsorbents and ion exchangers. Considering the reuse of the P recovered from the wastewater, concentrations of impurities, such as heavy metals, toxic organic materials and pathogens, should be very low. Hence, the solution used for the phosphate recovery should be clear. In addition, high phosphate concentration is beneficial for effective phosphate removal. Therefore, we applied zirconium sulfate-surfactant micelle mesostructure (ZS) as an ion exchanger to recover orthophosphate from P rich water. Although the use of ion exchangers for P recovery is relatively expensive, they have advantages of easy operation, high selectivity, high efficiency and no sludge production over other processes to obtain concentrated phosphate solution in high purity. Since a typical influent concentration of total P in sewage wastewater ranges from 5 mg-P/L to 10 mg-P /L, ZS was applied to the wastewater at higher phosphate concentration, such as reject water from an anaerobic digestion process. This thesis started with characterization (ion exchange capacity, isotherm, effects of pH and interfering ions, elution capacity) of ZS. Then ZS powders were immobilized on polymer matrix to avoid decomposition of ZS structure in regeneration process. P-ZS was used for recovery of phosphate in artificial solution and ground water containing phosphate of about 10 mg-P/L. Furthermore, we tried to obtain phosphate rich solution without suspended solids from excess sludge generated in a membrane bioreactor (MBR) by anaerobic digestion with an anaerobic MBR (AnMBR).

We investigated characterization of ZS. Ion exchange process reached to equilibrium within 60 min. The isotherms could be described by the Langmuir model. The ZS was an effective ion exchanger for phosphate with a very high ion exchange capacity (114 mg P/g ZS). The adsorbed phosphate was eluted effectively (85%) using NaOH solution at pH of higher than 13.3. In the regeneration process, the breakage of ZS particles occurred and the size of ZS powders regenerated with NaOH was below 0.5 μm. We can conclude that ZS is a highly effective ion exchanger for phosphate and enables the removal of phosphate from water. However, decomposition of ZS structure made it difficult to recover the regenerated ZS, for example by filtration or sedimentation.

To realize the reuse of ZS, ZS was immobilized on a polymer matrix (Aramid-Polymer). Scanning electron microscopy images of the cross-section of polymer-coated ZS (P-ZS) showed the ZS particles had angular outline and sharp edges, and the dimensions of ZS were in the range of 20 to 100 mm. Some smaller ZS particles still existed. ZS was densely packed with the polymer. P-ZS had considerable numbers of pores and skin surface, which could facilitate transfer of phosphate and prevent leakage of ZS particles that were broken down during the elution process. As expected, the ion exchange kinetics of P-ZS for phosphate were slow and it took 120 min for P-ZS to achieve equilibrium. This is probably explained by mass transfer resistance within the polymer structure. However, the contact time of 120 min is likely sufficient for P-ZS to achieve sorption equilibrium, because the amount of phosphate per unit mass of ZS for P-ZS in equilibrium was comparable to the ZS at 120 min. The phosphate ion exchange capacity increased with decrease in pH and the phosphate ion exchange capacity was highest at pH range of 3.0-5.0. Considering the acid dissociation constant values of phosphoric acid, the fraction of each phosphate species (H_3PO_4, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}) of the total orthophosphate, which was defined as the sum of these four chemical species, was calculated. A decrease in pH from 7.2 inevitably resulted in the formation of more $H_2PO_4^-$ than HPO_4^{2-}, indicating preferable of $H_2PO_4^-$ to ZS. This result indicates that phosphate removal by ZS requires pH adjustment to optimize phosphate removal efficiency. Since anions (e.g., bicarbonate, nitrate, chloride and acetate) other than phosphate were present in environmental waters, the interfering effect of the anions was investigated. The uptake and distribution coefficients (K_d) of these anions were evaluated. The selectivity order based on the K_d values was phosphate (K_d = 3390) ≈ bicarbonate (K_d = 3340) >> nitrate (K_d = 109) ≈ acetate (K_d = 84) > chloride (K_d = 1.7). At equilibrium, P-ZS could remove 107 mg P/g-ZS while 66 mg P/g-ZS of phosphate was removed in presence of carbonate. P-ZS was subjected to a 50-cycle P-removal-recovery test to investigate P-ZS reusability. The overall amount of phosphate removed and recovered in 50 cycles was 1300 and 1141 mg P/g P-ZS, respectively. The P-ZS retained its functionality and ion exchange and elution capacities over 50 cycles. An artificial phosphate solution and groundwater, both of which contained phosphate of about 10 mg P/L, was treated in columns packed with P-ZS. The phosphate could be removed completely onto P-ZS up to 1020 (an artificial solution) and 241 (groundwater) bed volumes, respectively. The reason for the lower removal efficiency was the presence of bicarbonate. These results indicated that P-ZS was a highly effective ion exchanger for phosphate and enabled the removal of phosphate from water.

AnMBR (20L) was operated for 165 days. Excess MBR sludge, which contained P at a relatively high concentration, was fed to the AnMBR at a sludge-loading rate of 3.8 g SS/reactor/day. COD removal efficiencies were > 88%. The average biogas production rate was 432 mL/reactor/day. Sludge has not been withdrawn except samples (500 mL) for analysis. P was released from the MBR sludge and collected as permeate of membrane. Concentration of phosphate in the permeate was 74 ± 19 mg P/L. However, by anaerobic digestion, 78% of P present in the MBR sludge was not transformed to soluble phosphate that could be filtered. The permeate was fed to the P-ZS column with a flow rate of 5 mL/hr (2 h of hydraulic retention time). Breakthrough occurred at 196 BV, during which 71 mg P of phosphate per g ZS in P-ZS was removed.

In summary, ZS could recover phosphate in pure water, transparent ground water and even filtered rejected water by an ion-exchange process with high capacity. Bicarbonate was the sole interfering anion among the anions tested. Adsorbed phosphate could be eluted from the ZS using NaOH solution. The P-ZS could be reused at least 50 times without loss of original functionality. A column packed with P-ZS could remove phosphate completely in groundwater (about 10 mg P/L of phosphate) and filtered reject water (88 mg P/L of phosphate) up to 241 and 196 bed volumes, respectively. Therefore, we concluded that ZS is a highly effective ion exchanger for phosphate and enabled the removal of phosphate from water. From an economic point of view, modification was required, such as simplification of the system and further increase in the number of reuse of P-ZS.

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Chapter 1

Introduction

Significance of Phosphorus

Phosphorus (P) is an essential nutrient for living organisms, which acts as a nutrient for growth, and also the vital components of the DNA and the key element of the energy supplier ATP (adenosine Triphosphate) (Chitrakar et al., 2006). As an essential cell component, P cannot be replaced by any other element. Dietary P is readily absorbed in the small intestine, and any excess P is excreted into urine through kidneys. P deficiency in human may cause symptoms related to bone mineralization, proximal myopathy and symptoms of nervous system dysfunction (Takeda et al., 2012). Symptoms of P deficiency in animals are decreased appetite, lowered blood pressure, reduced rate of gain, and in severe deficiency, skeletal problems are usually found (Johnson and Watt, 2006). P is a component of the complex nucleic acid structure of plants, which regulates protein synthesis. Thus, P is important in cell division and development of new tissue. P is also associated with complex energy transformation in the plant. Plants deficient in P are stunted in growth and often have an abnormal dark-green color.

Phosphorus cycle

P is a nutrient necessary to all living cells. It is an important component of adenosine triphosphate (ATP), nucleic acid (DNA and RNA), and phospholipid in cell membranes. In nature, phosphorus passes through several interconnected cycles. The inorganic cycle describes the cycles from erosion, transport to the oceans, sedimentation tectonic uplift and alteration of P-containing rocks into plant-available P in soils (Cornel et al., 2009). P transported into oceans can be considered as “lost” for agricultural use. Beside inorganic P cycle there are two organic cycles attached describing P as part of the food chain. One of the cycles takes place on land (soil-plants-human/ animals-organic waste-soil) the other in water. Large amount of phosphate present in wastewater is one of the main causes of eutrophication, which is considered as one of the water pollution. a significant reduction of P is obligatory in most countries. The average concentration of total phosphorus (sum of organic and inorganic forms; T-P) in wastewater is within the range of 10 - 20 mg/L, mostly comes from phosphate builders in detergents. Common forms of

P in wastewater are orthophosphate (50 - 70%), polyphosphates, and P tied to organic compounds. Orthophosphate comprises approximately 90% of P in biologically treated effluents (Cornel et al., 2009). There are several P removal technologies, such as enhanced biological phosphorus removal, metal precipitation, constructed wetland system, adsorption by various microorganisms, and several innovative engineering solutions.

Source of P and its availability

P is present in nature in the forms of inorganic and organic materials and from simple to complex molecules. There are two main types of phosphate rock deposits - sedimentary and igneous. Sedimentary phosphate deposits are exploited to produce more than 80 percent of the total world production of phosphate rock. The word phosphate rock is used; firstly as the apatite bearing rock with a content of P high enough to be used directly to make fertilizer or as a furnace charge to make elemental phosphorus, secondly as to designate a beneficiated apatite concentrates. Fertilizer grade of the phosphate rock is universally expressed by phosphate pentoxide (P_2O_5). Globally, on average, phosphate ores have a P_2O_5 content of around 30% (Smit et al., 2009).

Farming practices that are helping to feed billions of people include the application of phosphorus fertilizers manufactured from phosphate rock, a nonrenewable resource used increasingly since the end of the 19th century. The world P resource, phosphate rock, are mined and used extensively. In 2008, 161 million tons of P was mined around the world (Lu et al., 2009). In 2000, 418,000 ton-P was imported as phosphorous ore, and 174,000 ton-P was imported as foods for human and livestock. In addition, 139,000 ton-P was imported as mineral other than phosphate ore. 550,000 ton-P was used as a fertilizer, which corresponds to 75% of the total imported P, and 40,000 ton-P was disposed as waste and wastewater. 90,000 ton-P of slag was produced. In japan, 60,000 ton-P was discharge as sewage wastewater. The average P concentration of Japanese sewerage wastewater was 40,000 ton-P per year, and after treatment around 15,000 ton-P were remaining in the effluent. The USGS estimates that around 65 billion tons of phosphate

remain in the ground. In 2010, 176 million tons of phosphate were mined around the world (Martin et al., 2006). There is a prediction that within the year 2070, Phosphorus is going to be depleted, due to the excessively used. In addition to phosphorus depletion, the world's economy is totally dependent on P rock (Cordell et al., 2011). Although, fossil fuel are increasing its cost sharply recently, there are many alternative source of power supply such as solar energy or wind energy. However, in case of P, there is no substitute for phosphorus in crop growth and therefore food production. As mentioned, the critical point in time for P depletion is somewhere in the near future, while the demand for phosphorus is growing exponentially due to the higher demand of foods, make the price of the remaining phosphate rock become scarily expensive. A scarcity of phosphate rock will definitely increase the cost of raw materials of many food products, which definitely lead to the economic crisis.

The extensive use of phosphate inevitably results in discharge of large amounts of phosphate-bearing waste into municipal and industrial wastewaters, ultimately into the effluent streams (Babatunde et al., 2010). Human waste, food residues, and consumer products, such as detergents, contribute phosphorus to sewage. The release of phosphate to surface waters is of environmental concern. Eutrophication is characterized by excessive plant and algal growth due to the increased availability of one or more limiting growth factors needed for photosynthesis (Schindler 2006), such as sunlight, carbon dioxide, and nutrient fertilizers. Discharging effluent contains high concentration of phosphorus will accelerate the rate of eutrophication because phosphorus is one of the limiting factors (Chislock et al., 2013). Eutrophication results in the creation of dense blooms of noxious, foul-smelling phytoplankton that reduce water clarity and harm water quality (Blackall et al., 2002). Thus, developing the processes for phosphorus recovery from wastewaters is another alternative choice for preventing phosphorus depletion and water pollution.

Phosphorus recovery processes from wastewater

The broad categories of P removal from the effluent include physical, chemical, biological and crystallization methods. Chemical removal techniques are the most effective and well-established methods up to date, such as phosphate precipitation with calcium, aluminum and iron salts. However, the recover of P contains the toxic materials such as aluminum (Al), and organic toxic materials that cannot be used directly (de-Bashan et al., 2004). The biological method, especially, enhance biological phosphorus removal (EBPR) process needs a large space due of complex configuration. Moreover, the stability of phosphorus removal by EBPR is also depended on bacteria in activated sludge, which unable to control by non-professional workers. Adsorption and ion exchange reaction with solid sorbents has been largely used for the removal of pollutants from wastewaters (Jasinski, 2011). Adsorption is the process where the target molecules or particles bind to a surface of material, which have available adsorption site. Ion exchange is the process where ion from solution is exchanged for a similarly charged ion attached to an immobile solid particle. Details of P removal and recovery technology are discussed as following.

1) Natural phosphorus removal in activated sludge treatment plants

Before discharging wastewater into water bodies, removal of phosphorus is usually implemented. Primary treatment of wastewaters removes 5-10% of P, which is associated with particulate matter, and conventional biological treatment removes up to 10-25% (Cornel et al., 2009). There are 3 possible ways in which phosphorus is removed in the activated sludge process.

- Phosphorus assimilation

Microorganisms assimilate P, which enters in the composition of several macromolecules in the cell. Phosphorus is stored as polyphosphates in special granule. The stoichiometric composition of microorganisms and the composition of the wastewater is such that 20 to 30% of inlet phosphorus is removed by normal assimilation (Cornel et al., 2009).

- Chemical precipitation

Phosphorus removal in sludge may also be the result of natural simultaneous precipitation, if cations such as Ca, Fe, Al, Mg, and Zn are present. When precipitation occurs, there is formation of insoluble compounds such as $Ca_{10}(PO_4)\cdot 6(OH)_2$ or hydroxyapatite, vivianite $Fe_3(PO_4)_2\cdot 8H_2O$, or variscite $AlPO_4\cdot 2H_2O$ (de-Bashan et al., 2004). These compounds will be mixed with in sludge, which increases the biomass quantity.

- Biologically induced phosphate precipitation

At the head of a plug-flow aeration tank, microbial activity leads to low pH, which solubilized phosphate compounds. At the end of the tank, a biologically mediate pH increase leads to phosphate precipitation and incorporation into the sludge. Biologically mediated phosphate precipitation also occurs inside denitrifying biofilm. Since denitrification is an alkalinity-producing process, denitrifier activity leads to pH increase and subsequent calcium phospate precipitation inside biofilm (Cornel et al., 2009).

2) Chemical precipitation

This process falls under the category of tertiary treatment. Chemical precipitation is used to remove the inorganic forms of phosphate by the addition of a coagulant such as Ca, Fe, Al, and Mg into wastewater. These are generally added in the excess amount to compete with natural alkalinity to form precipitation. The chemical precipitation is designed to remove more than 95% of phosphorus from wastewater (Asano et al., 2007).

- Calcium

Lime ($Ca(OH)_2$) is usually used. As the pH value of the wastewater increases beyond about 10, excess calcium ions will then react with the phosphate, to precipitate in hydroxylapatite:

Equation 1: hydroxylapatite formation

$$\mathbf{10\ Ca^{2+} + 6\ PO_4^{3-} + 2\ OH^- \leftrightarrow Ca_{10}(PO_4)\cdot 6(OH)_2} \quad (1)$$

By using lime, phosphorus can be removed at 75-85% (de-Bashan et al., 2004).

- Aluminum

Alum or hydrated aluminum sulfate is widely used precipitating phosphate and aluminum phosphate ($AlPO_4$). The basic reaction is:

Equation 2: Aluminum phosphate formation

$$Al^{3+} + H_nPO_4^{3-n} \leftrightarrow AlPO_4 + nH^+ \quad (2)$$

By using aluminum, phosphorus can be removed at 80-90% (de-Bashan et al., 2004).

- Iron

Ferric chloride or sulfate and ferrous sulfate are all widely used for phosphorus removal, although the actual reactions are not fully understood. The basic reaction is:

Equation 3: Ferricphosphate formation

$$Fe^{3+} + H_nPO_4^{3-n} \leftrightarrow FePO_4 + nH^+ \quad (3)$$

By using iron, phosphorus can be removed at 75-85% (de-Bashan et al., 2004).

3) Constructed Wetlands

The wetland concept is widely used to treat wastewater for decades. Constructed wetlands are a cheap, low-tech process to control environmental pollution. Even though it is a commonplace report about their ability to clear wastewater, refining of the process, and validation of the concept of rural areas. Assessment of the contribution of duckweed Lemna gibba, and its associated microorganism is responsible for removing up to 75% of the nutrients in the wastewater (de-Bashan et al., 2004). Wetlands system is a possible approach for all wastewater treatment, and can be utilized in practically every location.

4) Enhances biological phosphorus removal (EBPR)

Various mechanisms have been proposed to explain the enhanced uptake of phosphorus by microorganisms in wastewater. Biomass first needs to pass through an oxygen and nitrate free phase, i.e. an anaerobic phase, before entering a phase where an electron acceptor is present in order to remove P (Figure 1). The oxygen and nitrate free phase can be achieved in a separate reactor, the first section of a plug flow reactor or part of a

sequencing batch reactor cycle (Cornel et al., 2009).

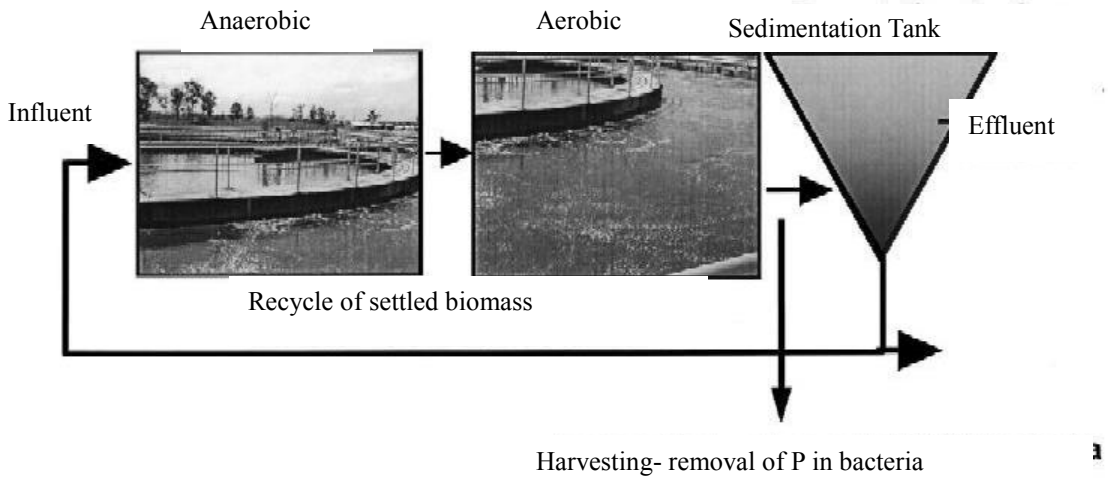

Figure 1: Enhances biological phosphorus removal (EBRP) configuration

When the wastewater enters the anaerobic phase, specialized organisms, called poly-phosphate accumulating bacteria (PAOs) accumulate carbon sources as an internal polymer called Poly-HydroxyAlkanoates (PHAs) and release soluble orthophosphate from the sludge. The energy to store in this polymer is obtained from breakdown of glycogen and hydrolysis of an energy rich internal phosphorus chain called poly-Phosphate (poly-P) (Biswas et al., 2007). Since poly-phosphorus is broken down to orthophosphate for energy supply, the phosphate concentration in the anaerobic phase increases (Liu et al., 2008).

When conditions in bioreactor changes to aerobic, PHA molecules serve as energy and carbon sources for uptake of even larger amount of orthophosphate than the amount originally released during the anaerobic process, and this enhanced uptake includes the phosphorus arriving with the new wastewater. The aerobic process reincorporates the orthophosphate into new intracellular microbial polyphosphate, this leaves the wastewater phosphate-poor and in case of complete EBPR success, phosphate free (Lu et al., 2009).

According to Batetens (2011), the most important disadvantage of EBPR concerns the

reversible nature of biological phosphate storage. Thus, the organisms can breakdown the internal phosphorus content and release it again to the environment. Sludge retention times in the settler should be limited and the oxygen supply to the aerobic phase should provide sufficient oxygen also to the outlet of the basin to prevent anaerobic conditions occurring in the secondary clarifier. Release of phosphorus can, however, is turned to advantage when coupled with chemical phosphorus recovery processes. The important advantages of EBPR are low sludge production and the fertilizer value of the sludge (Cornel et al., 2009).

5) Magnesium Ammonium Phosphate (MAP)

Phosphorus is recovered by converting the P-ion in wastewater into a solid fraction. This fraction can be an insoluble salt precipitate, a microbial mass in activated sludge, or a plant biomass in constructed wetland (de-Bashan et al., 2004). Recovered phosphorus cannot be used as truly sustainable products because it is removed with various other waste products, and some of which are toxic.

Phosphates recovered from wastewater plants might be a feasible source of industrial as raw material. The activated sludge (bio-solids) commonly discarded in fields from wastewater treatment plant contains considerable phosphorus. The most common approach for removing phosphate from wastewater is metal salt precipitation, which makes the precipitate unrecoverable for possible industrial processing into fertilizer (de-Bashan et al., 2004).

The most common compound for phosphorus recovery from wastewater is magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4 \cdot 6H_2O$) commonly known as struvite, which precipitates spontaneously in some wastewater process. Struvite precipitates spontaneously in wastewater treatment environments where high concentrations of soluble phosphorus and ammonium are present. Additional essential conditions are low concentration of suspended solids and pH above 7.5. Precipitation of struvite requires that its components are available simultaneously in the wastewater in the molecular ratio 1(magnesium): 1(ammonium): 1(phosphate) (Koilraj, Kannan, 2010). Normally,

ammonium concentration in municipal wastewater and several other wastewaters tend to be rich, but magnesium concentration is deficient, so supplementation of magnesium is required, and this helps to increase solution pH.

6) Phosphorus adsorption by adsorbents

Various methods have been applied to remove phosphorus from wastewater, but the removed phosphorus remained in the sludge in many forms. Further process is essential to recover phosphorus in order to get a very high purity phosphorus source. Several waste materials or by products such as fly ash, blast furnace slag, red mud spent alum sludge, and aluminum and iron-rich residues have been checking the ability to adsorb and desorb phosphorus for the maximum recovery. The studies of phosphorus adsorption by various adsorbents have been studied for decades. Many researchers used several types of by products to adsorb phosphorus from wastewater, and they were successful to adsorb phosphorus. The data of each adsorbent are shown in Table 1

Table 1: Adsorption capacity of adsorbents

Adsorbents	Adsorption capacity (mg/g)	Reference
Red mud	0.58	(Gibert, 2009)
Zr-loaded orange waste	57	(BAETENS, 2011)
Fe(III)-loaded orange waste	13.94	(Biswas et al., 2008)
Iron oxide tailings	12.65	(Zeng et al., 2004)
Waste slum sludge	31.9	(Babatunde et al., 2010)
ZrO(OH)2(Na_2O)0.051.5H_2O	17	(Blackall et al., 2002)
ZnAlZr-LDHs	91	(Jasinski, 2011)
Silica sand	0.049	(Iwamoto et al., 2002)
Activated alumina	3.33	(Iwamoto et al., 2002)
Anthracite coal	0.1	(Iwamoto et al., 2002)
ZM	51.74	(Yeon et al., 2008)
ZrO_2	29.71	(Koilraj, Kannan, 2010)

From Table l, the adsorption capacity of each adsorbent is varies, due to their specific surface area and pore structure. However, selection of adsorbent depends on the concentration of phosphorus in water to be treated.

7) Phosphorus removal by ion exchanger

Ion exchange is a chemical reaction where an ion from solution is exchanged for a similarly charged ion attached to an immobile solid particle.. Typical ion exchangers are ion exchange resins (functionalized porous or gel polymer), zeolites, montmorillonite, clay, and soil humus. Ion exchangers are either cation exchangers that exchange positively charged ions (cations) or anion exchangers that exchange negatively charged ions (anions). There are also amphoteric exchangers that are able to exchange both cations and anions simultaneously. However, the simultaneous exchange of cations and anions can be more efficiently performed in mixed beds that contain a mixture of anions and cations exchange resins, or passing the treated solution through several different ion exchange materials. Ion exchangers can be unselective or have binding preferences for certain ions or classes of ions. This depends on their chemical structure, which are the size of the ions, their charge, or their physical structure. Ion exchange is a reversible process and the ion exchanger can be regenerated or loaded with desirable ions by washing with an excess of these ions.

Table 2: Summary of advantages and disadvantages of P removal& recovery process

P removal technology	*Sludge production*	*System difficulties*	*Parameters to be controlled*	*Valued of Recovery Product*
Chemical Precipitation	Extra sludge produced	- Handling the precipitates - Prevention of corrosion	- pH - Dose - Mixing rate	Metals/ Chemical Contaminated sludge which required further process for recovery purpose
MAP	No extra sludge	- Scaling - Operation skills	- Aeration rate - pH - Magnesium dose - HRT	Struvite (contain both N and P) is easy to use as slow release fertilizer
Adsorption & Ion-exchanger	No extra sludge	- Synthesis of the materials - Competing ions Cost	- pH - HRT	P-rich solution materials (depends on eluents)

Zirconium sulfate Micelle Mesostructure

Since the discovery of a new family of silica-based mesoporous materials, various mesostructured materials have been reported for non-silica metal oxides such as zirconium oxide. A common problem of the non-silica hexagonal materials is destruction of their mesostructure upon heating treatment to eliminate the surfactant. In the study on mesostructure zirconium oxide with regular pore structure, a few research groups found that phosphoric acid treatment can stabilized the pore structure of Zirconium sulfate. The mesostructure materials containing the surfactant micelles could be used as adsorbent very effectively. Zirconium Sulfate surfactant micelle mesostructure (ZS) is an ion exchanger which has used to treat arsenate and selenite ions in wastewater (Huang et al., 2008), (Takada et al., 2004). ZS has ability to exchange ion with the elements in 5^{th} column in periodic table. Since the arsenic and phosphorus are in the same column in the periodic table, theoretically, the ZS powder must also be able to apply to recover phosphorus. From this hypothesis, the ability of ZS powders to exchange ion with phosphate has been tested, and finally, whether phosphate can be recovered from water samples with a very high effectiveness will be investigated.

Research objectives

In this study, ZS was used to recover phosphate from water sample. Isotherm, kinetic study, competition between anions, and column test of ZS based ion exchanger were examined. Moreover, the reutilizations of this ion exchanger were also observed. These objectives can contribute to the understanding of ZS ion exchange mechanisms, and operation parameters in order to use this ion exchanger with its maximum efficiency, and for real application for P-recovery from several waters.

Outline of dissertation

There are five chapters in this study, and the outline of this dissertation is as follow. The first chapter of this study provides the basic overview of phosphorus cycle and its depletion, which lead to the need of this study. The second chapter in this study deals with preparation of ZS to be used in the study, also the analysis technique for analyzing the sample. Chapter 3 explained the characteristic of P-ZS. Chapter 4 shows the results and findings obtained from experiment regarding application of P-ZS. Another application of P-ZS to recovery phosphorus from AnMBR permeate was explained in chapter 5. Chapter 6 summarized up this thesis, and emphasized the main contribution of this research together with some perspective for the future work.

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Chapter 2

Phosphate removal from water with Zirconium Sulfate Micelle Mesostructure (ZS)

Introduction

The release of phosphate into water bodies, such as bays, lakes, ponds, lagoons, rivers and seas, is one of environmental concern as it can lead to a deterioration in water quality. Phosphate can disturb the ecological balance of an aquatic environment by enhancing algae proliferation, termed eutrophication, and the subsequent depletion of dissolved oxygen, as the algae decay (Camargo et al. 2005). Furthermore, phosphorus is known to be a limited resource (Gilbert, 2009; Cordell et al. 2009). Published reports demonstrate that the lifetime of exploitable reserves of phosphate rock ranges from the next few decades (Yoshida and Galinada, 2002) to several hundreds of years (Bloecher et al. 2012). Hence, phosphorus recovery from phosphate-containing wastewater as an alternative source of phosphate becomes increasingly important to compensate (Bloecher et al. 2012).

Since the discovery of a new family of silica-based mesoporous materials, various mesostructured materials have been reported for non-silica metal oxides such as zirconium oxide (Wu et al., 2005). A common problem of the non-silica hexagonal materials is destruction of the mesostructure upon heating treatment to eliminate the surfactant (Wu et al., 2005). In the study on mesosturcture zirconium oxide with regular pore structure, a few research group found that phosphoric acid treatment can stabilized the pore structure of Zirconium sulfate (Wu et al., 2005). The mesostructure materials containing the surfactant micelles could be used as ion exchanger for removed unfavorable ions in water very effectively. ZS is an ion exchanger, which successfully removed arsenate and selenite ions out of water (Iwamoto et al., 2002; Takada et al., 2004). ZS can remove arsenate at 1.8 mol/mol-ZS and 2.4 mmol/g for selenite ions. Figure 2 shows picture of ZS.

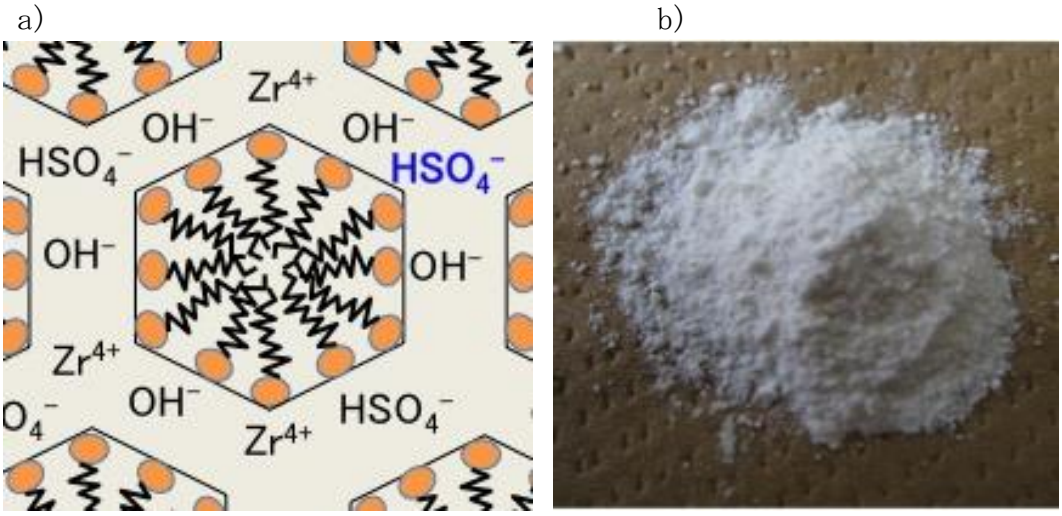


Figure 2: a) Schematic illustration of ZS structure and b) ZS powder

As mentioned above, phosphate can stabilized the hexagonal structure of ZS, which means that some phosphate species might be able to be removed by ZS. Moreover, since arsenic and phosphorus are in the same column in the periodic table, theoretically, the ZS powder must also be able to apply to phosphorus recovery. In this chapter, several experiments were done to investigate ability of ZS to remove phosphate and other parameters affected phosphate sorption.

Materials and methods

Preparation of ZS

ZS was prepared according to the procedure reported in the previous study (Iwamoto, 2002). $Zr(SO_4)_2 \cdot 4H_2O$ (48.5 g) was added into 160 g of milli-Q™ water. Hexadecyl-trimethylammonium bromide as template (C_{16}T-MABr, 24.64 g) was gently added drop-wise into the 838.5 g of $Zr(SO_4)_2$ solution by titration technique while stirring it for at least 2 hours. The mixture was stirred over night and autoclaved at 110°C for 48 hours. The white precipitate was created. It was dried to obtain the wet cake, and finally was ground into fine powder.

Batch experiment

Batch experiments were carried out to examine the ion exchange behavior of phosphate on ZS. Briefly, 200 mg of ZS was added into a 500 mL flask with various concentrations of phosphate standard solutions prepared using Milli-Q water (200 mL). Three drops of chloroform were added to each flask to inhibit bacterial growth. pH in the initial phosphate standard solution was adjusted to 7.0 by adding NaOH or HCl to minimize pH variations owing to the different amounts of KH_2PO_4 added. The solutions were shaken continually at 25°C for 120 min to achieve adsorption equilibrium (i.e., no further uptake). During the adsorption process, a 1 mL sample was withdrawn at preset time intervals. After the sample had been filtered using a 0.2 μm pore size membrane (Advantec Co., Ltd., Tokyo, Japan), the phosphate concentration in the solution was determined using ascorbic acid method (Eaton et al., 2005).

The elution experiments were carried in a batch-wise test to determine the desorption capacity of ZS at various sodium hydroxide (NaOH) concentrations. Phosphate desorption was studied using a phosphate-loaded ZS, prepared by treatment of 310 mg P/L (10 mM) of a phosphate solution as described above. The phosphate-loaded ZS (1 g) was immersed in 50 mL NaOH solution for 30 min at various solution pH values. During the desorption process, a 1 mL sample was taken at preset time intervals. After the sample had been filtered through a 0.45 μm pore size membrane (Advantec Co., Ltd., Tokyo, Japan), the phosphate concentration in solution was determined as described above. The amount of desorbed phosphate was determined based on the amount of phosphate in solution.

Particle size measurement

After the elution test, ZS particles were measure their diameter by Laser Diffraction Particle Size Analyzer (SALD-3100, Shimadzu).

Analysis of isotherm

Several isotherm models have been used to describe the experimental isotherm data, and the two most commonly used are:

Equation 4: Langmuir equation

$$q_e = \frac{Q_m b_A C_e}{1 + b_A C_e} \quad (4)$$

where q_e = Equilibrium adsorbent-phase concentration of adsorbate (mg/g),

Q_m = Maximum concentration of adsorbate when surface sites are saturated with adsorbate (mg/g)

C_e = Equilibrium concentration of adsorbate (mg/L)

b_A = Langmuir adsorption constant of adsorbate (L/mg)

Equation 5: Freundlich equation

$$q_e = K_A C_e^{1/n} \quad (5)$$

where K_A = Freundlich capacity factor, $(mg/g)(L/mg)^{1/n}$

$1/n$ = Freundlich adsorption intensity parameter, unitless

The best-fit equation using the linear regression analysis was commonly used technique to determine the best-fit isotherm and the method of least squares has been used for finding the parameters of the isotherms. The Langmuir isotherm can be linearized into at least four different types and simple linear regression will result in different parameter estimates.

Table 3: Isotherm model equation, corresponding linear forms.

Type	Linear form	Plot	Parameters
Langmuir Type 1	$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{bq_m}$	C_e/q_e vs. C_e	q_m = 1/slope b = slope/intercept
Langmuir Type 2	$\frac{1}{q_e} = \left(\frac{1}{bq_m}\right)\frac{1}{C_e} + \frac{1}{q_m}$	$1/q_e$ vs. $1/C_e$	q_m = 1/intercept b = intercept/slope
Langmuir Type 3	$q_e = q_m - \frac{1}{b}\frac{q_e}{C_e}$	q_e vs. q_e/C_e	q_m = intercept b = -1/ slope
Langmuir Type 4	$\frac{q_e}{C_e} = bq_m - bq_e$	q_e/C_e vs. q_e	q_m = -intercept/slope b = -slope
Freundlich	$q_e = KC_e^{\frac{1}{n}}$	log (q_e) vs. log (C_e)	K = 10^intercept n = 1/slope

Kinetic study can be carried out by batch experiments at various initial sorbate concentrations, sorbent doses, agitation speeds, pH values and temperatures. The equilibrium adsorption amount of sorbate per unit weight of adsorbent (i.e., adsorption capacity) was calculated according to Equation 6 (Asano et al., 2007).

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{6}$$

where
- q_e = equilibrium adsorption amount of sorbate (mg P/g ZS)
- C_0 = initial phosphate concentration (mg PO_4^{3-}/L)
- C_e= equilibrium phosphate concentration (mg PO_4^{3-}/L)
- V = the solution volume (L)
- m = the anion exchange mass (g ZS)

The linear regressions are frequently used to determine the best-fitting kinetic models, and the method of least squares is used for finding parameters of the kinetic models. In

this study, the coefficient of determination, r^2, was used to test the best-fitting of the kinetic model to the experimental data (Equation 7: coefficient of determination).

$$r = \frac{\sum \left(q_m - \overline{q_t}\right)^2}{\sum \left(q_m - \overline{q_t}\right)^2 + \sum \left(q_m - q_t\right)^2} \tag{7}$$

where q_m is maximum amount of phosphate on the surface of the ZS at equilibrium, obtained from experiment (mg/g), q_t, is the amount of phosphate on the surface of ZS at any time, t, obtained from experiment (mg/g), and $\overline{q_t}$ is the average of q_t (mg/g).

Sample analysis

Phosphate concentrations in sample were analyzed by ascorbic acid colorimetric method (APHA, 2005; Method 4500-P-E) Ammonium molybdate and antimony potassium tartrate in acid medium with orthophosphate will form a heteropoly acid-phosphomolybdic acid- that is reduced to intensely colored molybdenum blue by ascorbic acid. Detectable P range from 10μg-P/L to 2mg-P/L. After mixing the reagent with samples, the mixed solutions were measured by using Spectrophotometer system (V-630; Jasco). The pH was measured using pH meter (Horiba, Ltd. D-51).

Results and Discussion

Phosphate Mass transferred

For the adsorption process, an analysis of the kinetic data is important because the kinetics describe the uptake rate of ion exchanger, which in turn controls the resident time in the adsorbent-solution interface (Asano et al., 2007). Experimental data with are shown in Figure 3. The results showed that ion exchange completed with in 60 minutes. Very few amount of phosphate were taken up by ZS after 90 minutes. Therefore, 120 minutes was set as the equilibrium time of this technology.

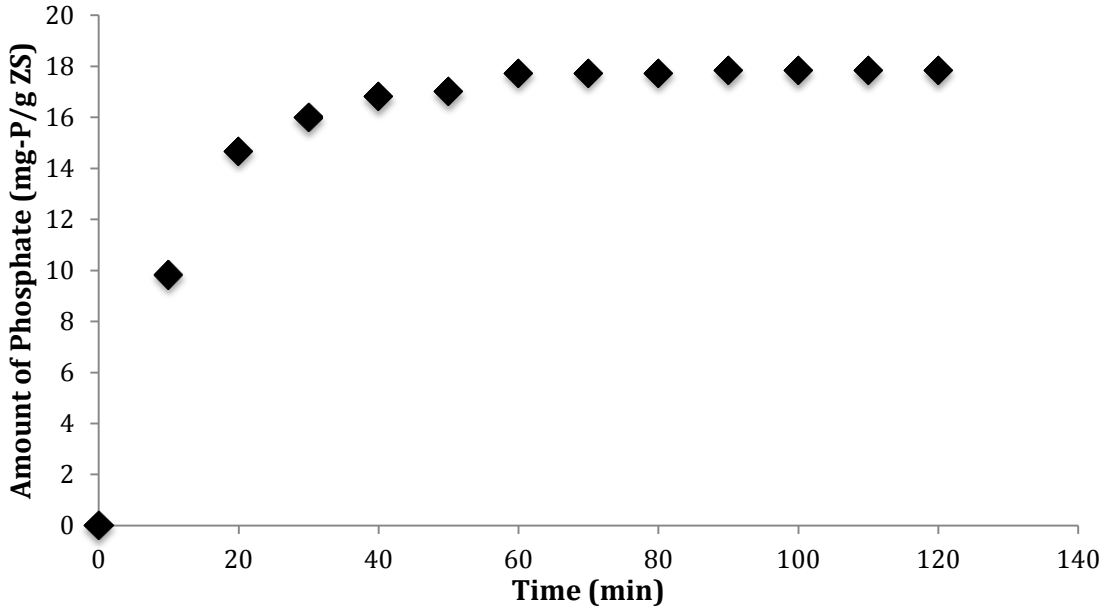


Figure 3: Phosphate mass transferred data regarding time

Isotherms

Isotherms are generally used to describe the amount of solute that can be adsorbed/ exchange ion onto an adsorbent/ ion exchanger at equilibrium at a constant temperature. In this study, isotherms were carried out to determine the condition for maximum ion exchange of phosphate to ZS. The y-axis shows the amount of phosphate adsorbed onto

ZS or known as q_e. q_e was calculated by equation 1, and the data obtained were plotted in figure 4 which showed the adsorption isotherm of ZS.

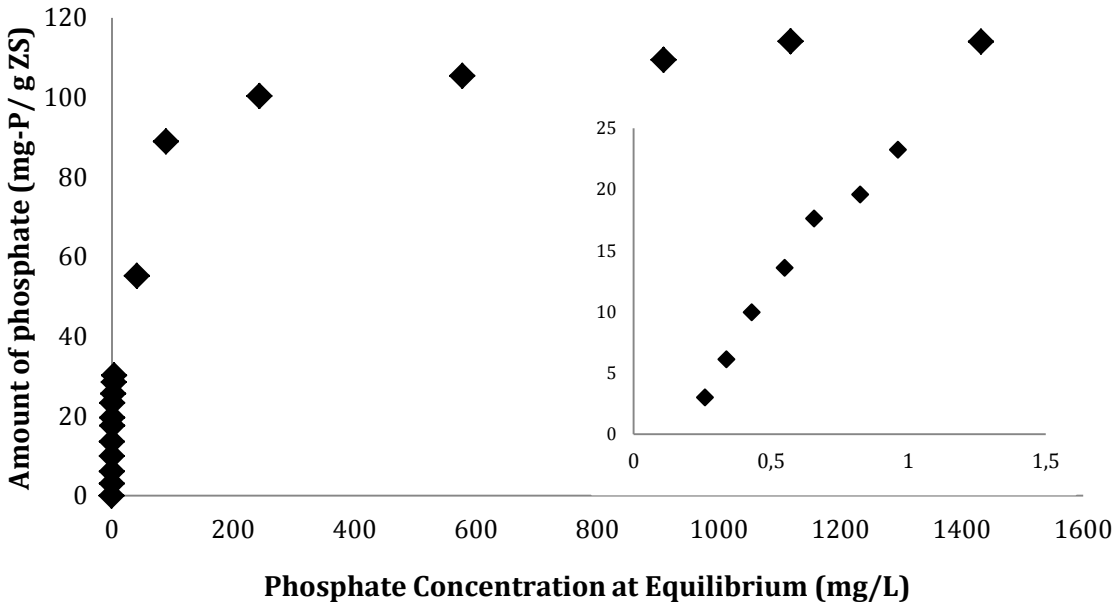
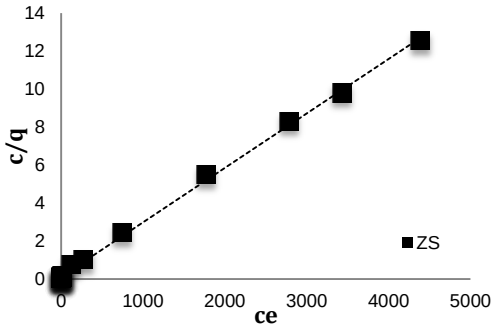


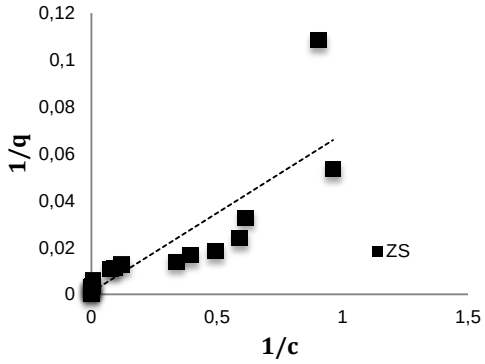
Figure 4: ZS isotherm according to the experimental data

As the equilibrium concentration of phosphate increased, q_e, which used to explain the adsorption amount, increased gradually, and finally reached to the equilibrium state. Equilibrium state of the ion exchange process indicates the limitation of exchangeable ions of the ion exchangers.

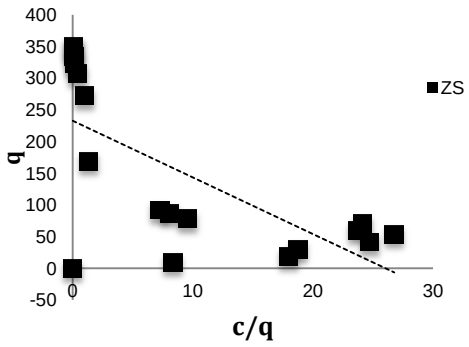
a) Langmuir Isotherm type 1



b) Langmuir Isotherm type 2



c) Langmuir Isotherm type 3



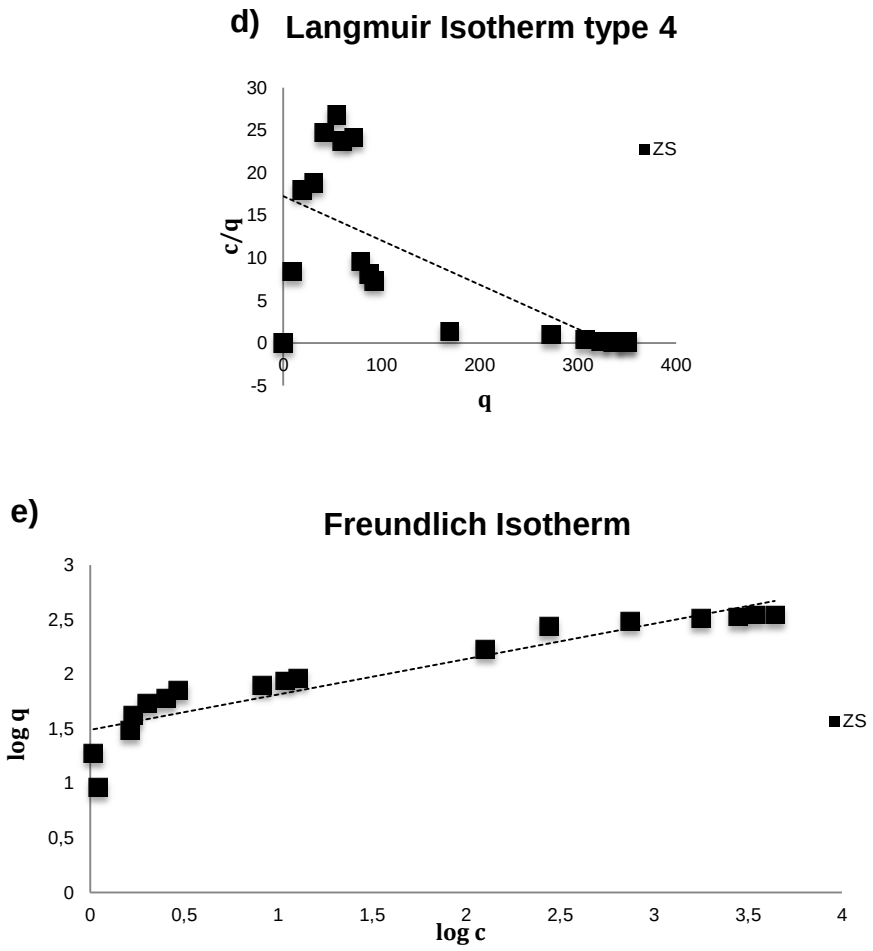


Figure 5: Plots for phosphate ion exchange by ZS. a) Linearize-Langmuir equation type 1, b) Linearize-Langmuir equation type 2, c) Linearize-Langmuir equation type 3, d) Linearize-Langmuir equation type 4, and e) Freundlich equations.

Experimental data with linear equations of the four Langmuir equations and Freundlich equation are shown in Figure 5. The calculated q_m and b values and the coefficient of determination values were shown in Table 4.

From Table 4, the data obtain from 4 linearized Langmuir equations were varies. The coefficient of determination for Langmuir type 1 was found to be relatively higher than the others for the ZS isotherm. However, the coefficient of determination, r^2, of all types

of linearized Langmuir equation were varied, so this means that the transformation of Langmuir equation into linearized equations implicitly altered their error structures and may also violates the error variance and normality assumption of standard least squares methods. In addition, the differences of the axis of all curves might contribute to the variation of data in Table 4. From Table 4, it was also observed that the equilibrium ion exchange capacity of ZS for phosphate was found to be 106.65 mg P/g (based on Langmuir type 1 equation), which was similar to the experiment results.

The equilibrium data were further analyzed by the linearized form of Freundlich equation using the same set of experimental data, by plotting log (q_e) versus log(C_e). The calculated Freundlich isotherm parameters and the corresponding r^2 values were shown in Table 4. From Table 4, it was observed that at all solutions, the r^2 values were found to be relatively less fit than linearized Langmuir isotherm. This suggests that the Langmuir isotherm is the most appropriate isotherm than the Freundlich isotherm for the present system.

Table 4: Parameters obtained from the plots according to linearization and non-linear Langmuir equation.

Equation	Parameter	Linear ZS	Non-linear ZS
Langmuir type 1	q_m (mg/g-zs)	113.64	106.65
	B (L/mg)	0.07	0.08
	r^2	0.95	0.95
Langmuir type 2	q_m (mg/g-zs)	82.64	106.65
	B (L/mg)	0.32	0.08
	r^2	0.87	0.95
Langmuir type 3	q_m (mg/g-zs)	76.02	106.65
	B (L/mg)	0.34	0.08
	r^2	0.83	0.95
Langmuir type 4	q_m (mg/g-zs)	108.16	106.65
	B (L/mg)	0.16	0.08
	r^2	0.93	0.95
Freundlich	k ((mg/g)(mg/L)^n)	14.52	12.88
	N	3.08	3.08
	r^2	0.89	0.92

These different outcomes from Table 4 show the real complexities and problems in estimating the isotherm parameters by linearization technique. Various outcomes for the four linearized equations are also due to the different axial settings, that would alter the result of linear regression and influence the determination process (Ebie et al., 2008). Thus, it will be more appropriate to use non-linear method to estimate the parameters involved in the isotherm or any rate equation. Also, non-linear method had an advantage that the error distribution does not get altered as in linear technique, as all the isotherm parameters are fixed in the same axis.

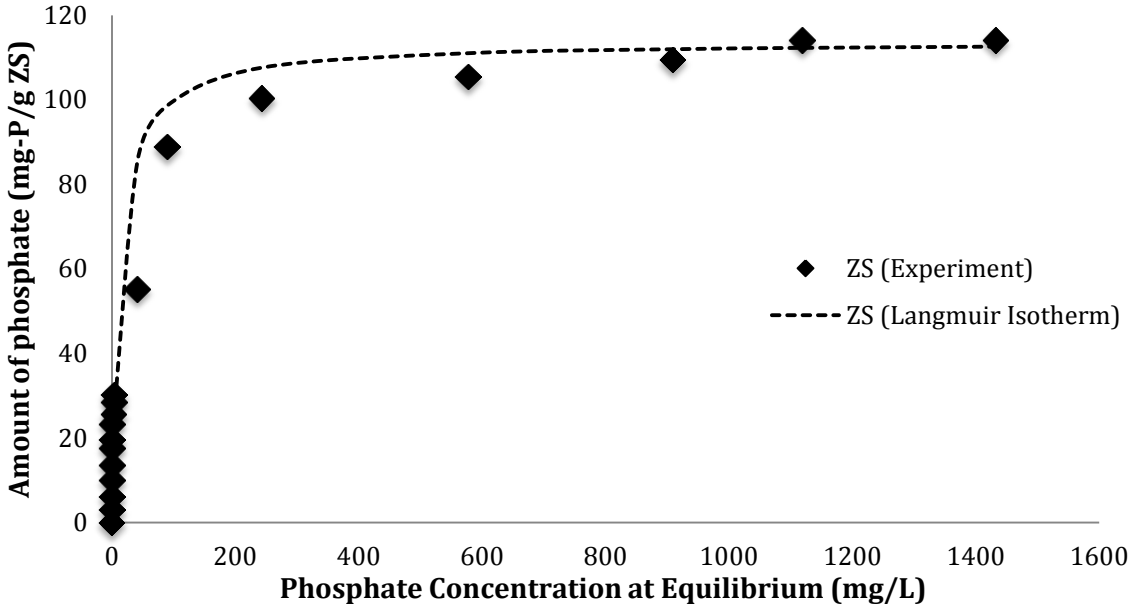


Figure 6: Adsorption isotherm of phosphate onto ZS.

For non-linear method, a trial and error procedure, which is applicable to computer operation, was developed to determine the isotherm parameters by minimizing the respective coefficient of determination between experimental data and isotherms using the solver add-in with Microsoft's spreadsheet, Microsoft Excel. Figure 6 shows experimental data and the predicted equilibrium curve using non-linear method for the Langmuir-equilibrium isotherm. The obtained isotherm parameters were listed in Table 4. In the case of Langmuir isotherm, the results from the four Langmuir linear equations are the same. By using non-linear method, there are no problems with transformations of

non-linear Langmuir isotherm equation to linear forms, and also they are in the same error structures. A q_m value, which is used to indicate the maximum adsorption efficiency of ZS, was approximately 106.65 mg P/L. Further, r^2 values (0.95) suggest that the Langmuir isotherms fit the experimental data equally well.

Elution Efficiency

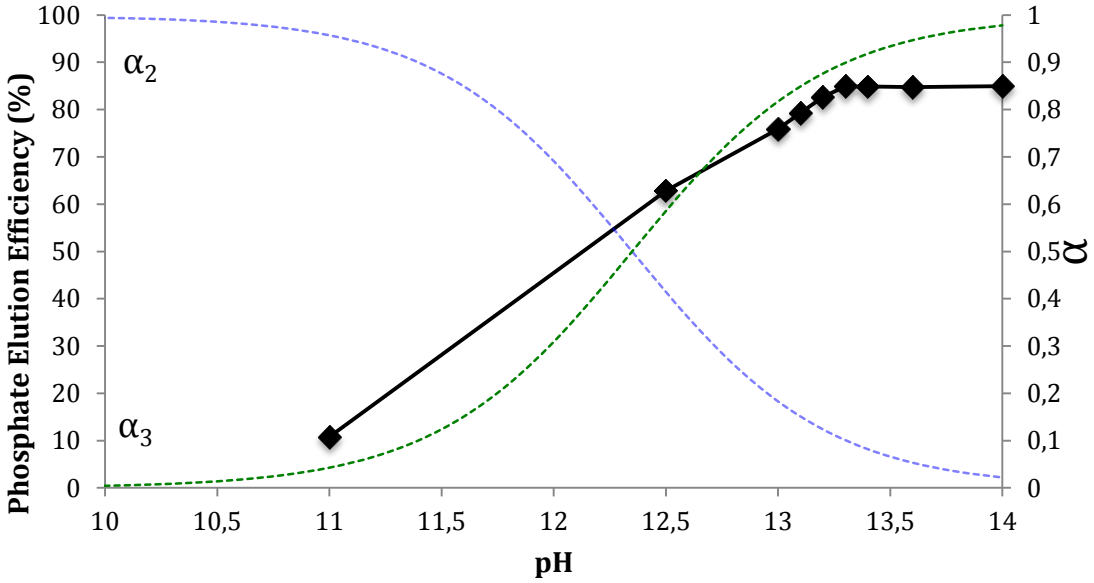


Figure 7: Elution efficiency at various pH

The applicability of ZS as a potential ion exchanger depends not only on the ion exchange capacity, but also on the elution performance, which eventually leads to its reusability. Since the mechanism of removal of phosphate by ZS is by ion exchange, the anion could be considered as eluent for the adsorbed phosphate. It has been reported that hydroxide is the hardest Lewis base among common inorganic anions (Awual et al., 2011). Therefore, aqueous NaOH behaves as an effective reagent for elution (Zhu and Jyo, 2005). Figure 7 shows phosphate elution efficiency at a variety of pH values of the elutent. Phosphate adsorbed on ZS could be eluted with aqueous NaOH within 10 min. The data shown in Figure 7 were taken after 30 min of the elution process. The phosphate elution efficiency increased as pH increased to 13.3 and was unchanged with pH above 13.3. The maximal phosphate elution efficiency was about 85%. These results indicate

that ZS can be regenerated. Phosphate elution occurred through an ion-exchange mechanism involving the release of phosphate and the uptake of hydroxide (Iwamoto et al., 2002). Furthermore, shift of phosphate species from HPO_4^{2-} (α_2) to PO_4^{3-} (α_3) might also affect elution of phosphate from ZS, because ZS prefers HPO_4^{2-} as compared with PO_4^{3-} (Figure 7). Results from the elution study also indicate that ion exchange of ZS is not completely reversible. In addition, the bonding between ZS and phosphate is probably strong under neutral pH conditions and it is relatively difficult for the adsorbed phosphate to be eluted.

Particles size distribution

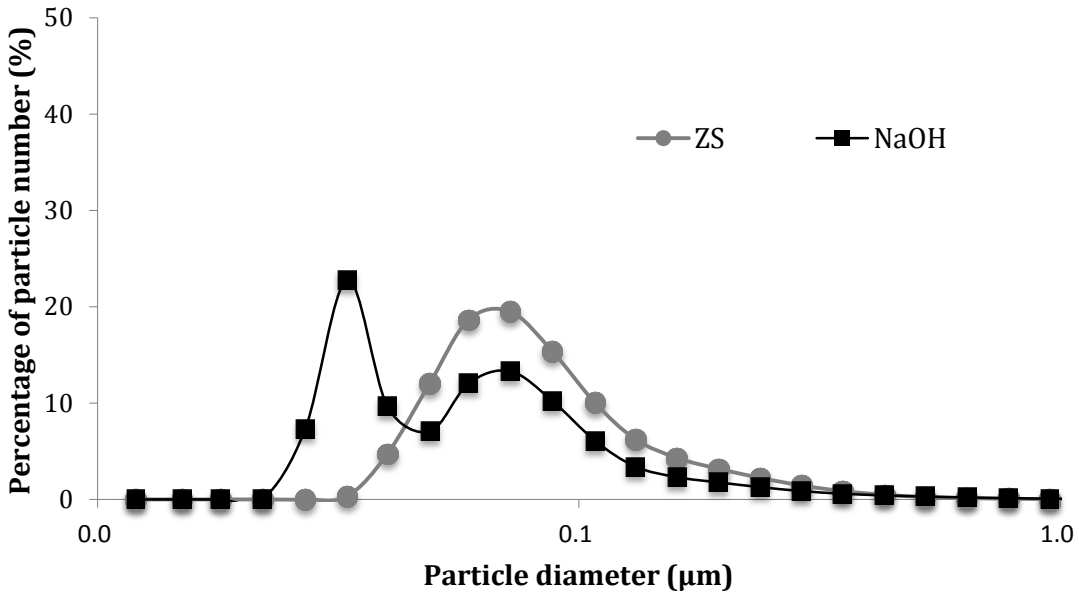


Figure 8: ZS particles size distribution

However, it was found the decomposition of the ZS structure after elution process, which led to the non-reusable problem. Figure 8 shows the size distribution of ZS before and after exposed to NaOH. ZS particle shrank after exposed to NaOH because NaOH destroyed the hexagonal structure of the ZS. Although phosphate was eluted effectively from ZS using NaOH solution, the breakage of ZS particles occurred and the ZS size regenerated with NaOH was below 0.5 μm. This changes in particle size compromised the reusability of ZS.

Structure of ZS and possible adsorption Mechanism

$$Zr(HSO_4)(C_{19}H_{42}N)_{0.5}(OH)_{3.5}\cdot 2H_2O + \mathbf{HPO_4^-} \rightarrow Zr(\mathbf{H_2PO_4})(C_{19}H_{42}N)_{0.5}(OH)_{3.5}\cdot 2H_2O + HSO_4^- \quad (8)$$

$$Zr(\mathbf{H_2PO_4})(C_{19}H_{42}N)_{0.5}(OH)_{3.5}\cdot 2H_2O + \mathbf{HPO_4^-} \rightarrow Zr(\mathbf{H_2PO_4})(C_{19}H_{42}N)_{0.5}(\mathbf{H_2PO_4})_{3.5}\cdot 2H_2O + OH^- \quad (9)$$

$$Zr(\mathbf{H_2PO_4})(C_{19}H_{42}N)_{0.5}(\mathbf{H_2PO_4})_{3.5}\cdot 2H_2O + \mathbf{OH^-} \rightarrow Zr(\mathbf{OH})(C_{19}H_{42}N)_{0.5}(\mathbf{OH})_{3.5}\cdot 2H_2O \quad (10)$$

Equation (8)-(10) showed the possible ion exchange mechanism which the operation condition of pH 7 and at 20-30° C while the condition for elution is at pH 13 and 20-30° C. Phosphate bound to the ZS at the position of sulfate in ion exchange process. For the first time used of ZS, pH drops from 7 to around 3, which indicated the acid released (SO_4^{2-}) from ZS since there was no other ions in the system, equation 8. After elution, in which hydroxide (OH^-) replaced to the phosphate position in ZS, equation (10), pH had increased from 7 to around 8.5, indicating that P can be recovered from ZS. In addition, there was another adsorption mechanism in which P replaced at the OH^- position at the deeper layer of the ZS surface (9).

Conclusion

ZS was used to recover phosphate ion in water sample. Two isotherm equations were applied to determine maximum ion exchange efficiency. The experiment data showed that the Langmuir equation was better fit to the experimental data more than the Freundlich equation. However, the coefficient of determination of both equations was relatively low, while the non-linear method showed the higher coefficient of determination of 0.956 for ZS. From the non-linear Langmuir equation, the maximum ion exchange amount of ZS was 106.65 mg/g-ZS. As ion exchange process depends on temperature, pH, and the surface structure, improvement of sorption capacity would be control all the parameters to be stable through all experiment. Moreover, the more amount of ZS used will increase the amount of P removed.

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Chapter 3

Immobilization of Zirconium Sulfate Micelle Mesostructure with Polymer (P-ZS)

Introduction

Among the P-recovery process, ion exchange is one of the most popular methods because of its simplicity, and high selectivity. The most important reason is that the ion exchanger can be recovered. Many types of ion exchangers have been used to recover phosphorus from sewerage and industrial wastewaters.

Zirconium (Zr) is a superior ion exchanger owing to its strong surface complexing ability for phosphate and high chemical stability under acidic and basic conditions (Chitrakar et al., 2006; Biswas et al., 2008; Liu et al., 2008; Ohura et al., 2011; Yeon et al. 2008). For example, Biswas et al. (2008) reported on the high adsorption capacity of phosphate on orange waste gel loaded with Zr. Liu et al. (2008) described the effective adsorption of phosphate on mesoporous zirconium oxide. Yeon et al. (2008) synthesized the mesoporous structures of zirconium sulfate by using a template of surfactants, which showed higher adsorption capacity for phosphate than those for the adsorbents based on zirconium hydroxides and oxides.

In the previous chapter, ZS the ion exchanger that was used to recover Arsenate and Selenite, was examined its capacity to recover P. ZS could be used as an ion exchanger to recover phosphate from water with a very high sorption amount (106.65 mg P/g ZS).
However, the decomposition of the ZS structure was found after elution process, which led to difficulty for the materials reused. Figure 8 showed the size distribution of ZS before and after exposed to NaOH. The size of the ZS particles decreased after exposure to NaOH because NaOH destroyed the hexagonal structure of the ZS. Although the ZS structures were broken down after exposed to high basic condition, the broken ZS could still function. But the broken ZS could not be recovered by filtration. Therefore, reduction in size of the ZS was thought to be a problem of our process because this would lead to the non-reutilization problem. To solve the problem, ZS powder has been embedded with polymer in order to prevent the washout of regenerated ZS particles. Moreover, immobilization of ZS could be easier to handle. The immobilized ZS is referred to as Polymer Coated Zirconium Sulfate Micelle Mesostructure (P-ZS). In this

chapter, the P-ZS was used to recover phosphate from water samples. Isotherm, reuse times, and interference by other anions were examined.

Materials and methods

P-ZS preparation

ZS powder was prepared according to the procedure described in Chapter 1. The ZS powder was immobilized on a polymer (Aramid-Polymer). ZS (8 wt%) and the polymer (8 wt%) were added to solvent (N-methyl-2-pyrrolidone) (84 wt%) and mixed at room temperature. The obtained mixture was dropped into coagulation liquid (98 wt% water and 2 wt% N-methyl-2-pyrrolidone). In this manner, the porous polymer-coated ZS particles with ZS/polymer ratio of 8 to 2 (abbreviated as P-ZS) were formed as a result of the spinodal decomposition. The morphology of P-ZS was characterized by a scanning electron microscopy (SEM, Hitachi High-Tech Fielding Co. S-2400).

Isotherm

Batch mode ion exchange experiments were carried out to examine the ion exchange behavior of phosphate on ZS and P-ZS. Briefly, 200 mg of ZS and P-ZS (corresponding to 160 mg ZS) were added into 200 mL of Milli-Q™ in a 500 mL flask at various concentrations of phosphate. Three drops of chloroform were added to each flask to inhibit bacterial growth. pH in the initial phosphate standard solution was adjusted to 7.0 by adding NaOH or HCl to minimize pH variations owing to the different amounts of KH_2PO_4 added. The solutions were shaken continually at 25°C for 120 min to achieve equilibrium. During the ion exchange process, a 1 mL of the sample was taken at preset time intervals. The sample had been filtered using a 0.2 μm pore size membrane (Advantec Co., Ltd., Tokyo, Japan) and the phosphate concentration in the samples was determined using ascorbic method (APHA, 2005; Method 4500-P-E).

Interference by other anions

The ion exchange capacity of possible interfering anions on P-ZS was examined. Batch mode adsorption experiments were conducted as described above. One g of P-ZS was added into 200 mL of Milli-Q™ in a 500 mL flask at 10 mM of bicarbonate (HCO_3^-),

nitrate (NO_3^-), chloride (Cl^-) and acetate (CH_3COO^-). The molar ratio of each anion to phosphate was 1:1. The pH was adjusted to 7.0. Furthermore, interference by HCO_3^- was investigated in detail. The solutions at a variety of phosphate concentration and 1000 mg/L of HCO_3^- were prepared with Milli-Q™. ZS powder (0.2 g) was added to 200 mL of the solutions at room temperature (20-25°C). The experiments were conducted at the pH range of 5-7 with continuous stirring for 2 hours. Samples were collected at the time 0, 30, 60, 90, and 120, respectively. The isotherm was compared with that for ZS in the solution containing only phosphate.

Effect of pH on P-ZS ion exchange capacity

The batch mode ion exchange experiments as described above were conducted at various pH. The fluctuation of pH in the solution was adjusted within 0.1 of pH unit throughout the test period using 0.1 M HCl or NaOH. The P-ZS and initial phosphate concentrations were 0.2 g P-ZS/L and 500 mg phosphate/L (5 mM).

Reusability test

To examine stabilization and reutilization abilities of P-ZS, P-ZS was repeatedly subjected to removal-recovery test. The removal process was done in the same way as the isotherm determination experiment with 1000 mg phosphate/L of phosphate concentration. The experiments were conducted at pH 7.0. The removal and recovery cycles were repeated 50 times.

Sample Analysis

Phosphate concentrations in the samples were analyzed by ascorbic method (APHA, 2005; Method 4500-P-E). Detectable phosphorous range from 10 μg-P/L to 2 mg-P/L. After mixing the reagents with samples, the solutions were measured by using a spectrophotometer (V-630; Jasco). The pH was measured using pH meter (Horiba, Ltd. D-51, Range from pH 0.00 ~ pH 14.00). HCO_3^- concentration was determined by a high-performance liquid chromatography system (LC-10AD system; Shimadsu Co., Kyoto Japan) equipped with a shimadzu Shim-pack CR-102H column (0.8 by 30 cm). NO_3^-

and Cl^- concentrations were determined by an ion chromatography system (ICS-90 system; DIONEX, USA) equipped with automate sampler AS40 DIONEX.

Results and Discussion

Characteristic of P-ZS

The scanning electron microscope (SEM) uses a focused beam of electrons to create a variety of signals at the surface of solid specimens, and the signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. The morphology of P-ZS was investigated by SEM. The ZS particles exhibited angular outline and sharp edges (Figure 9A). The dimensions of ZS were in the range of 20 to 100 μm and some smaller size ZS also existed. ZS particles were densely packed within polymer (Figure 9B). P-ZS had skin surface and considerable numbers of pores (Figure 9B), which could allow phosphate to penetrate in the polymer and also prevent leakage of ZS particles that were broken down during the desorption process.

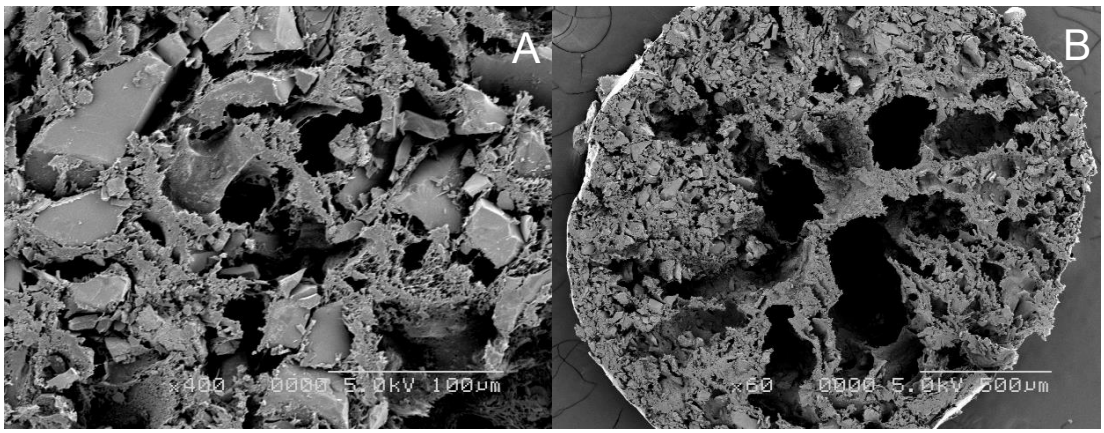

Figure 9: SEM images of the cross-section of P-ZS at ×400 (A) and ×60 magnifications (B).

Ion exchange time

Figure 10 shows the time series of the phosphate removal by the P-ZS. The equilibrium state of the process must be determined in order to know the amount of time required for

the saturation of the ion exchanger binding sites. The ion exchange process of P-ZS finished at 90 min although little amount of phosphate was adsorbed after 90 min. The equilibrium state of the ion exchange process was reached at 90 min under the condition of phosphate concentrations of 3 to 260 mg P/L. Thus, the ion exchange process was set to be finished at 120 min.

The final phosphate concentrations for the initial concentrations of 3, 16, 81, 130, and 260 mg P/L were 0.1, 1.12, 11.12, 19.08, and 44.94 mg P/L, respectively (Figure 10). At the low phosphate concentration ZS removal efficiency was almost 100% of phosphate, but when the phosphate concentrations of the samples were higher the efficiency decreased (Jellali, 2010). One of the important factors affecting ion exchange process is the amount of binding sites. Because the ion exchanger used in this experiment was 0.2 g in all tests, the available binding sites were the same at each concentration. Thus, the amount of phosphate adsorbed decreased at higher phosphate concentrations, resulting in the lower ion exchange efficiency.

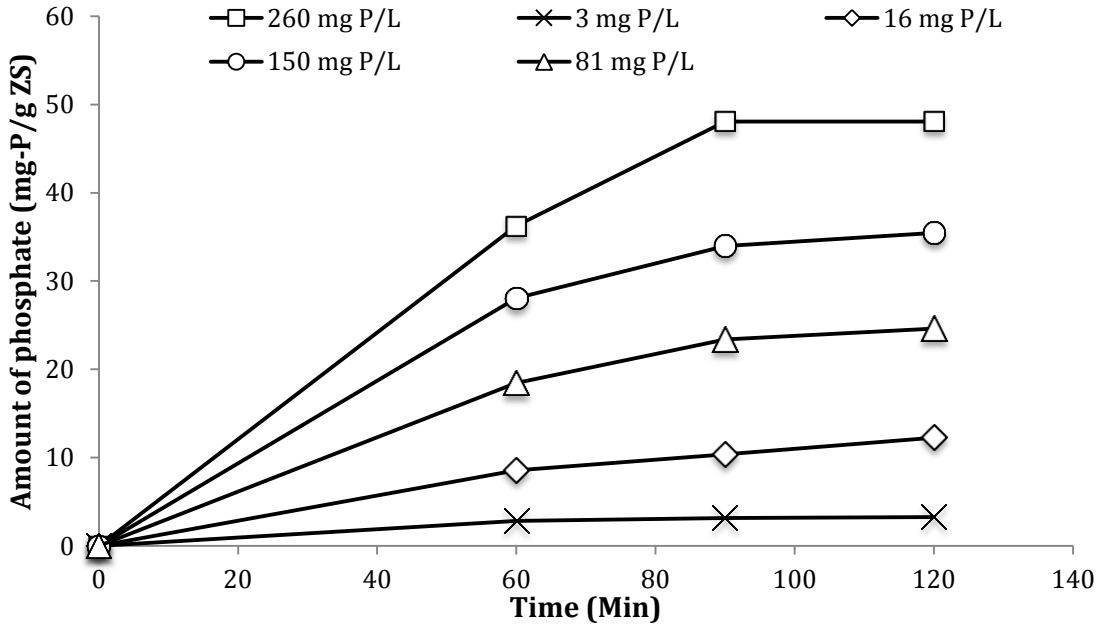

Figure 10: The time series of phosphate concentrations in the ion exchange tests

Effect of pH

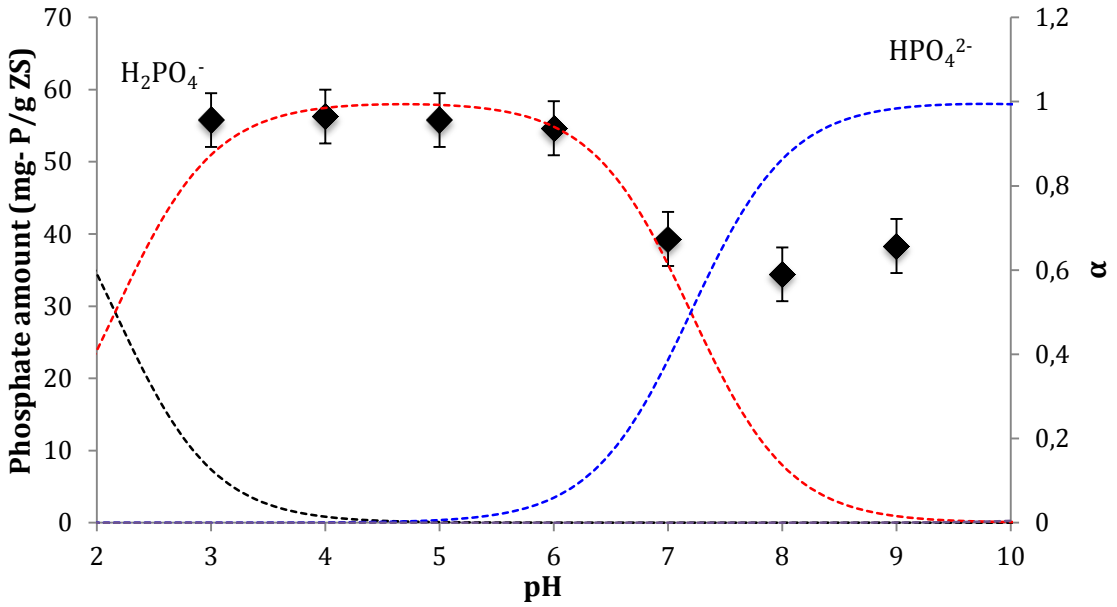

Figure 11: Effect of pH in the solution at equilibrium on phosphate ion exchange to P-ZS.

Figure 11 illustrated the effect of solution pH on phosphate ion exchange to P-ZS. As observed, the phosphate ion exchange capacity increased with decrease in pH. The maximum phosphate ion exchange capacity was 28.38 mg P/g ZS at pH 3.0 (corresponding to 89%). Considering the acid dissociation constant values of phosphoric acid (pKa_1 = 2.16, pKa_2 = 7.20 and pKa_3 = 12.35) (Benjamin, 2002), the fraction (α_i) of each phosphate species (H_3PO_4, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}) of the total phosphate, which was defined as the sum of H_3PO_4, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}, was calculated (Figure 11). An increase in pH from 7.2 inevitably makes the phosphate species more negatively charged, i.e., it results in the formation of more HPO_4^{2-} (α_2) than $H_2PO_4^-$ (α_1), indicating preferable ion exchange species of $H_2PO_4^-$ to P-ZS. This indicates that phosphate removal by ZS requires pH adjustment to optimize phosphate removal efficiency.

Interfere ions

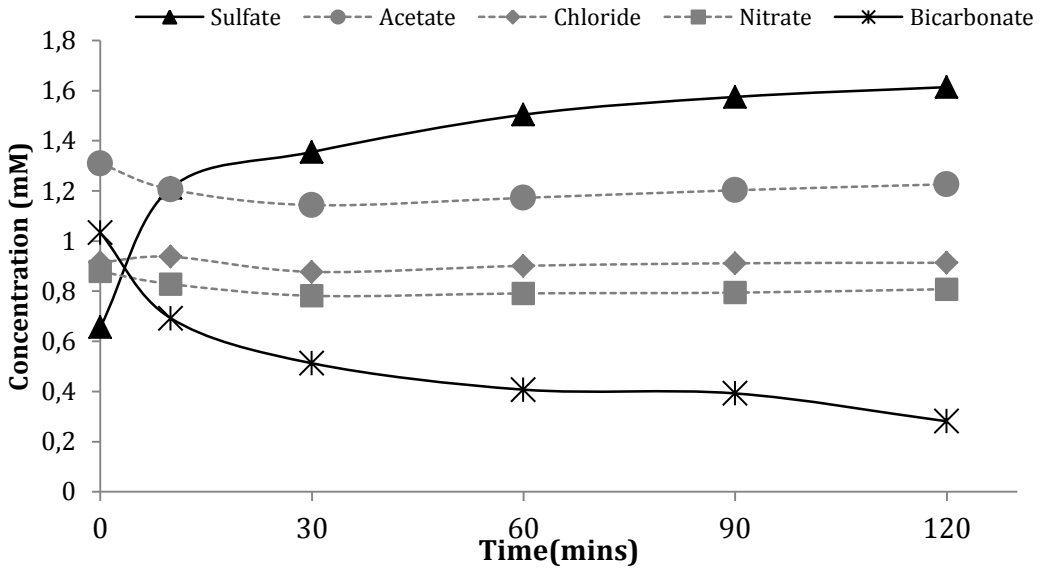

Figure 12: Changes in the interfering anions concentrations overtime with P-ZS

The removal of phosphate from the reject water of digested sludge is one of the possible applications of the technology. Since there would be other anions rather than phosphate in the reject waters (Takabatake, 2004), the other anions competition experiment was conducted. The wastewater and environmental water can contain common anions (for example, bicarbonate, nitrate, chloride and acetate), which may compete with the target phosphate for binding sites, thereby reducing the ion exchange capacity of P-ZS. Therefore, the ion exchange kinetics of P-ZS was investigated for bicarbonate, nitrate, chloride and acetate. The uptake (q_e) and distribution coefficients (K_d) of these anions are calculated from the data. K_d can be estimated as follows:

Equation 11: distribution coefficients

$$K_d(mL/g) = \frac{q_e(mmol/g)}{C_e(mmol/mL)} \tag{11}$$

where C_e = phosphate concentration in solution at equilibrium.

q_e = phosphate concentration in P-ZS at equilibrium.

The values of q_e were 0.97 mmol/g-ZS (phosphate), 10^{-3} mmol/g-ZS (chloride), 10^{-2} mmol/g-ZS (nitrate), 0.1 mmol/g-ZS (acetate), and 0.94 mmol/g-ZS (bicarbonate). A higher K_d value was observed for phosphate than for the other anions except for bicarbonate. The selectivity order based on the K_d values was phosphate (K_d = 3390) ≈ bicarbonate (K_d = 3340) >> nitrate (K_d = 109) ≈ acetate (K_d = 84) > chloride (K_d = 1.7). The selectivity of ZS was comparable to that of an adsorbent reported in another study (Chitrakar et al., 2006). These results indicate that P-ZS has a high selectivity toward phosphate, but bicarbonate should be considered as a possible interfering anion.

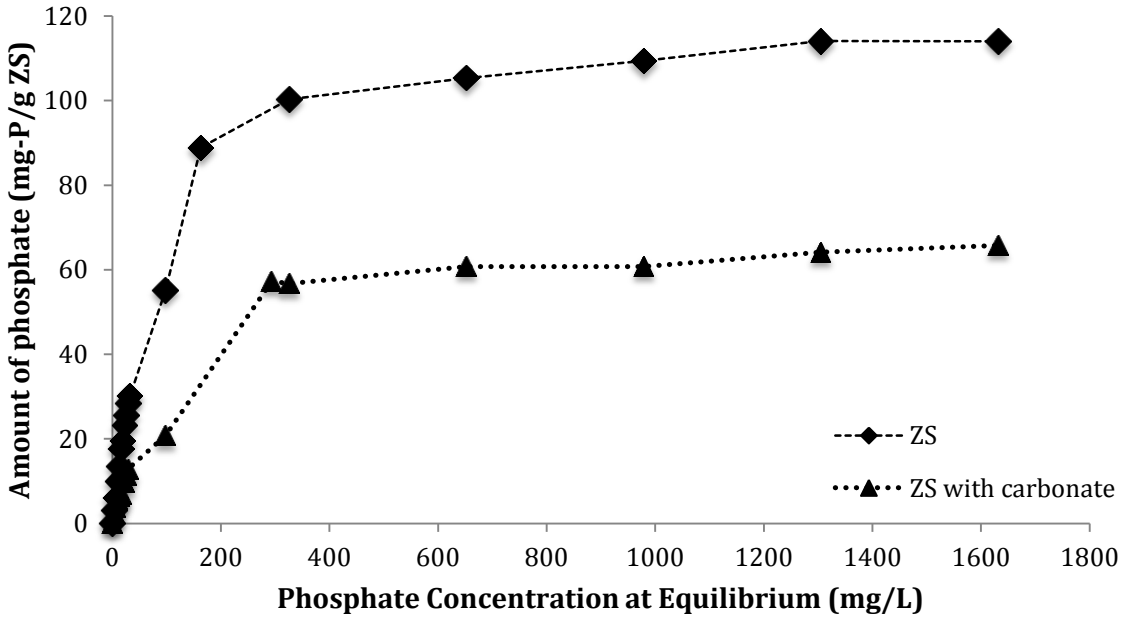

Figure 13: Adsorption Isotherm with Bicarbonate completion

Isotherm was used to examine the competition between phosphate ion and bicarbonate ion adsorbed onto ZS. As mentioned, isotherms are performed by exposing a known quantity of solute in a fixed volume of liquid to various dosage of ion exchanger, or various concentration of the solute with the fixed amount of ion exchanger. At the end of the equilibration period, the aqueous phase concentration of the solute is measured. Figure 13 has clearly shown that the presences of bicarbonate in the system have a huge

effect on phosphate ion exchange. According to the data obtained from isotherm, which q_m of ZS is equal to 106.65 mg P /g-ZS. At equilibrium, ZS can remove 65.57 mg P/g-ZS, which contributed to 58% removal efficiency, if there was bicarbonate in the system. From this result, bicarbonate removal is necessary before applied the P-ZS in order to reach its maximum efficiency.

Isotherms

As discussed in the previous chapter (Chapter 2), ZS ion exchange follows the Langmuir equation, and the non-linear regression has been applied to minimize variation of the parameters effecting ion exchange. For P-ZS, isotherm was calculated according to the result obtained from ZS isotherm. Isotherm experiments were performed at pH 7.0 for 120 min, which is sufficient to reach equilibrium according to the kinetic studies as described above (Figure 3). Figure 14 shows phosphate isotherms onto ZS and P-ZS.

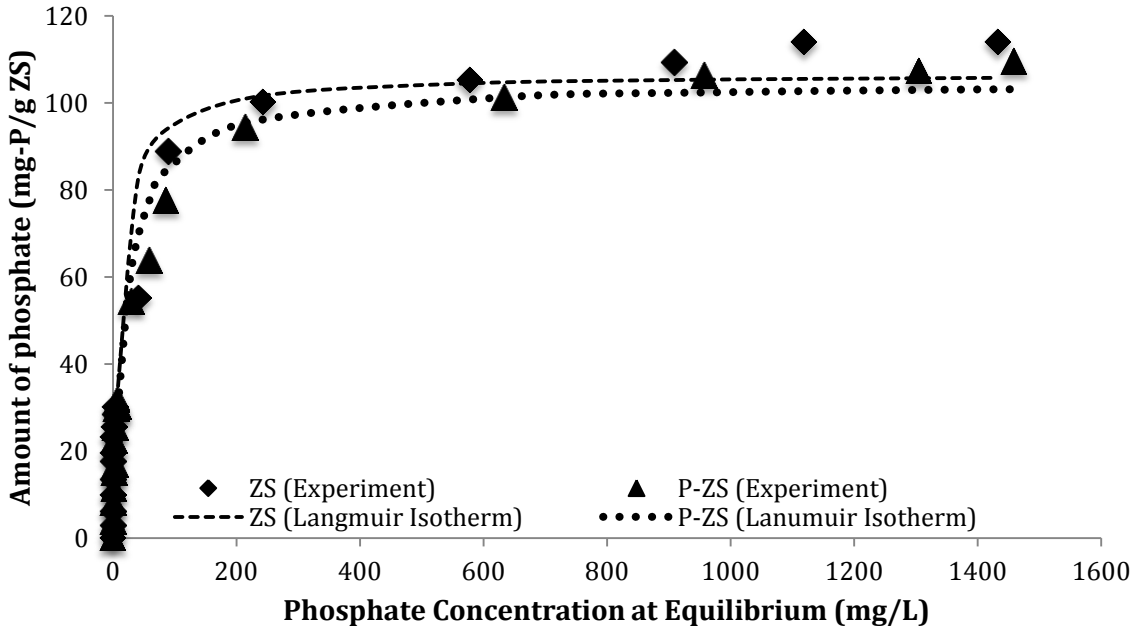

Figure 14: Adsorption isotherm of phosphate onto ZS and P-ZS

The isotherms are characterized by a steep initial rise followed by a plateau, indicating that the shapes of the curves appeared Langmuirian in nature (Naeem et al., 2007). The

experimental data were analyzed with non-linear Langmuir and Freundlich isotherm models. The Langmuir model assumes the adsorbent surface to be homogenous and the adsorption energies for each adsorption site to be equivalent (Naeem et al., 2007). Solute immobilization occurs without mutual interactions between the molecules adsorbed at the surface. Conversely, the Freundlich model is based on an exponential distribution of adsorption sites and energies, and mutual interaction between adsorbed molecules is possible (Naeem et al., 2007). As shown in Table 5, the values of both the correlation coefficients (r^2) demonstrate that the data are better fitted to the Langmuir equation than the Freundlich equation. The maximum phosphate ion exchange capacities of ZS and P-ZS were estimated to be 106.65 mg P/g ZS for ZS, 104.63 mg P/g ZS for P-ZS. The isotherm curve for P-ZS was almost the same as that of ZS, indicating that polymer coating ZS did not affect the ion exchange ability of ZS in P-ZS.

The lower maximum phosphate ion exchange capacity of P-ZS compared with ZS may result from complete immobilization of a part of ZS within the polymer structure. Such a high capacity has not been reported previously (Table 1). Hence, P-ZS should be applicable for advanced wastewater treatment of industrial wastewaters (Chimenos et al. 2006; Chimenos et al. 2003) and supernatant of anaerobically digested wastewater sludge (van Rensburg et al. 2003).

Table 5: Langmuir & Freundlich isotherm parameter

Equation	Parameter	linear ZS	non-linear ZS	linear P-ZS	non-linear P-ZS
Langmuir type 1	Qm	113.64	109.89	106.65	104.63
	B	0.07	0.05	0.08	0.05
	r^2	0.95	0.97	0.95	0.98
Langmuir type 2	Qm	82.64	73.53	106.65	104.63
	B	0.32	0.14	0.08	0.05
	r^2	0.87	0.73	0.95	0.98
Langmuir type 3	Qm	76.02	246.17	106.65	104.63
	B	0.34	0.04	0.08	0.05
	r^2	0.83	0.66	0.95	0.98
Langmuir type 4	Qm	108.16	102.33	106.65	104.63
	B	0.16	0.07	0.08	0.05
	r^2	0.93	0.97	0.95	1.00
Freundlich	K	14.52	11.80	12.88	11.80
	n	3.08	2.83	3.08	2.83
	r^2	0.89	0.89	0.92	0.89

P-ZS reusability

The applicability of P-ZS as a potential ion exchanger depends not only on the removal capacity, but also on the recovery performance, which eventually leads to its reusability. From the elution study also indicated that phosphate on ZS is not completely reversible. In addition, the bonding between ZS and adsorbed phosphate is probably strong under neutral pH conditions and it is relatively difficult for the adsorbed phosphate to be recovered.

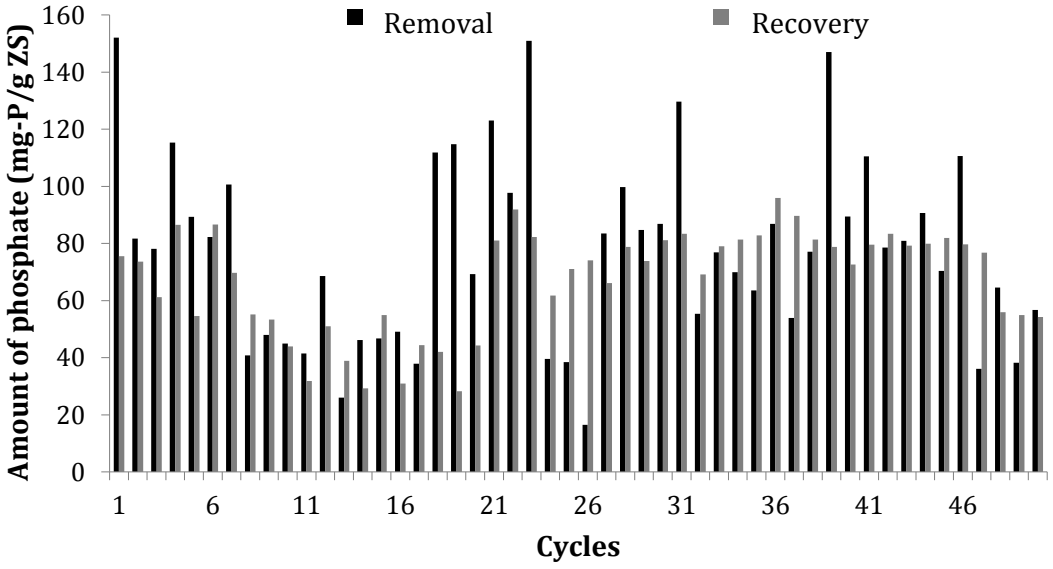

Figure 15: P-ZS reusability data

Although phosphate was eluted effectively from ZS using NaOH solution, the breakage of ZS particles occurred and the ZS size regenerated with NaOH was below 0.5 μm. This change in particle size compromised the reusability of ZS. Adsorbed phosphate on the P-ZS was eluted by aqueous NaOH solution at pH 13.5. The removal-recovery cycles were repeated for 50 times and results on phosphate removal-recovery capacities are shown in Figure 15. The phosphate removal-recovery capacities fluctuated, but could retain functionality over the 50 cycles. The total amount of phosphate removal-recovery over 50 cycles was 1260 and 1100 mg P/g P-ZS, respectively. Although the dry weight of P-ZS decreased to 55 % over the five initial cycles, no measurable loss of P-ZS occurred

thereafter. It is probably because the washout of the small size P-ZS (i.e., P-ZS powder) occurred and the leakage of ZS from P-ZS was insignificant. Owing to the high ion exchange capacity of ZS to phosphate and its reusability over many operating cycles without noticeable deterioration, the relatively high cost of the P-ZS raw materials (i.e., zirconium sulfate) will not be a barrier in practical application.

Conclusion

We synthesized a zirconium sulfate-surfactant micelle mesostructure (ZS) as an ion exchanger for phosphate removal from water. ZS could exchange phosphate in water by an ion-exchange process with high ion exchange capacity as compared with other phosphate adsorbents and ion exchangers. The phosphate removal capacity increased with decrease in pH. Bicarbonate was the sole interfering anion among the anions tested. Phosphate adsorbed could be eluted from the ZS using NaOH solution. The P-ZS could be regenerated at least 50 times without loss of original functionality. Therefore, we concluded that ZS was a highly effective ion exchanger for phosphate and enabled the removal of phosphate from water.

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Chapter 4

Application of Polymer Coated Zirconium Sulfate Mesostructure (P-ZS) for Phosphorus recovery

Introduction

A wide range of ion exchangers (granulated as well as finely powdered) including zeolite, ion exchange resin, and etc. are used in wastewater treatment for the removal of heavy metals, dissolved organic compound, and nutrients. P-ZS showed its efficiency of phosphorus removal in the batch experiment. Therefore, application of P-ZS to remove phosphorus from environmental samples is very interesting.

In the wastewater treatment plant, most types of the ion exchanger are used as the tertiary treatment due to the fact that passing wastewater with high-suspended solids concentration required high energy for pumping and mixing. Treated water from several wastewater treatment plants may be one of the choices for phosphorus recovery test. However, the amount of P in those water seemed to be relatively low that it could be easily discharged into the natural water.

An interesting resource for phosphorus recovery is the groundwater. Usually, concentrations of dissolved phosphorus (DP) in groundwater are typically low because phosphorus tends to be absorbed into soil and aquifer sediments and is not readily transported in groundwater (Holman et al. 2008). The principal sources of phosphorus to groundwater systems include overlying soils, dissolution of minerals that contain phosphate in aquifer sediments, agricultural fertilizer, animal waste, and leaking septic systems or infiltration of wastewater (Heather et al. 1999). However, Dubrovsky et al. (2010) noted that dissolved phosphorus concentrations in groundwater showed no correlation to fertilizer and manure use in agricultural areas, and similarities to concentrations in deep groundwater suggest that natural geologic sources might have a greater influence on concentrations in groundwater than anthropogenic sources. Therefore, there are many reports about phosphorus contamination in groundwater throughout the world. (Domagalski et al. 2012).

Groundwater was found to be suitable sample for this technology because it contains low suspended solids concentration, and high concentration of phosphate. In this chapter, artificial groundwater and groundwater samples were used as phosphorus resources for

phosphate recovery in a column mode. Column mode is usually used in the real water treatment, therefore the data obtained from this experiment can be utilized for real application of this technology.

Materials and methods

Experimental Setup

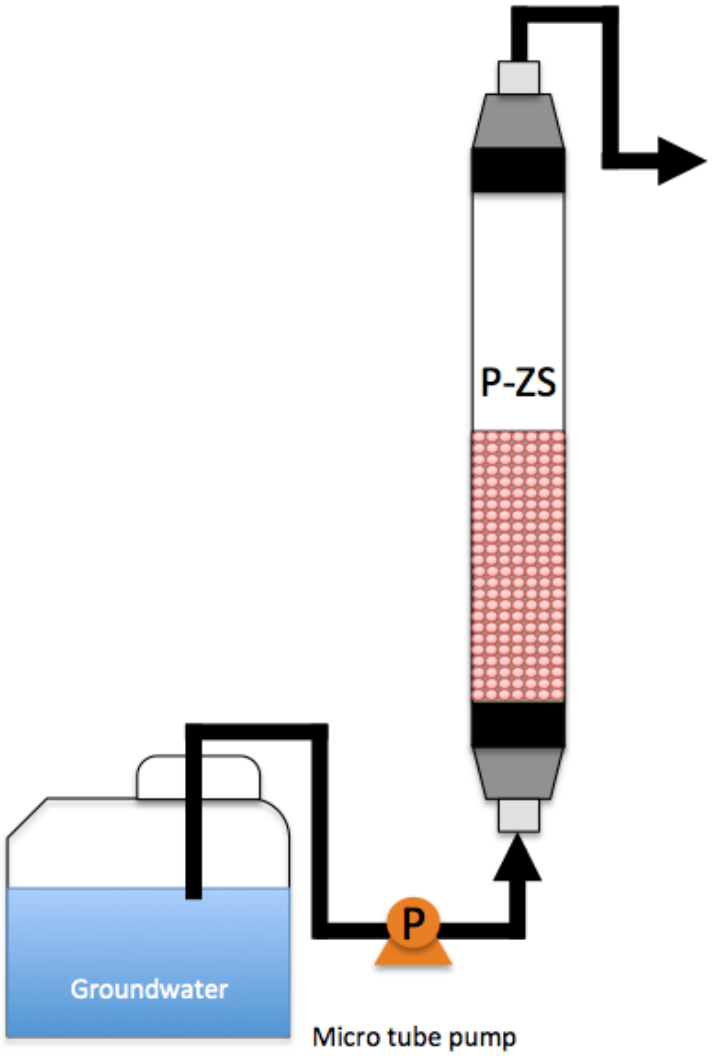

Figure 16: P-ZS column set up

The ion exchange column was carried out by using a transparent glass column of 3.5 cm diameter with 53 cm height. The column was place in the room with constant temperature at 25°C. 24.5 g of (100 ml) of P-ZS was put into the column and filled with deionized water at the beginning. After that the solution of 10 mg-P/L (Milli-Q^{TM} water with KH_2PO_4) was fed into the column with the flow rate of 40 ml/hr. Samples were collected at every hour and determine the phosphate concentration by using the ascorbic method.

Another column experiment was conducted with the groundwater to examine phosphate removal. Glass columns (2.5 cm internal diameter and a length of 20 cm) were packed with 3 g (10 ml) of P-ZS. The column was operated in an upflow mode, to maximize the contact between the water and the adsorbent at a flowrate of 5 mL/hr. The flowrate was controlled with a microtube pump MP-1000 (EYELA), and the tubing was checked regularly to ensure that there were no kinks or clogs. Samples were collected every day, and the samples were analyzed for pH and Bicarbonate (HCO_3^-), phosphate.

Phosphate and phosphorus concentration measurement

Phosphate concentrations in the sample were analyzed by ascorbic method. (APHA, 2005; Method 4500-P-E) Ammonium molybdate and antimony potassium tartrate in acid medium with orthophosphate will form a heteropoly acid-phosphomolybdic acid- that is reduced to intensely colored molybdenum blue by ascorbic acid. Detectable phosphorus range from 10ug/L-2mg/L. After mixing the reagent with samples, the mixed solutions were measured by using Spectrophotometer system (V-630; Jasco)

pH measurement

The pH was measured using pH meter (Horiba, Ltd. D-51, Range pH 0.00 ~ pH 14.00).

Carboxylic acid and bicarbonate concentration measurement

Concentrations were determined by a high-performance liquid chromatography system (LC-10AD system; Shimadsu Co., Kyoto Japan) equipped with a shimadzu Shim-pack CR-102H column (0.8 by 30 cm).

Results and Discussion

Mass transfer zone (MTZ) is the area of the bed ion exchanger in which ion exchange is occurred. After the water containing the constituent to be removed passes through a region of the bed whose depth is equal to the MTZ, the concentration of the contaminant in the water is reduced to its minimum value. No further ion exchange occurs within the bed below the MTZ. As the top layers of carbon granules become saturated with organic material, the MTZ will move down to the bed until breakthrough occurs (Asano et al. 2007).

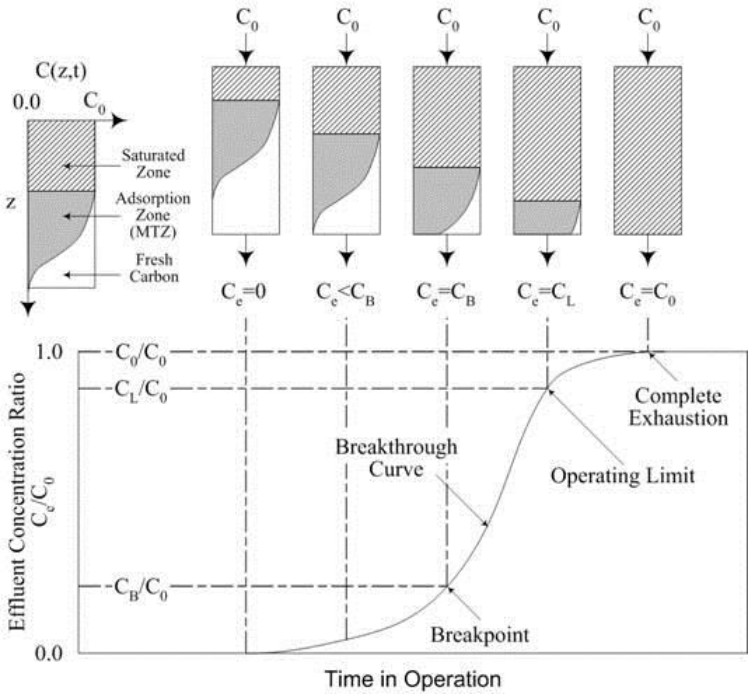

Figure 17: Mass transfer zone and breakthrough curve

Where

C_0 = the concentration of adsorbate in the influent

C_e = the concentration of adsorbate in the effluent

C_B = the breakthrough concentration of the adsorbate

C_L = operating limit concentration

Typically, breakthrough is said to have occurred when the effluent concentration reaches five percent of the influent value. Exhaustion of the ion exchanger bed is assumed to have occurred when the effluent concentration is equal to 95 % of the influent concentration. Composition of groundwater obtained from Akita prefecture is given in table 6

Table 6: Groundwater composition

Nutrients	Concentration	Detection limit
Phosphate mg P/L	29	0.003
Total phosphorus (T-P) mg/L	29	0.003
Chloride (Cl^-) mg/L	69	1
Sodium (Na) mg/L	290	0.1
Calcium (Ca) mg/L	0.4	0.1
Magnesium (Mg) mg/L	1.6	0.1
Sulfate (SO_4^{2-})mg/L	30	1

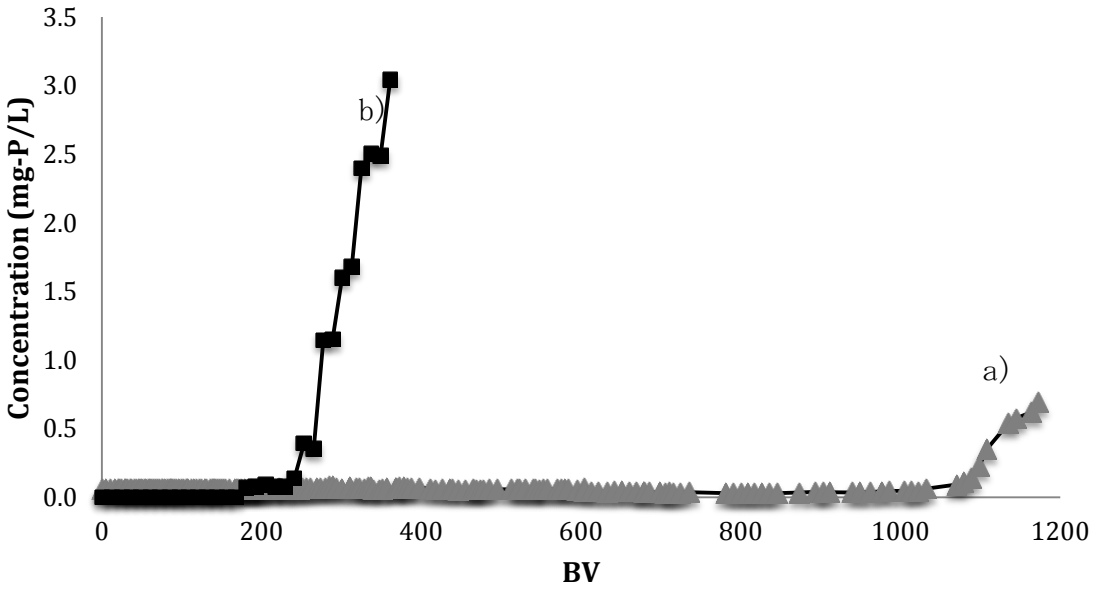

Figure 18: Breakthrough data of a) artificial groundwater and b) groundwater

Table 7: P-ZS breakthrough details for artificial ground water and groundwater

Details	Artificial Groundwater	Groundwater
P-ZS amount (g)	24.50	3.00
BV	1088	240
Total **phosphate** adsorbed (mg P)	1065.24	26.02
phosphate adsorbed (mg P/g P-ZS)	42.12	8.09
phosphate adsorbed (mg P/g ZS)	56.65	10.11

To further evaluate the phosphate removal capacity of P-ZS, column experiments were conducted on a phosphate standard solution (10 mg P/L at pH 7.0). Figure 18 shows breakthrough profiles of phosphate, using columns packed with P-ZS in continuous-mode operation where the solutions were percolated continuously at a hydraulic retention time (HRT) of 2 hr. From this result, it is perceived that breakthrough, which is defined as the point where the phosphate concentration exceeded the analytical detection limit (0.5 mg P/L), occurred at 1020 bed volumes for the phosphate solution. This means that phosphate could be completely removed (with more than 99 % efficiency) up to the mentioned bed volumes. These values were much higher than those reported in other studies (Biswas et al., 2008; Ohura et al., 2011; Awual et al., 2011). The effective ion exchange capacity for P-ZS calculated from the breakthrough profile for the phosphate standard solution was 56.65 mg P/g ZS, which was almost identical to that (50 mg P/g ZS) evaluated in the batch test (Figure 14).

The test of groundwater was also evaluated for phosphorus ion exchange by the water treatment residuals in a column apparatus. A column containing P-ZS was constructed in the same method as for artificial groundwater column as described earlier. In order to reduce the breakthrough volume, amount of P-ZS was reduced to 3 g (corresponding to 10 mL). Data form figure 18 showed the breakthrough occurred at 240 bed volumes for the phosphate solution. The effective removal capacity for P-ZS calculated from the breakthrough profile for the phosphate standard solution was 10.11 mg P/g ZS, which was lower than that of the artificial groundwater result. The reason of this reduction of

phosphate removal amount was the presence of other interfered ions, i.e. HCO_3^-. The data from this experiment showed the same trend that was found in the batch test in which the adsorption efficiency reduced by 57% if HCO_3^- were present in the environment.

Conclusion

A column packed with P-ZS could remove phosphate completely in a phosphate solution including about 10 mg P/L of phosphate up to 1020 and 240 bed volumes, for artificial groundwater and groundwater respectively. Therefore, ion exchange column studies using a fixed bed suggests that the P-ZS can be used in a continuous-mode operation to remove phosphate from wastewater and other industrial effluents contaminated with phosphate.

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Chapter 5

Application of Polymer Coated Zirconium Sulfate Micelle Mesostructure(P-ZS) for Phosphorus Recovery from Anaerobic Membrane Bioreactor (AnMBR) Permeate

Introduction

Anaerobic wastewater treatment is considered to be a more cost effective technology than the aerobic treatment of different kinds of wastewater ranging from medium to high strength, including sewage and industrial wastewater (Wijekoon et al., 2010). The success of anaerobic treatment is attributed to low biomass yield, high loading potential, less nutrient demand, smaller reactor and low operations & maintenance cost (Smith et al., 2012). In addition, biogas recovery from anaerobic treatment ensures renewable energy source and reduces green house gas emission.

The composition of sludge is complex, however, they can be a source valuable of materials such as nitrogen, phosphorous and metals that have uses as nutrients in agricultural applications and more recently for the production of microalgae (Gerardo et al., 2013). Moreover, recent trends of sludge in wastewater treatment have also included the production of biogas to recover energy (Visvanathan, & Abeynayaka., 2012)

In general, the available nutrient recovery technologies target one or two specific materials within the waste effluent (Gerardo et al., 2013). The recovery of phosphorous with hydrogels in aquaculture waste effluent (Kioussis et al., 1999) and precipitation as calcium phosphate (Hosni et al., 2008 and Lu and Liu, 2010), have been reported. Absorption of phosphate by adsorbents is popular due to its simplicity and cost effective (Pitakteeratham et al., 2012).

In anaerobic treatment, researchers have obtained permeates which reduce on chemical oxygen demand (COD) and total dissolved solids (TDS) above 95% (Galambos et al., 2004 and Tay and Jeyaseelan, 1995). The advantages of membrane filtration have been widely reported and these include physical separations free of chemical additives, lower operating and maintenance costs than other competing separation technologies, together with the particle and pathogens free permeates (Chen et al., 2006). However, discharge permeate into the aquatic environment or water reuse is not possible without further nitrogen and phosphorus removal (Ruiz-Martinez et al. 2012). Therefore, treating

AnMBR's permeates with P-ZS column is another alternative solution to remove phosphorus from water and also able to recover phosphate.

Materials and methods

Wastewater source

The wastewater was obtained from pilot-scale Baffled membrane reactor (BMBR) excess sludge operated at Sosiegawa wastewater treatment center, Sapporo, Japan. The total chemical oxidation demand (COD) concentration fluctuated in the range of 5.44 ± 1.34 g-COD/L, the suspended solid concentration of 5.49 ± 1.13 g/L, and the pH of 7. The T-P concentration was 123.41 ± 31.5 g P/L.

Experimental Setup

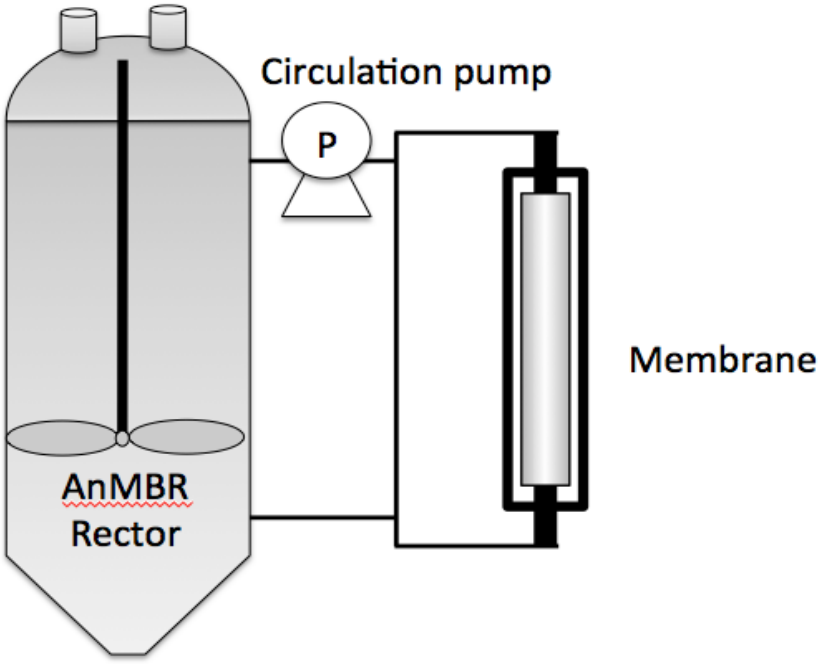

Figure 19: AnMBR configuration set up

A flow diagram of the AnMBR pilot plant (20 L) is shown in Figure 19 The system included an anaerobic reactor, membrane modules and a circulate pump. Excess sludge from a pilot-scale Baffled membrane reactor (BMBR) operated at Sosiegawa wastewater treatment center, Sapporo, Japan) (Kimura et al., 2008) was screened through 1 mm mesh and pumped into the reactor daily. The AnMBR system was made of stainless steel. The anaerobic sludge was circulated inside the anaerobic reactor by FISCIAER PORTER flow pump and KANKI MIXER (Oriental Motor) mixer. The membrane tank had a 0.405 m^2 microfiltration membrane module (Sumitomo Electric Industries Membrane Systems, 1 μm pore size). HRT was 2 days.

Wastewater source

Anaerobic seed sludge was obtained from Ebisu Joka Center wastewater treatment plant, Hokkaido, Japan. 500 mL of BMBR excess sludge, obtained from Sosiegawa wastewater treatment center, was added to the reactor daily as a feed solution. pH for the first 170 days was not control. The temperature of the reactor was controlled at 38°C by As-One TR-K temperature controller. The AnMBR permeate was collected and taken to the laboratory each day to test for COD, T-P, D-P, SS & VSS, Biogas, pH, ORP.

P-ZS column for phosphate removal

Glass columns (2.5 cm internal diameter and a length of 20 cm) were packed with 3 g (10 ml) of P-ZS. The column was operated in an upflow mode, to maximize the contact between the water and the adsorbent at a flow rate of 5 mL/hr. The flow rate was controlled with a peristaltic pump (Masterflex), and the tubing was checked regularly to ensure that there were no kinks or clogs. Samples were collected every day, and the samples were analyzed for pH and, phosphate.

Biogas composition

All gas compositions (CH_4, CO_2, N_2, and H_2) produced from AnMBR were measured by a gas chromatography system (GC-14B, Shimadzu Co., Kyoto, Japan) equipped with a

thermal-conductivity detector and a Shincarbon-ST column. The biogas volumes were measured at ambient temperature.

Volatile fatty acids concentration measurement

Concentrations of volatile fatty acids (VFAs; formate, acetate, propionate, lactate, i-butyrate, and n-butyrate) were determined by a high-performance liquid chromatography system (LC-10AD system; Shimadsu Co., Kyoto Japan) equipped with a shimadzu Shim-pack CR-102H column (0.8 by 30 cm) after filtering it through a 0.2-μm-pore-size membrane.

Phosphate concentration measurement

The concentrations of total phosphorus (T-P) were measured using the Molybdovanadate Test 'N Tube™ Method (Hach Method 10127), detection range from 1.0 - 100.0 mg phosphate/L. The concentrations of Reactive Phosphorus (orthophosphate) were measured by using the Molybdovanadate Test 'N Tube™ Method (Hach Method 8114), detection range from 1.0 - 100.0 mg phosphate/L.

Chemical oxygen demand (COD)

The concentrations of total COD (T-COD) were measured using a Reactor Digestion method (Method 8000) approved by US EPA for wastewater analysis Range: 3-150 mg/L COD.

pH& ORP

The oxidation–reduction potential (ORP) and pH were directly determined by using an ORP and a pH electrode, respectively.

Results and discussion

Anaerobic treatment performance

The AnMBR reactor was operated for 170 days. Hydraulic retention time (HRT) was set to be 20 days. Sludge losses from the system were only due to sampling which leads to an infinite SRT. The pH of the reactor was not controlled, but only pH range above 7 throughout the operation period (Fig. 20).

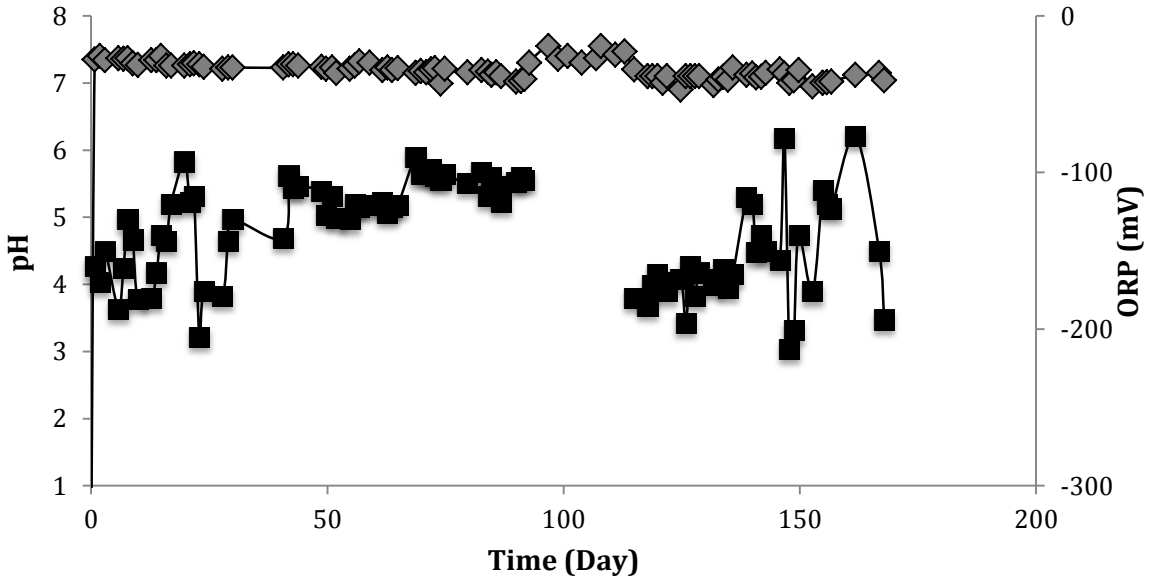

Figure 20: Operational condition pH and ORP

Concentrations of influent T-COD and effluent T-COD from AnMBR were measured (Figure 20). The average T-COD concentration (± standard deviation) of the BMBR excess sludge was 15.69 ± 1.82 g-COD /L. The average effluent D-COD concentration was 0.269 ± 0.19 g-COD /L, resulting in a COD removal efficiency as high as 95 ± 2%.

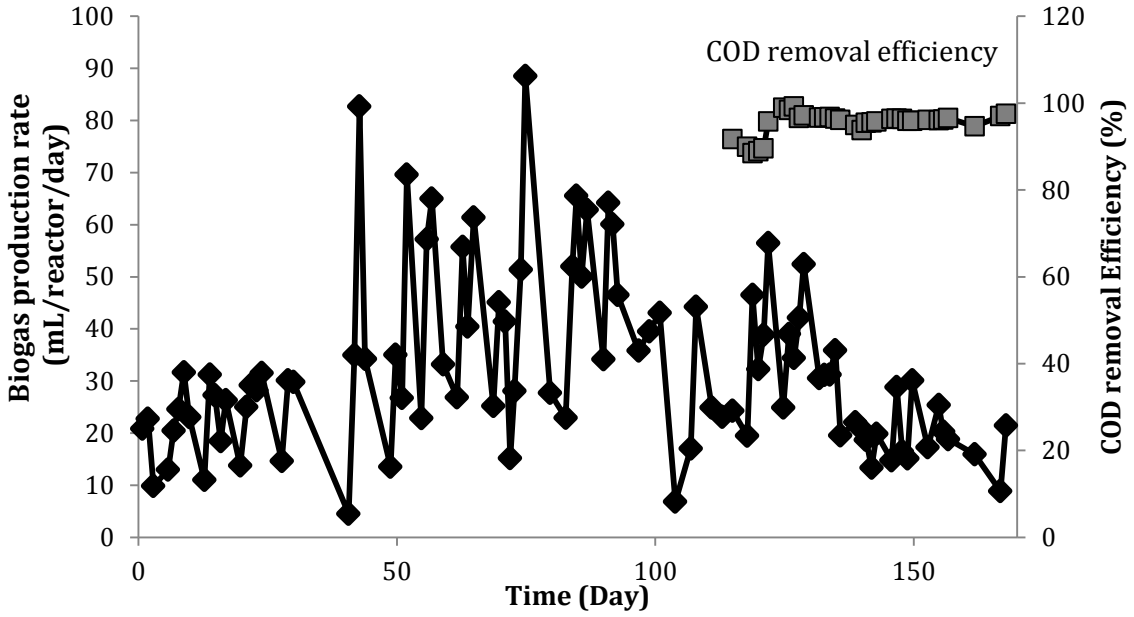

Figure 21: Biogas production rate and COD removal efficiency for 170 days

COD removal efficiencies were in the range from 88 to 98% (Fig. 20). The relative high COD removal efficiencies achieved can be related to two factors. The influent COD had a significant amount of readily biodegraded COD. On the other hand, the membrane is able to retain all particulates and colloidal matters inside the reactor, which clearly contributes to improve the quality of the effluent. Average biogas generation of the reactor was 26.74 ± 14.04 mL/reactor/hr, with a methane composition of about 38.14%

Phosphorus concentration in AnMBR

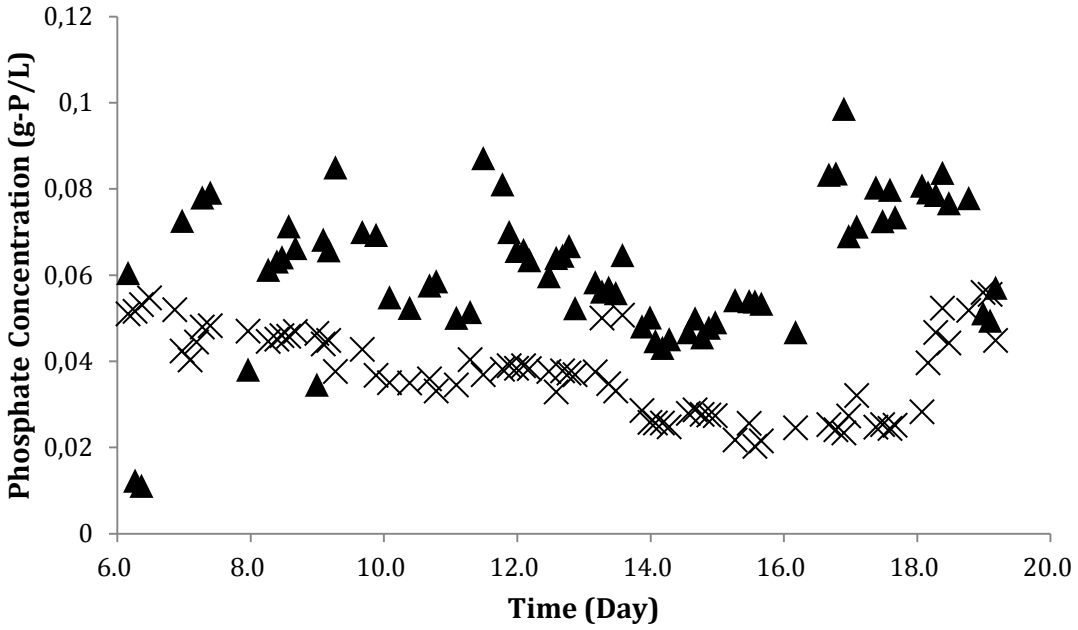

Figure 22: Phosphate concentration from a) BMBR sludge and b) AnMBR permeate

Figure 22 provides an overview of the quality of the effluent of AnMBR in T-P and dissolved phosphate species. Anaerobic digestion does not reduce the mass of P, but it only converts the organic P to the inorganic forms, e.g. phosphate that is soluble in aqueous phase. Phosphate concentration was found to be very high in permeate 74.176 ± 18.57 mg-P/L. Therefore, AnMBR permeate was found to be a source for P-recovery.

P recovery by P-ZS column

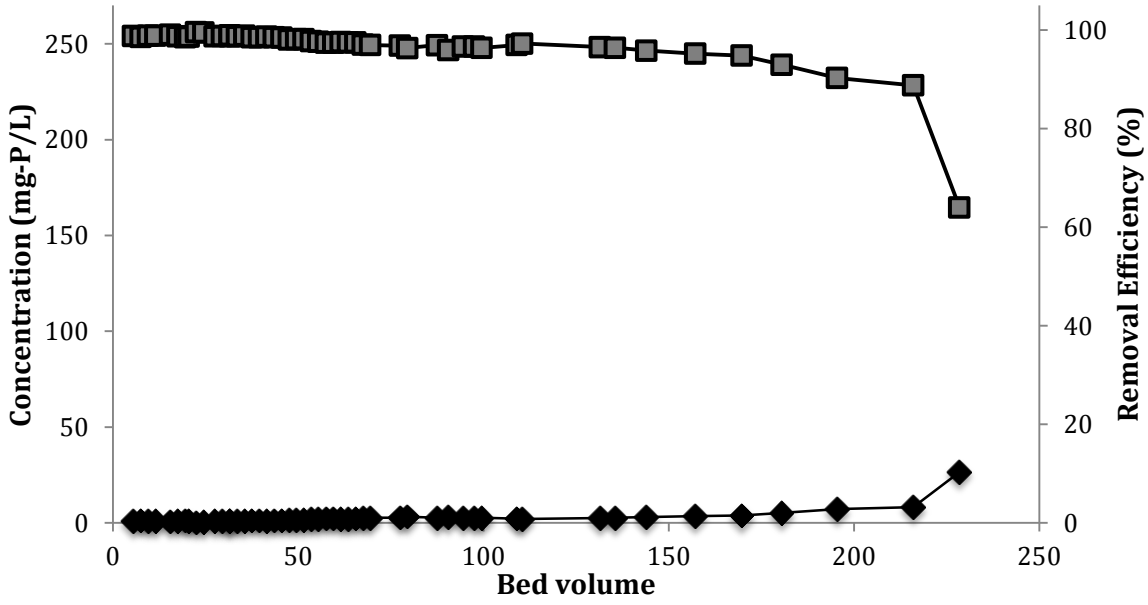

Figure 23: P-ZS breakthrough profile treated AnMBR permeate

AnMBR permeate was pumped into the column pack with P-ZS. Figure 23 shows breakthrough profiles of phosphate. A column test was also performed to determine the breakthrough curve behavior at flow rates of 5 mL/hr to promote P-recovery. The results in chapter 3 confirmed the lower the pH, the more favorable ion-exchange conditions were achieved, therefore pH of permeate was adjusted to 5 before pumped into P-ZS column. Moreover, at pH 5 carbonate species will be in the form of H_2CO_3 which is not in the ion form, therefore we can prevent interference of bicarbonate by adjusting pH. Figure 23 represents the experimental results obtained on P-ZS with the AnMBR permeate feed rates of 5 ml/hr and solution initial concentration of 81 mg P/L. The effluent solution concentration reached to 5% of its feed concentration (the breakthrough points) at 144 BV. Total amount of P that can be removed by ZS was 48.32 mg P/g-ZS, which was higher than that in the groundwater because of pH pretreatment.

Table 8: Breakthrough profile for AnMBR permeate

Constituents	Artificial Groundwater	Groundwater	AnMBR Permeate
P-ZS amount (g)	24.50	3.00	3.00
BV	1088	240	144
Total phosphate adsorbed (mg P)	1065.24	26.02	116
Phosphate adsorbed (mg P/ g P-ZS)	42.12	8.09	38.67
Phosphate adsorbed (mg P/g ZS)	56.65	10.11	48.33

Elution of phosphate

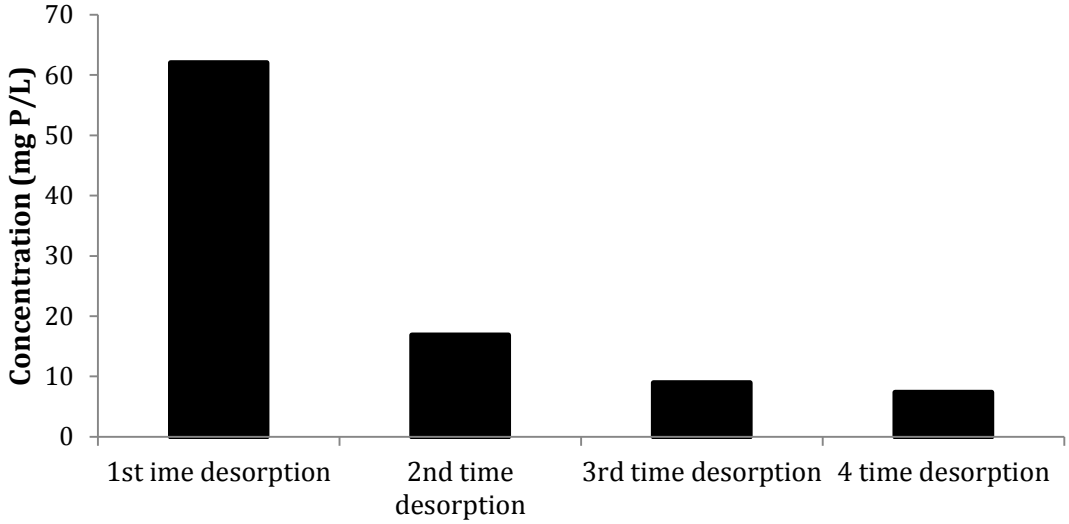

Figure 24: Eluted solutions concentration

Phosphate removed by P-ZS could be eluted with aqueous NaOH. The data discussed in Figure 7 (Chapter 2) has already shown the mechanism that NaOH with pH more than 13 could elute phosphate up to about 85%. Results from elution study also indicate that phosphate removed by ZS is not completely reversible. Therefore, only 25.8 mg P/g ZS can be desorb for the first time. However, for the 2nd, 3rd, and 4th time of repeated elution process, 7.03, 3.73, and 3.05 mg P/g ZS were found (Figure 24). The total amount of phosphate eluted from P-ZS was 39 mg P/ g ZS corresponding to 82.12% of the removed

amount.

Conclusion

Application of anaerobic membrane bioreactor (AnMBR) to treat excess sludge from Baffle membrane bioreactor was successful in term of COD removal (95 ± 2%). However, the main aim for this experiment was to recover high concentration of dissolved phosphate. High concentration of phosphate (74.176 ± 18.57 mg-P/L) was found in the AnMBR permeate. The permeate was pumped into polymer coated zirconium phosphate micelle mesostructure (P-ZS) packed column for phosphorus recovery. The breakthrough occurred at 144 BV corresponding to 48.32 mg P/g ZS. 3 times elution by NaOH showed that 39.68 mg (82.1 %) of phosphate can be recovered. Moreover, acid treatment shows higher dissolution efficiency when pH of the solution was low. Therefore, acid treatment is recommended to dissolute phosphate to soluble form. Using P-ZS can be one of the alternatives for phosphate recovery in water treatment system.

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Chapter 6

Conclusion and Recommendation

The main aim of this research was to investigate the characteristic of "Zirconium Sulfate Micelle Mesostructure (ZS)" and its application to phosphate recovery from several water samples. ZS could remove phosphate in water by an ion-exchange process with high removal capacity as compared to other phosphate adsorbents and ion exchangers. Langmuir equation showed that the maximum ion exchange amount of ZS was 106.65 mg/g-ZS. Sodium Hydroxide (NaOH) with pH more than 13 was used as an eluent, and the elution efficiency was 85%. However, NaOH contributed to the decomposition of the ZS structure after elution process, which led to the non-reusability.

ZS powder has been embedded with polymer in order to prevent the leakage of the breakdown of ZS particles. Moreover, the bigger size of the packed ZS was thought to be easier for the reusability purpose. The newly synthesis ZS material was named "Polymer Coated Zirconium Sulfate Micelle Mesostructure (P-ZS)." It was found that the phosphate removal capacity increased with a decrease in pH. Bicarbonate was the sole interfering anion among the anions tested. The P-ZS could be regenerated at least 50 times without loss of original functionality. A column packed with P-ZS could remove phosphate completely in a phosphate solution including about 10 mg P/L of phosphate up to 1020 and 240 bed volumes, for artificial groundwater and groundwater respectively.

High concentration of phosphate (74.176 ± 18.57 mg-P/L) was found in the Anaerobic membrane bioreactor (AnMBR) permeate. The permeate was pumped into polymer coated zirconium phosphate micelle mesostructure (P-ZS) packed column for phosphorus recovery. The breakthrough occurred at 144 BV corresponding to 48.32 mg P/g ZS. 3 times elution by NaOH showed that 39.68 mg (82.1 %) of phosphate can be recovered.

Therefore, we concluded that ZS was a highly effective ion exchanger for phosphate and enabled the removal of phosphate from water.