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Removal of Phosphorus in Agricultural Run-off Water by Utilization of Lignocellulosic Biomass Filters

Study case: utilization of common reed as an adsorbent

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<p>Fertilizers used on agricultural farms contain a significant amount of phosphorus along with other nutrients, which are essential for crop growth. When it rains, phosphorus can be partially washed away from the farm, leaches into the surrounding ditching system and eventually ends up in lakes, seas, etc., which thus reduces the quality of the farming soil as well as contributes to the eutrophication phenomenon.</p> <p>The use of filters made from different types of lignocellulosic biomass modified with certain chemicals that can capture this nutrient before the run-off water reaches the ditching system would help solving this issue. In addition, this biomass and phosphorus containing filter material can be recycled back to the field to enhance the soil quality. Furthermore, the modification of biomass should be inexpensive and free from harmful chemicals.</p> <p>In this thesis, common reed, an abundant biomass in Finland, was first quaternized with modifying chemicals, including urea, chlorocholine chloride and imidazole. After that, it was employed to test its phosphorus uptake capacity. From the results, it seems that common reed naturally releases an amount of phosphorus into the water. The use of chemicals to integrate this biomass seems to even increase the phosphorus concentration rather than mitigation. However, this could be due to the experimental errors, and since the number of the conducted experiments was not sufficient, proper conclusion cannot be made.</p>	
Keywords	phosphorus removal, biomass filters, common reeds, adsorption, quaternization

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List of Abbreviation

DNA	Deoxyribonucleic Acid
RNA	Ribonucleic Acid
ATP	Adenosine Triphosphate
EBPR	Enhanced Biological Phosphorus Removal
EPI	Epichlorohydrin
EDA	Ethylenediamine
DMA	Dimethylamine
TEA	Triethylamine
DMF	<i>N,N</i> -dimethylformamide
MP-AES	Microwave Plasma Atomic Emission Spectroscopy
FAAS	Flame Atomic Absorption Spectroscopy
DES	Deep Eutectic Solvent

1 Introduction

Phosphorus, together with nitrogen and potassium, are the three most essential macronutrients for plants' flourish. Specifically, phosphorus compounds are a constituent in DNA, RNA, ATP as well as phospholipids, the molecules that make up every cell's membrane in a plant. A deficiency in either of these nutrients would, thus, result in a slow crop growth rate, which is undesired by the farmers. Therefore, fertilizers, which provide the necessary nourishments under available forms that plants can easily absorb, are widely utilized on agricultural farms to overcome this issue (HowStuffWorks, 2000).

However, the use of fertilizers seems to lead to another issue. As it rains, the nutrients in the fertilized soil can be partially washed away from the fields, leach into the surrounding ditching system and eventually end up in the sea. Thus, the soil's quality will gradually deteriorate. In addition, excess nutrients, noticeably phosphorus and nitrogen, released into aquatic ecosystem will accelerate the rate of cultural eutrophication (Carpenter et al., 1998, cited in Chislock et al., 2013), a phenomenon that has become a major concern in recent years due to its consequences. Therefore, a solution with proper efficiency and a reasonable financial cost to solve this leaching issue is essential.

Up to now, various technologies have been applied to control the phosphorus discharged from different sources, including the agricultural activities mentioned above. They are categorized into three major groups, namely chemical, physical and biological methods. Adsorption, one of the chemical approaches, has been proven to be a feasible alternative to mitigate phosphorus leach from the agricultural fields. Specifically, adsorbents made from certain types of biomass, after going under a modification process, can be used to adsorb phosphorus before the run-off water reaches the ditching system. Later, the post product, which is a mixture of biomass and the nutrients can be recycled back to the field to enhance the soil quality.

In this thesis, the potential of phosphorus removal by utilization of quaternized common reeds as adsorbents is studied. In more detail, in the first section, different available methods of biomass modifications are summarized. Additionally, quaternization method, which was used in this study will be focused on. Moreover, relevant issues including

adsorption definitions, eutrophication phenomenon, and current technologies in phosphorus removal will be discussed. In the second section, the preparation and procedure of experiments will be provided and brief conclusion on the adsorption efficiency will be drawn from the recorded result data.

2 Literature review

2.1 Eutrophication phenomenon

2.1.1 Definition

Photosynthesis marine organisms need sunlight, oxygen, carbon, nitrogen, phosphorus and other essential elements in different ratios to produce new organic molecules to maintain their life. An insufficient provision of either of these components, i.e. limiting factors, will restrict the growth of those species, and such state is called limiting condition. On the other hand, when at least a limiting factor is abundant in amount, for example, excessive nutrients (nitrogen and phosphorus), the organisms will thrive quickly until the new limiting condition is met, this accelerated growth is characterized as eutrophication (National Research Council Staff et al., 2000).

2.1.2 Consequences

The most noticeable consequence due to nutrient enrichment is the significant increase in phytoplankton biomass productivity. Although the blooms provide dissolved oxygen during the day through photosynthesis, they demand dissolved oxygen for their respiration during night hours. Therefore, the oxygen saturation in water is reduced. Moreover, dead phytoplankton cells settle to the bottom of the lakes, oceans and are consumed by bacteria, which further contribute to oxygen depletion. At some point, the oxygen concentration cannot meet the standards to sustain a healthy aquatic environment, resulting in hypoxia or anoxia phenomenon (Wikipedia, 2017). Hypoxia occurs when the oxygen is still available, but its level is smaller or equal to 2 mg/L whereas anoxia is the condition when oxygen is completely absent.

Hypoxia and anoxia interrupt the standard living conditions of many marine organisms, for instance, commercially important fishes, invertebrates and benthic species, thus restricting their normal growth or even causing death to them. The depletion of dead bodies creates an unpleasant odour as well as reduces the quality and clarity of water, which

affect activities in the area, such as swimming, boating, etc. In addition, hypoxia causes changes in the structure of benthic community. Specifically, there is a shift from the dominance of large long-lived species to the dominance of smaller short-lived species.



Figure 1. Dead Salmon (Ableman, 2010)

Other considerable consequences to be named are degradation of coral reefs and submerged vegetation and harmful algal blooms. As major coral reefs grow in nutrient deficiency, nutrient enrichment discourages their development while encourages the blooms of algae. Thus, there will be a shift from corals to algal turfs and macroalgae, reducing coral diversity. Also, among the algal blooms, certain types of them produce toxic chemicals, and these blooms could cause a mass mortality of wild and farmed fish species (Figure 1), seabirds and other mammals. Furthermore, consumption of those marine products where the harmful blooms take place could affect human health (National Research Council Staff et al., 2000).

2.2 Current phosphorus removal technologies

To prevent the consequences due to the presence phosphorus in wastewater, many approaches have been carried out to minimize this nutrient. These technologies can be categorized as chemical methods (precipitation, anion exchange and adsorption), biological methods (constructed wetlands and enhanced biological phosphorus removal), and physical methods (filtration, reverse osmosis). A brief introduction to the above alternatives including their pros and cons will be provided in this section.

2.2.1 Chemical methods

2.2.1.1 *Precipitation*

In chemical precipitation method, metal salts of calcium, aluminium or iron are commonly utilized as the coagulating reagents. These coagulants neutralize the phosphorus compounds, forming precipitation (Figure 2) (Tchobanoglous et al., 2003, cited in Strom, 2006). The coagulated particles will form a floc during flocculation and settle to the bottom. Phosphorus, thus, can be separated from the effluent.

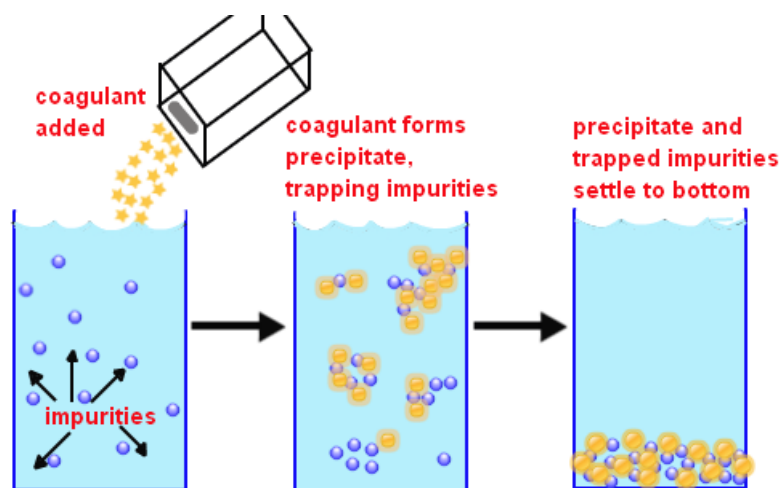
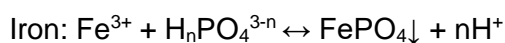
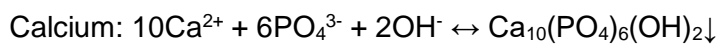


Figure 2. Coagulation (TutorVista, n.d.)

The reactions are presented below:



This technology has been employed widely in commercial scale for a long time. Nevertheless, the major disadvantages of such process are the generation of additional sludge, especially in the case of calcium application (Tchobanoglous et al., 2003, cited in Strom, 2006), the high cost of the metal chemicals, the need for further neutralization of the effluent and the insufficiency when the concentrate of phosphate is low (Kumar et al., 2010, Mallampati and Valiyaveetil, 2013 and Zhang et al., 2011, cited in Nguyen et al., 2014).

2.2.1.2 *Anion exchange*

Anion exchange, one type of ion exchange, is the process of removing the anions in the incoming solution by replacing them with the provided similarly-charged anions. The exchange medium is a natural or synthetic solid resin loaded with a stationary functional acid group and anions, most often Cl^- , which can move freely (Figure 3). These mobile anions are then exchanged with phosphate anions in the influent due to their smaller affinity towards the functional acid group. The transference takes place until the resin is used up.

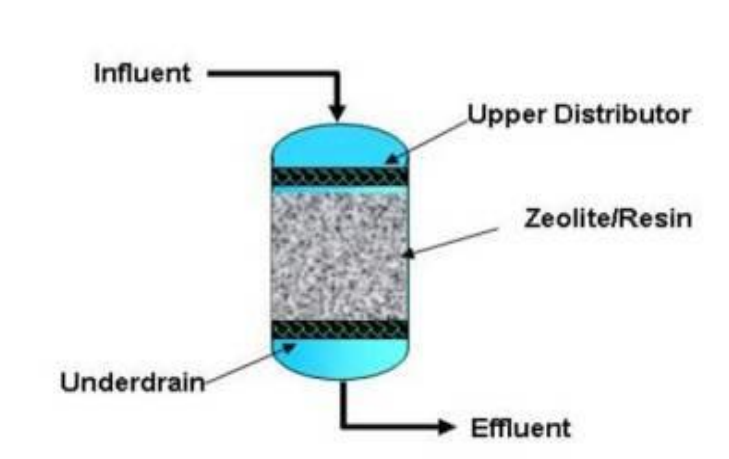


Figure 3. Typical ion exchange configuration (US EPA, n.d.)

At this point, a saturated solution of the exchanged anions (Cl^-) can be used to wash the resin so that it returns to initial condition, ready for the next run. One possible issue with this method is fouling due to accumulation of minerals and chemicals, hence pretreatment should be carried out to prevent such problem (US EPA, n.d.).

2.2.1.3 *Adsorption*

This section is treated in more details in part 2.3 of the thesis.

2.2.2 Biological methods

2.2.2.1 *Constructed wetlands*

Constructed wetland is a relatively simple, location feasible and cost effective process that has been utilized to treat wastewater for a long time. Specifically, in this method, aquatic plants are cultivated in treatment ponds, through which the wastewater will be

introduced. The roots of these plants behave as the biological filters, which will capture the nutrients in the wastewater when it flows horizontally from one end to the other end of the pond, leaving a cleaner output flow that can be disposed safely or used for other purposes. The phosphorus is then consumed by these plants for their photosynthesis (Figure 4) (de-Bashan and Bashan, 2004).

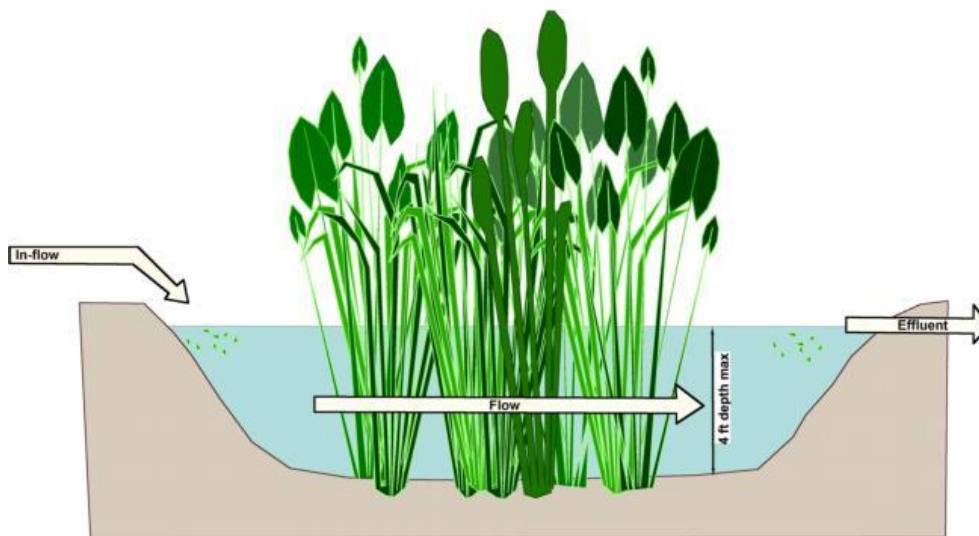


Figure 4. Surface flow wetland designed for treating nutrient rich runoff from agricultural production areas (White, 2012)

A wide range of aquatic plants have been researched for their ability to remove phosphorus, for instance duckweeds, reeds, water hyacinth, etc. In their published article, de-Bashan and Bashan (2004) summarized different plant types that have been utilized for this purpose. These plants are usually replaced periodically to avoid their degradation that might lead to re-release of phosphorus.

2.2.2.2 *Enhanced biological phosphorus removal*

Enhanced biological phosphorus removal (EBPR) has shown better performance compared to constructed wetlands in removing phosphorus. This method makes use of the bacteria residing in the sludge from previous treatment cycle and consists of two stages, anaerobic followed by aerobic (Figure 5).

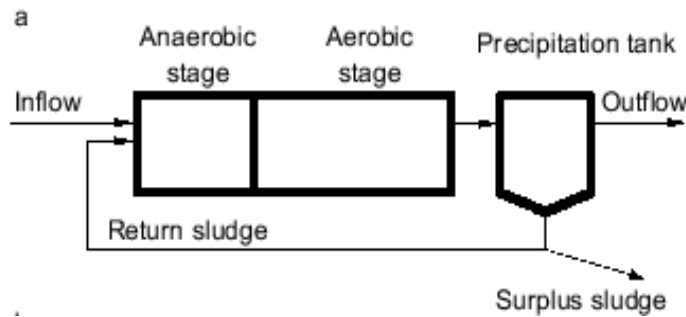


Figure 5. Basic concept of anaerobic-aerobic process for EBPR (Adapted from Mino, 1999)

When the carbon rich wastewater flow is introduced to the anaerobic phase, the microbes, using their stored polyphosphate as a source of energy, will ingest the organic matters and carbon sources in the wastewater to produce the storage biopolymers, which will be stored in their cells. At the same time, the derived soluble orthophosphate is released back into the environment.

In contrast, in aerobic phase, the produced biopolymers will act as the energy and carbon source, which enables the bacteria to take up the orthophosphate at an even greater amount compared to which they released in the previous phase and synthesize them back to polyphosphate. As a result, the phosphorus in the wastewater is consumed, thus removed from the stream. The post product is a phosphate enriched activated sludge, which later can be disposed or partly recycled for the next cycle. In some cases, nutrients, mainly acetate and sugar are added to this step as an extra carbon source for the microbes to utilize (de-Bashan and Bashan, 2004).

2.2.3 Physical methods

2.2.3.1 *Filtration*

Microfiltration and ultrafiltration are membrane filtration processes that are commonly employed to eliminate particulates (suspended solids, colloids) and microbial contaminants (bacteria, viruses). Phosphorus is normally removed by filtration after coagulation and flocculation process, in which coagulants (iron or aluminum ions) are used to form agglomeration, and hence it is usually called physical-chemical method. The stages within the method is illustrated in Figure 6.

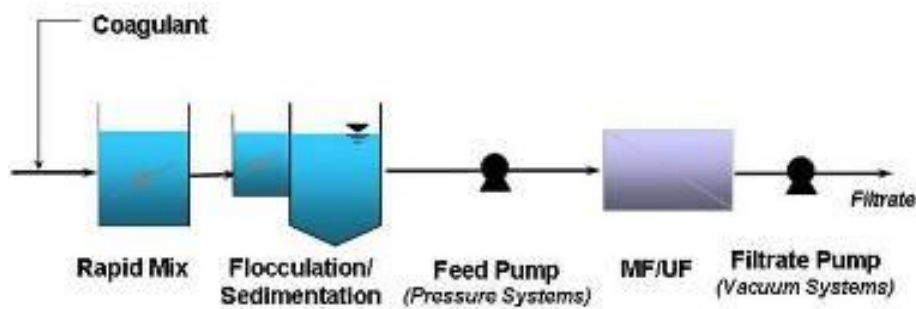


Figure 6. Typical membrane filtration configuration (US EPA, n.d.)

The pore size of microfiltration's membrane is between 0.1 to 0.5 μm while that of ultra-filtration's is between 0.01 to 0.1 μm . Both can be operated under positive pressure (3 to 40 psi) or negative pressure (-3 to -12 psi). The pressure difference ensures the water is pushed through the membrane where contaminants are captured, leaving behind the filtrate stream. These retained contaminants can be removed by backwashing stage (US EPA, n.d.).

2.2.3.2 Reverse Osmosis

Reverse Osmosis is a membrane technology whose principle is based on the natural tendency to maintain balance. Specifically, when two solutions containing two different solute concentrations come in contact at a fixed permeable membrane, the one with lower concentration will flow through the membrane to the other side, which has higher concentration. Gradually, a difference in fluid height between two sides of the membrane, i.e. osmosis pressure, is established. This phenomenon is called osmosis.

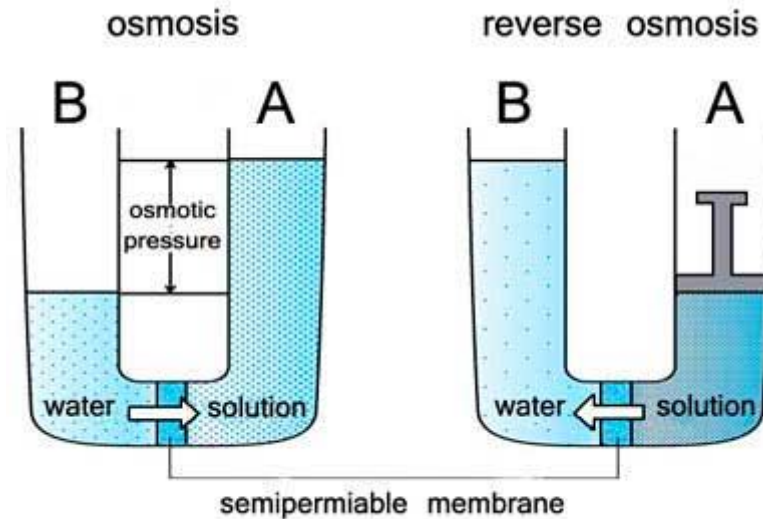


Figure 7. Reverse osmosis (Zeetu, 2017)

In contrast to osmosis, reverse osmosis only occurs when external pressure is applied (Figure 7). Additionally, this pressure must overcome the osmosis pressure mentioned above to reverse the osmosis process. At the end of the procedure, the water in the column with higher dissolved solid content is pushed to the other side, leaving behind the solutes including phosphorus that cannot go through the membrane (Lenntech, n.d.)

2.3 Adsorption

2.3.1 Definition

Adsorption is an exothermic transfer process in which the molecules or ions from a fluid phase (gas or liquid) adhere and accumulate onto a solid or liquid surface. Thus, they are removed from the fluid. In the context of this thesis, adsorption is ions removal from aqueous solution onto a solid surface (biomass).

The substance that allows the molecules or ions to attach to its surface is called the adsorbent. Whereas the substance that is adsorbed is called adsorbate.

The reverse process, through which the molecules are returned into the aqueous solution by adjustment in concentration, temperature or pH of the liquid phase, is called desorption (Worch, 2012).

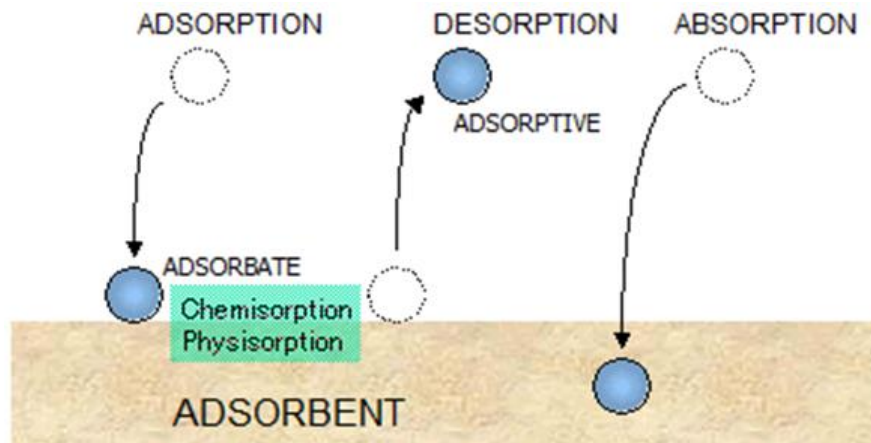


Figure 8. Adsorption state (MicrotracBEL, n.d.)

The term adsorption should not be confused with absorption, which is another type of sorption. In absorption, the incoming fluid is completely dissolved by a solid or liquid absorbent whereas in adsorption, the phenomenon takes place at the surface of the material (Figure 8).

2.3.2 Types of adsorption

Adsorption is classified into physical adsorption (physisorption) or chemical adsorption (chemisorption) based on the value of adsorption enthalpy.

In physisorption, the forces between adsorbate and adsorbent are weak van der Waals forces of attraction. The enthalpy in this case is relatively low, normally <50 kJ/mol (Worch, 2012). In addition, physisorption takes place at low temperature and results in multilayer of adsorbate on the surface of the adsorbent (Chemistry learning, 2009).

On the other hand, in chemisorption, the driving forces are chemical forces (chemical bonds). The enthalpy in this case is high (>50 kJ/mol) (Worch, 2012). Moreover, chemisorption occurs at any temperature and forms unilayer of adsorbate on the adsorbent (Chemistry learning, 2009).

2.3.3 Adsorption process theory

The adsorption theory explains the relations between the (adsorbent) loading q , which is the amount of adsorbate uptake per mass unit of adsorbent, and the process parameters.

It comprises three constituents: adsorption equilibrium, adsorption kinetics and adsorption dynamics. Among these components, the adsorption equilibrium plays a prime role that leads to the determination of the other two elements' models (Worch, 2012).

The adsorption equilibrium represents the dependence of loading on adsorbate concentration and temperature or merely concentration (adsorption isotherm):

$$q = f(c, T) \text{ or } q = f(c), T = \text{constant}$$

Equilibrium data is essential in selecting a suitable adsorbent, recognizing the adsorption ability of the water pollutant or designing adsorbents.

The adsorption kinetics describes the dependence of loading on contacting time:

$$q = f(t)$$

The adsorption dynamics describes the dependence of loading on both contacting time and space:

$$q = f(t, z)$$

2.3.4 Types of adsorbents

Up to now, there has been extensive use of adsorbents in many practical applications. The selection of a particular adsorbent mainly depends on the user's desired specific properties including density, porosity, external and internal surface area, pore-size distribution and surface chemistry, which vary among different substances. In the field of waste water removal, adsorbents are categorized into three major groups according to their origins: engineered adsorbents, natural and low cost adsorbents, and geosorbents.

Engineered adsorbents are produced under a strict process. They usually demonstrate a higher adsorption efficiency with constant properties compared to other two types. In addition, their provided surface area is much larger, which enhances the transfer process. Activated carbon (Figure 9), polymeric and oxidic adsorbents, synthetic zeolites belong to this group. However, one drawback of this type is its high cost.



Figure 9. Activated carbon (Ravedave, 2006)

Natural and low cost adsorbents have been studied extensively in recent years due to their appealing low price. They are normally derived from nature, agricultural wastes or industrial by products. The materials can be used either directly, or after going under some modification process to change the intrinsic characteristics. For example, natural clay, wood, sawdust, straw, fly ash, and sludge belong to this group. One disadvantage of natural adsorbents is their smaller surface area compared to engineered adsorbents. This group of adsorbent is the main interest in this study.



Figure 10. Sawdust made with hand saw (Rasbak, 2009)



Figure 11. Alluvial soil (Anon., n.d.)

Geosorbents usually comprise mineral and organic constituents. The mineral fraction will adsorb ionic species while the organic component will adsorb organic species. Unlike engineered and natural low cost adsorbents, geosorbents cannot be modified as desired and thus should be used as they are. An example of this is the bank filtration in which the soil is considered a geosorbent (Worch, 2012).

2.4 Current researches on the phosphorus removal by lignocellulosic biomass adsorption

2.4.1 Biomass, the potential material

Lignocellulosic biomass is a source of raw material that has a wide range of utility. It is categorized into 3 major groups:

- Virgin biomass is those that can be found growing in nature (common reeds, bushes, etc.).
- Waste biomass is defined as the byproduct of agricultural activities (sugarcane bagasse, wheat stalks, etc.) or of forestry (sawdust, wood residues, etc.).
- Energy crops are crops that produce products to be later used as raw material for bio-fuels production purposes (switch grasses, elephant grass, etc.).

Lignocellulosic biomass is composed of carbohydrate polymers (cellulose and hemicellulose), which are chains of different sugar monomers (5C and 6C). These polymers are

strongly attached to an aromatic polymer, so called lignin (Wikipedia, 2017). Since cellulose and hemicellulose structures have many hydroxyl groups, they can easily get involved in condensation, polymerization reactions to form other functional polymers that can be later employed as an anion exchange resin (Varma, Kennedy and Galgali, 2004, cited in Xu et al., 2010b). The production of resin from a low-cost and abundant source might help reduce the cost of phosphorus treatment (Liu et al., 2012, cited in Nguyen et al., 2014).

This modification process is essential since the original lignocellulosic biomass demonstrates an extremely low phosphorus removal efficiency, which is because most available functional groups are negatively charged (-OH, -COOH), whereas the number of positively charged functional groups on the surface of the materials is limited.

2.4.2 Different biomass modification methods

Different approaches have been applied to modify the lignocellulosic biomass. They can be classified into three major groups: activation (thermal, chemical, or steam), cationization (metal loading, quaternization), and anionization (sulfate surface coating). Among these, cationization is the method that is mostly applied.

2.4.2.1 *Cationization*

2.4.2.1.1 Metal loading

In this method, before adding the metal salts, the biomass is usually grafted with more carboxyl groups or treated with basic solutions to maximize its metal sorption ability. The carboxyl groups grafting reaction can be either esterification with succinic anhydride, oxidation with sodium chlorite or etherification with monochloroacetic acid. On the other hand, in the base treatment process (saponification), the base could change the ester groups in the biomass to carboxylate or alternatively break the ester bonds to form more hydroxyl groups (Nguyen et al., 2014).

The metal salts for loading vary, including Fe^{2+} , Fe^{3+} , Cu^{2+} , Zr^{4+} , La^{3+} , etc. The adsorption uptake capacity studied also varies depending on the metal, the lignocellulosic biomass materials as well as the operating parameters used. Nguyen et al. (2014) summarized a list of current studies using this modification method in their review. It is shown that the maximum adsorption capacity (q_{max}) in the studies was ranged from 5 to 174.68 mg/g.

Biswas et al. (2008) conducted the most efficient research by using orange waste gel pretreated with base $\text{Ca}(\text{OH})_2$ and loaded with $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, the value of which was 175 mg/g. In the research conducted by Carvalho et al. (2011), bagasse fibers were first etherificated using monochloroacetic acid and then loaded with FeCl_2 , and the phosphorus uptake capacity was 152 mg/g.

Though the method exhibits good outcome, it is not a preferable alternative in this thesis study. This is due to the possible leakage of metals during operation. Moreover, since the adsorbents are later deposited back onto the farms to recycle the phosphorus, the accumulation of metal-containing post-product might cause an extra burden to the site soil.

2.4.2.1.2 Quaternization

Modification of biomass through quaternization can be done by two alternative pathways, and each of which involves two stages: either converting the material into epoxy cellulose, followed by grafting with quaternizing ammonium compounds, or alternatively creating aminated intermediate, followed by creating aminated material.

In the first pathway, a cross-linking agent will be first used to convert the material to epoxy cellulose. This step is essential since cellulose and quaternary ammonium compounds have relatively poor interactivity towards each other. The cross-linking agents that have been employed include epichlorohydrin (EPI), choline chloride derivative, *N*-(3-chloro-2-hydroxypropyl), and ethylenediamine (EDA).

After the epoxy cellulose is formed, it is grafted with quaternizing ammonium compounds to create an exchange resin. Ammonium compounds could be chloro-2-hydroxypropyltrimethylammonium chloride, dimethylamine (DMA), triethylamine (TEA), or urea. This step is done with the presence of a solvent, for instance *N,N*-dimethylformamide (DMF) or methanol, as the cross-linking agent and the ammonium compound do not dissolve each other. Karachalios and Wazne (n.d.) utilized imidazole and Xu et al. (2010a) utilized pyridine to open the ring of epoxide group in the base medium.

In the second pathway, the cross-linking agents, instead of reacting with the cellulose at the beginning, are mixed with ammonium compounds to form a so-called aminated intermediate. After that, this intermediate will be grafted onto the cellulose (Nguyen et al., 2014).

A summary of different types of quaternized biomass which had been used to remove phosphorus shows that a significant amount of phosphorus can be adsorbed by this method. Specifically, the highest uptake capacity was of coconut shell fibers modified with 2-hydroxypropyltrimethylammonium chloride (De Lima et al., 2012). Similarly, wheat residue treated with EPI, DMF, EDA and TEA in the study conducted by Xu et al. (2010b) exhibited a capacity of 171 mg/g.

However, this method, in some aspects, is a concern to the environment quality because hazardous agents and solvents are used in the process. Therefore, Karachalios and Wazne (n.d.) proposed the use of urea and chlorocholine chloride derivative in imidazole, which is an environmental friendly and low cost approach, in their study. This option is the most feasible method in the context of this thesis, concerning the agricultural farming condition in real application. Therefore, a study following this pathway on another lignocellulosic biomass type (common reed) instead of the original wood residues will be carried out in this thesis.

2.4.2.2 *Activation and Anionization*

Activation is defined as the process of carbonization or calcination of organic matters either by applying high temperature, steam (thermal and steam activation) or by employing inorganic chemicals. This method is ideal for biomass types that have high porous structure and high content of CaCO_3 . However, it yields certain drawbacks, noticeably the high energy consumption, the requirement for its specialized equipment and the possibility to contaminate the environment. These issues make it less attractive for usage.

Anionization (sulfate surface coating) is another modification approach. Unfortunately, this method has not been studied in the case of lignocellulosic biomass, but only on the traditional adsorbents. Thus, its application is limited in this context (Nguyen et al., 2014).

2.5 Microwave Plasma Atomic Emission Spectroscopy (MP-AES)

2.5.1 Working principle

In this thesis, the concentration of the phosphorus solution after the treatment was analyzed using Microwave Plasma Atomic Emission Spectroscopy (MP-AES). MP-AES is an atomic emission technique which is used to identify an analyte element by its electromagnetic spectrum. Its working principle is relatively simple and can be illustrated in the figure below:

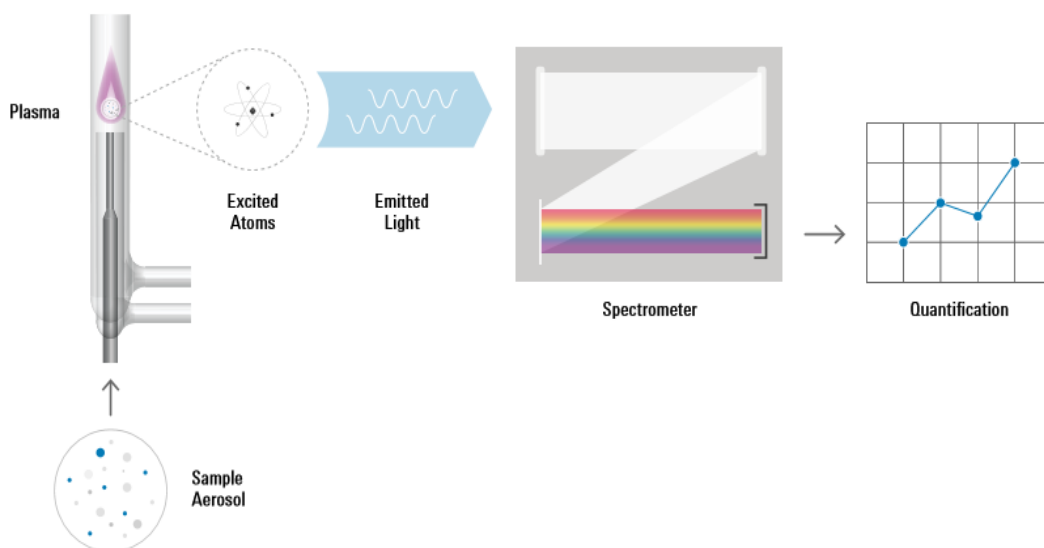


Figure 12. Schematic diagram of a microwave plasma atomic emission spectrometer (Agilent Technologies, 2016)

At the beginning, a microwave energy is used to create a plasma from nitrogen, which is drawn either from the ambient air or from the cylinders. This microwave plasma acts as a perfect excitation source for atomic emission. After that, the analyte liquid sample is turned into an aerosol by the nebulizer and a spray chamber. This aerosol is then introduced into the center of the created plasma, where it will be dried, decompose and atomized. Once an atom of a specific element is excited, it will emit light in a characteristic pattern of wavelength, i.e. an emission spectrum, as it returns to the ground state. The light is led to a fast scanning monochromator and imaged on a CCD detector. At the end, by comparing the emitted spectrum with a known concentration of the element, i.e. the calibration curve that is drawn from the standard solutions, one can identify the concentration of the test sample (Agilent Technologies, 2016).

2.5.2 Advantages of MP-AES technique

MP-AES technique has many advantages over its competitor, FAAS (Flame Atomic Absorption Spectroscopy), which explains the gradual shift to its use in analytical tasks. These pros would include performance, safety, cost and operation convenience.

MP-AES has higher sensitivity with detection limits down to ppb and it is also possible to analyze elements with high detection limit, for example phosphorus. This larger detective range would reduce the dilution tasks and thus, save time. Additionally, the work is done faster when performing multi-elements analysis and the interference of unwanted chemical compounds is reduced thanks to the high operating temperature of the plasma.

The instrument can use nitrogen extracted straight from the air instead of using acetylene and nitrous oxide as in FAAS. This replacement with flammable gases diminishes the probability of gas leakage or fire in case of improperly storage or handling. Moreover, there is no more need for changing different burners to determine full range of different analyte elements, which enhances safety level.

In elemental analysis, the greatest cost is due to the use of gas cylinders. MP-AES eliminates this limiting factor and thus becomes a cheaper option compared to FAAS. In addition, the preparation step is simpler and the machine is relatively easy to operate, which requires only a short training period. Also, since only electricity is needed, it is more flexible regarding operating location. In other words, MP-AES instrument can be put at the sampling location instead of a conventional laboratory (Agilent Technologies, 2016).

3 Experiment

3.1 Materials

The common reeds used in this thesis were taken at a sea site. After being collected, they were cut into a smaller size (Figure 13) from an original length of 2-2.5 meters, washed and air dried. Later, they were dried at 110°C in the oven for approximately 7 hours to discard the remaining moisture content.



Figure 13. Common reed collected

After that, they were shredded in a mechanical cutter and sieved to attain the size of 0.25-0.5 mm (Figure 14) for the experiments.

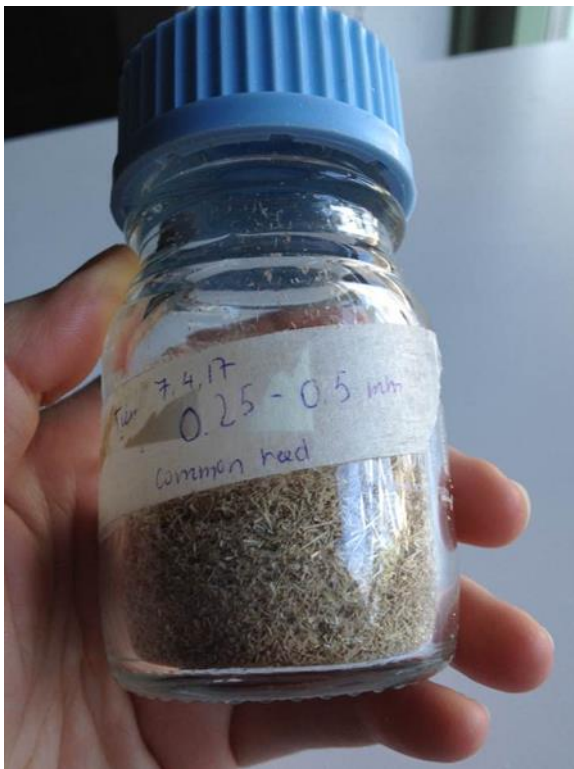


Figure 14. Sieved size 0.25-0.5 mm

The modification process for the common reed was done according to the preparation conducted by Karachalios and Wazne (n.d.). First, the mixture of Chlorocholine chloride

and urea (with mole ratio of Chlorocholine chloride: urea = 1:2) was heated on a hot plate at 75 °C for approximately 30 minutes. This would produce a so-called deep eutectic solvent (DES), which has a lower melting point compared to its individual components (choline at 302 °C and urea at 133 °C). Due to its safety, efficiency and low cost, DES is a preferable solvent in different applications.



Figure 15. Quaternization set-up



Figure 16. Quaternization product mixture

After that, 10 mL of the above solvent was added to 0.2 g of the prepared common reed in the presence of 0.784 g imidazole. The mixture was heated at 150°C in a heating mantle for approximately 3 hours, then let cool down (Figure 15 and Figure 16). Later, the modified common reed was washed with distilled water to remove the redundant chemicals, ready to be used for the experiments.

Maintaining the temperature at a constant during the quaternization process using the heating mantle was challenging. Specifically, the temperature fluctuated between 135-165°C in this experiment. This issue could have been improved by using an oil bath instead of the heating mantle as this would keep the surrounding temperature at a more stable value.

Moreover, due to the small size of the biomass and the viscosity of the modifying chemicals, it was difficult to completely separate the common reed and the redundant chemicals by merely washing with distilled water, which might lead to an unexpected adsorption experimental result. To solve this issue, the common reed could have been placed in a thimble or filter before being dipped in the modifying solution.

3.2 Phosphate solution preparation

$(\text{NH}_4)_2\text{H}_2\text{PO}_4$ ($M = 115 \text{ g/mol}$) was used to prepare phosphate containing solutions used in the thesis work.

In total, 3 solutions with concentration of 25 mg/L, 50 mg/L and 100 mg/L were prepared and used as standards for the MP-AES instrument. Additionally, a solution with concentration of 150 mg/L was prepared and used as the test sample.

3.3 Procedure

In each of the test, a dose of 0.1g adsorbent was added to 50 mL solution in a beaker. After that, the mixture was stirred on a plate over a period of 90 minutes. Then, the mixture was vacuum filtered to eliminate the biomass portion, leaving the liquid for MP-AES analysis.

No	Adsorbent Type	Initial Concentration (mg/L)
1	Unmodified	0 (distilled water)
2	Unmodified	150
3	Modified	150

Table 1. Experiments

The first test was done to check whether common reed would naturally release a certain amount of phosphorus into water. The second test was done to study the adsorption ability of original/ unmodified common reed. And the last test was done to study adsorption ability of modified common reed.

4 Results

The MP-AES used the 213.618 nm wavelength for the analysis. The standards' intensities (Table 2) were used to get the calibration curve (Calibration error 5%).

Standards	Method Concentration (mg/L)	Intensity
Blank	0	-0.23
Standard 1	25	1794.76
Standard 2	50	3389.55
Standard 3	100	6658.04

Table 2. Standards result

The calibration curve is presented in Figure 17 below:

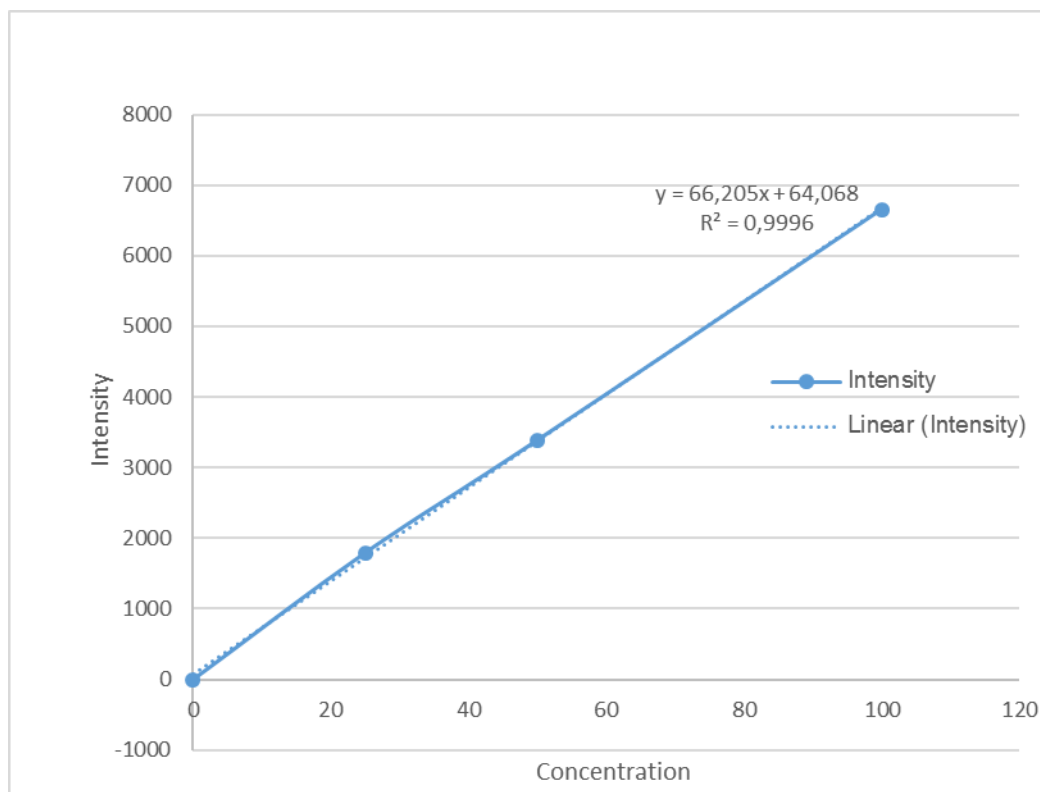


Figure 17. Calibration curve

The solutions with initial concentration of 150 mg/L were diluted 10 times to get the concentration of 15 mg/L, which fit in the calibration range. The intensities of the biomass samples recorded are given in Table 3.

No	Adsorbent type	Initial Concentration (mg/L)	Intensity
1	Unmodified	0 (distilled water)	340.15
2	Unmodified	150	1041.12
3	Modified	150	1304.34

Table 3. Samples' intensities

From these intensities and the linearity equation drawn from Figure 17, the concentrations of the samples were calculated and the result is given in Table 4 (the concentrations of the diluted solutions were multiplied with 10 to get their real values).

No	Adsorbent type	Initial Concentration (mg/L)	Final Concentration (mg/L)
1	Unmodified	0 (distilled water)	4.17
2	Unmodified	150	147.58
3	Modified	150	187.34

Table 4. Samples' concentrations

5 Conclusion

From the results, it seems that common reeds naturally release an amount of phosphorus into the water. This is in accordance with the results obtained from the previous similar experiments.

The final concentration of unmodified material using initial concentration of 150 mg/L shows a slight amount of adsorbed phosphorus. However, this might be a result of experimental error rather than an actual adsorption since natural common reed would release phosphorus into the water. Without doing replicates, it is impossible to make a proper conclusion on this.

The use of chemicals to integrate the common reeds seems to even increase the phosphorus concentration rather than mitigation. But again, similar to above, proper conclusion cannot be made based on only one measurement. One possible way to solve this issue is to have 5-8 replicates for each of the above experiment to reduce the experimental errors and have more reliable results.

In conclusion, the results obtained were not as good as expected due to certain issues, i.e. temperature control, biomass separation, data analysis, which were mentioned in the previous sections. To overcome these limitations, in the future, the proposed solutions should be taken into consideration when similar experimental process is carried out.

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