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PHOSPHORUS REMOVAL FROM WATER USING ALUMINUM BASED WATER TREATMENT RESIDUAL MATERIAL

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<p>Abstract</p> <p>The problem of lake eutrophication is a phenomenon observed around the World. A large number of nutrients enter water body due to both natural environmental factors and human activities, and gradually changing water lakes from poor nutrient status to high productivity in the eutrophic state.</p> <p>In this thesis, aluminium sludge from the flocculation process (Kuopion Vesi Oy) was used as a low-cost adsorbent for phosphorous removal from lake water. Adsorption kinetic tests were conducted to analyse the adsorbent capability for phosphorous removal from the aquatic solution under various conditions. Experiments were carried out in the lab-scale, and the effect of adsorbent dose, the initial concentration of phosphorus and solution pH on phosphorus process efficiency was investigated.</p>			
Keywords			
Eutrophication, aluminium sludge, phosphorus, nitrogen, adsorption			

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1 INTRODUCTION

The formation and evolution of lakes are not only influenced by the natural environmental factors and changes of the river basin but also affected by human activities. The problem of lake eutrophication is a phenomenon observed around the World. A large number of nutrients enter water body and gradually changing water lakes from poor nutrient status to high productivity in the eutrophic state. With the change of natural environmental conditions, the lake has its own inevitable process of occurrence, development, aging, and extinction. In the natural state, the evolution process of the lake is very slow, but due to the human activities, the evolution significantly accelerates, and the environmental problems caused by eutrophication are becoming more and more serious. (Pant, 1980; Bennett, 2001; Paer, 2006; Qin, 2002; Wu, 2012)

In surface freshwater systems, phosphate is usually a limiting factor for plant growth, and in seawater systems, ammonia and nitrate often restrict the growth and total production of plants. Eutrophication is often caused by nutrients that are limited in these water systems. For example, the phosphorus content is usually limited in normal freshwater systems, so increasing phosphate can lead to overgrowth of plants. In seawater systems, phosphorus is indispensable, but nitrogen content is limited. So, this restrictive factor will be eliminated and the overgrowth of plants will occur.

The existing methods of phosphorus removal include biological, chemical and physical methods, but their removal efficiency vary in a wide range. Aluminium-based water treatment residual, which is a convenient and simple treatment method for phosphorus-containing sewage, is becoming more and more popular (Khan, Fareed & Ansari, 2005). Some studies have shown that the dehydrated aluminium sludge has a certain adsorption capacity for phosphorus present in the water body (Yizhong, Liping, Erdeng, 2011). Therefore, it may be promising to use aluminium sludge as a low-cost adsorbent to remove phosphorus from nutrients-rich waters and agricultural effluents.

2 LITERATURE REVIEW

2.1 Eutrophication process and its effect on natural environment.

Eutrophication is defined as an enrichment of a water body with excessive amount of nutrients. Eutrophication (from the Greek word for "good nutrition") refers to the increase in the output of primary producers, resulting in a decrease in the stability of the ecosystem. Over the past 30 years, excess nutrients (usually nitrogen and phosphate) have been shown to be the main cause of eutrophication. Eutrophication as a water quality issue has had a high profile since the late 1980s, following the widespread occurrence of blue-green algal blooms in some fresh waters. Some blue-green algae can produce toxins, which are harmful to humans and all other living organisms.

The excess plant and algae growth responsible for eutrophication, is due to increased availability of one or more growth limiting factors required for photosynthesis, such as sunlight, carbon dioxide, and nutrient fertilizers (Sundull, 2006). As the lake ages, eutrophication occurs naturally; however, human activities and development have accelerated the rate and degree of eutrophication process (i.e. through point source discharge) (Carpenter, 1981).

In aquatic environment where eutrophication occurs, the excess of nutrients such as nitrate, phosphate, or organic waste can cause an imbalance in the "production versus consumption" of living material (biomass) in an ecosystem. The system then reacts by producing more phytoplankton/vegetation that can be consumed by the ecosystem. This overproduction can lead to a variety of problems including anoxic waters (through decomposition), toxic algal blooms and decrease in diversity, food supply, and habitat destruction. The reduction of oxygen level may lead to an increase in mortality of aquatic living organisms and other effects reducing biodiversity.

The large growth of algae and aquatic plants or phytoplankton destroys the normal functioning of the ecosystem and causes various problems. The water becomes cloudy, often with shades of green, yellow, brown or red. Eutrophication also reduces the value and aesthetic enjoyment of rivers and lakes. Health problems occur when eutrophication conditions interfere with drinking water treatment. Water eutrophication endangering aquaculture and fishing as well.

Eutrophication of water body increases costs of water treatment, both for drinking and industrial purposes. The eutrophic water contains not only a large amount of algae but also may increase the number of bacteria and toxins. Moreover, it aggravates the odour of water and reduces the visual and tactile quality.

The decline in the quality of eutrophic water is a great threat to human health. Aside from unexcepted smell and taste, such water may contain pathogenic toxins, which can accumulate in fish. After fish consumption, the toxin can be transferred to the human body and endanger human health. The red tide algal blooms caused by some species of phytoplankton and dinoflagellates, is also very problematic and harmful to wildlife and human. After contact with the skin, it can make the skin itching, prickle, and rash. If it is splashed into the eyes, the pain is hard to bear, and the vapor of red tide toxin can cause inflammation of the respiratory tract.

2.2 Eutrophication in Finland.

2.2.1 Current situation.

Finland is a country of thousands of lakes – it's about 188,000 lakes (larger than 500 m²). Lakes in Finland are generally shallow with small water volume and long retention time, what make Finnish lakes vulnerable to external nutrient loads and consequently to eutrophication (Figure 1).



Figure 1. Lakes in Finland.

It will take decades to solve the problem of eutrophication in Finland's inland waters and the Baltic sea. Over time, some water can recover from the presence of excess nutrients through natural processes if further input of phosphorus and nitrogen will be maintained at acceptable levels. But with at least 1,500 lakes around Finland, more active ecological restoration measures, such as selective fishing, oxidation or removal of aquatic vegetation, are needed to effectively prevent eutrophication. These measures have been applied to almost a thousand lakes.

Eutrophication is an example of a gradual and problematic change in the environment, and therefore attracts public attention. The issue of eutrophication in Finland first became the subject of widespread debate in the summer of 1997, when massive algae blooms took place in the Gulf of Finland. Blue-green algae occur naturally in Finnish waters, but this giant flower is a visible result of decades of excess nutrient loads.

2.2.2 The reasons of nutrients loading in Finland.

In Finland, phosphorus is the common limiting factor of primary production in inland waters and its concentration has a great impact on the eutrophication of waterways. Phosphorus loading in waterways is mostly caused by agriculture, but also by wastewater discharge, forestry or fish farming (Figure 2).

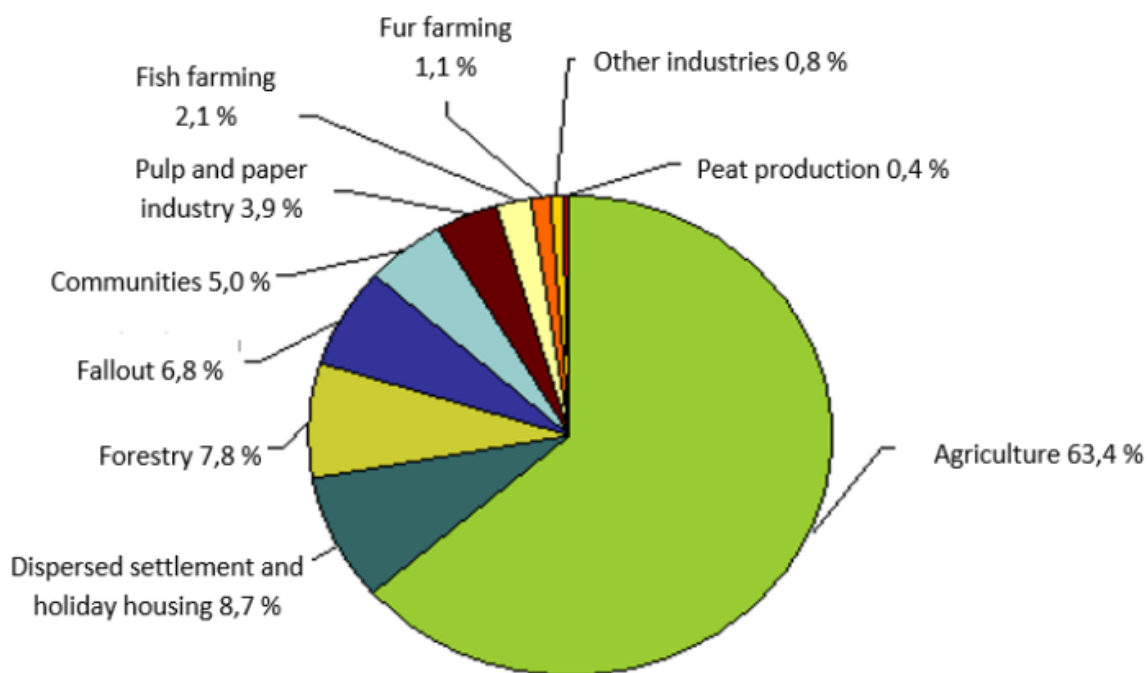


Figure 2. Incoming phosphorus load in inland water by sector (Finnish Environment Institute, 2005).

In addition to phosphorus, nitrogen is among the main nutrients in primary production and can act as minimum nutrient especially in the Baltic Sea but also in some inland waters. The most significant polluters as to nitrogen are agriculture (Figure 3).

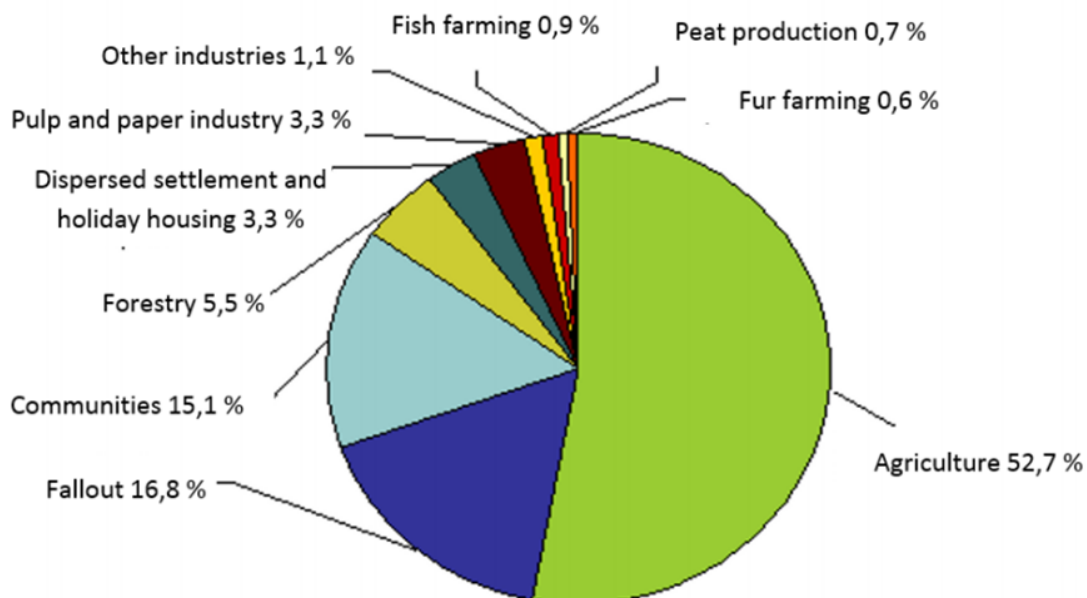


Figure 3. Nitrogen loading in inland waters by sector (Finnish Environment Institute, 2005).

2.3 Eutrophication in China.

2.3.1 Current situation.

The study of eutrophication has a long history, and many countries in the world are facing this problem. In recent 20 years, eutrophication of lakes in China has increased rapidly.

Lake is a node that interacts with the elements of the land surface system. It is an important freshwater resource bank, flood storage and species gene bank on the earth. It is closely related to human production and life and plays an irreplaceable function of ecosystem services. In recent years, China has strengthened the control of foreign pollutants in lakes, but the situation of lake eutrophication has not been effectively handled. This situation seriously endangering the regional water supply safety and the sustainable development of social and economic development, which has aroused great concern in the state and academia. As shown in Table 1, large areas of water bloom occurred in Taihu Lake, Chaohu Lake, and Dianchi Lake in 2007. The outbreak of large area of water bloom in Taihu Lake in 5-6 months affects the drinking water safety of hundreds of thousands of people in Wuxi.

The second survey of lakes status in China (2011) showed that 85.4% of the 138 lakes, which are more than 10 km², have exceeded the standard of eutrophication, and 40.1% have reached the heavy eutrophication standards. The Lugu Lake was the only lake among them, which reached the poor nutrition level throughout the year (Wan, 2015).

Table 1. The water bloom data of three typical eutrophic lakes in China

Name of lake	TN (mg/L)	TP (mg/L)	Chla (mg/m ³)
Tai lake	4.00	0.91	83.99
Dianchi Lake	2.62	0.20	0.074
ChaoLake	422	0.16	/

(TN – total nitrogen; TP – total phosphorus; Chla – Chlorophyll a)

The development trend of eutrophication of lakes, reservoirs, and rivers in China is very rapid. The major eutrophic sea areas are mainly concentrated in the nearshore areas, such as Liaodong Bay, the Yangtze Estuary, the Hangzhou Bay, the Pearl River Estuary etc. At the same time, most of the municipal and industrial sewage treatment plants which have been built and are being built in China are effective in reduction of chemical oxygen demand (COD), biochemical oxygen demand (BOD), ammonia nitrogen, total phosphorus, solid suspension in discharged effluents, but their performance in removal of total nitrogen was unsatisfactory. Despite the fact, that the current highest standard for total nitrogen in China is 10 mg/L (which is still 3 times the world's most stringent US index) the problem still exists.

Quite large amount of nitrogen and phosphorus come from industrial effluents, including iron and steel industry, chemical and pharmaceutical sector as well as from papermaking industry. In 2001, the discharge of industrial wastewater reached 20 billion 100 million T. Because of the technical and resource reasons, most industrial wastewaters have simple treatment or even are directly discharged into the receiving waters without any treatment. Apart from industrial wastewaters, also domestic sewage is a reason of lake eutrophication, since it contains a large amount of nitrogen, phosphorus

(mainly from detergents) and organic matter. In 2001, the national sewage discharged was up to 22 billion 700 million T.

According to statistics, the total amount of chemical oxygen demand (COD) in wastewater discharged in 2001 was 14.065 million tons, which was 2.7% less than that in 2000 and 6.07 million tons were discharged from industrial wastewater, which rose by 13.8%. And COD emissions from domestic sewage increased by 7.99 million tons, which went up 8%. It can be seen that domestic sewage gradually takes the place of industrial wastewater and becomes the main reason of water eutrophication in China.

Additionally, heavy use of chemical fertilizers and pesticides in a modern agricultural production pollute the environment to a large extent. Pesticides and fertilizers remain in the soil and are constantly leached into the surrounding environment, especially into water bodies contributing to water eutrophication.

2.3.2 Dianchi Lake as an example of eutrophicate lake in China.

Dianchi Lake, also known as Lake Dian and Kunming Lake, is a large lake located on the Yunnan-Guizhou Plateau close to Kunming, Yunnan, in southern China. Its nickname is the "Sparkling Pearl Embedded in a Highland". It is a freshwater fault lake at 1 886.5 m above sea level. The lake covers 298 km². It is 39 km long from north to south, and the average depth is 4.4 m. It is the eighth largest lake in China and the largest in Yunnan Province (Figure 4).



Figure 4. The original scenery of Dianchi Lake (Baidu).

According to the sampling analysis of 40 points from September 2001 to August 2002, the contents of total nitrogen, total phosphorus and chlorophyll a (Chla) in Dianchi sea were 2.62 mg /L, 0.20 mg /L, and 0.074 mg /L, respectively. According to the surface water environmental quality standard (GB3838 - 2002), it is a super V water quality and heavy eutrophication. Li Yuan (2005) studied the

cyanobacteria bloom in Dianchi from September 2001 to July 2002. The results showed that *Microcystis* Kiitz. and *Aphanizomenon* Morr. were formed in the algal bloom in China. The total number of cyanobacteria was 3.45×10^6 cell /L $\sim 1080.8 \times 10^6$ cell /L, with an average annual rate of 130.87×10^6 cell /L, accounting for 66.44% to 90.66% of the total phytoplankton cells. The number of *Microcystis* was 3.45×10^6 cell /L ~ 103 cell /L, 0.8×10^6 cell /L, and the average annual is 125.1×10^6 cell /L, accounting for 35.69% to 87.97% of the total phytoplankton, which is the single dominant genus of phytoplankton community in Dianchi. *Microcystis* bloom can be seen throughout the whole year. Sporadic algae bloom occurred only in March (Figure 5).



Figure 5. The eutrophic Dianchi Lake (Baidu).

2.3.3 Other eutrophic lakes in China.

The problem of eutrophication of lakes in some cities in China is serious. For example, the floating algae in West Lake are dominated by blue-green algae and the lake belongs to the heavy eutrophic lakes of blue and green algae. Wuhan East Lake, Guozheng Lake, Shuakei Lake, Yujia Lake and Temple Lake are characterized by high concentration of nitrogen and phosphorus and are eutrophic and heavy polluted.

The water quality of some urban lakes in China is listed in Table 2. It can be seen that the concentration of total nitrogen and total phosphorus in urban lakes is generally high, and the problem of eutrophication is serious.

Table 2. The water quality of some urban lakes in China

Name of lake	TN (mg/L)	TP (mg/L)	Chla (mg/m ³)
Hangzhou West Lake	3.10	0.170	56.58
Guangzhou Lu Lake	3.00	0.220	86.41
Huangshi Ci Lake	2.20	0.090	12.21
Xinjiang mushroom Lake	2.40	0.600	30.21
Huizhou West Lake	2.13	0.165	-
Changchun South Lake	4.80	0.310	-
Huhan Ink Lake	20.80	0.740	153.59

The Haihe River Basin is the political, economic and cultural centre of China, including the capital Beijing and more than 20 large and medium-sized cities. The natural runoff decreasing year by year leads to the weakening of the natural recharge process of the river, and the discharge of industrial wastewater and domestic sewage increases year by year, which makes the river of unconventional water supply. The amount of nitrogen and phosphorus has entered the river with the discharge of wastewater, which leads to their excessive amount in the main rivers. At the same time, river basin irrigation area is densely distributed, water conservancy facilities are built, resulting in poor physical continuity of plain rivers and their slow flow which additionally enhance the eutrophication process in the river basin, especially in plain section.

The survey of surface water quality includes the monthly monitoring data from 88 main monitoring sites located in the key area in 2009 (Haihe Water Conservancy Commission) and the data of 350 samples in the Haihe River Basin from 7 to October 2009. The sampling of phytoplankton is synchronized with the water quality survey, and the distribution of sample points is shown in Figure 6.



Figure 6. Distribution of sampling points for water quality survey in the Haihe River Basin.

The concentration distribution of total nitrogen (TN), ammonia nitrogen ($\text{NH}_3\text{-N}$) and nitrate ($\text{NO}_3\text{-N}$) in the main rivers of the Haihe River Basin in 2009 is shown in Figure 7. The average content of the river TN is 8.13 mg/L, exceeding 4 times standard of the surface water environment (GB3838 - 2002). $\text{NO}_3\text{-N}$ and average content are all over 4 mg/L, in which $\text{NH}_3\text{-N}$ (average content of 4.34 mg/L) exceeds class V standard (2 mg/L) more than 2 times. $\text{NH}_3\text{-N}$ is to control the pollution of nitrogen organic matter and protect the aquatic ecosystem, with ammonium (NH_4^+) and free ammonia (NH_3).



Figure 7. Distribution of nitrogen in the rivers of the Haihe River Basin.

2.4 Eutrophication in nonpoint sources.

Nonpoint source pollution (also known as 'diffuse' or 'runoff' pollution) is a pollution which comes from ill-defined and diffuse sources. Nonpoint sources are difficult to regulate and usually vary spatially and temporally (with the season, precipitation and other irregular events).

The reasons of the occurrence of eutrophication in nonpoint sources include soil retention, runoff to surface water and leaching to groundwater as well as atmospheric deposition.

■ Soil retention.

Nutrients from human activity accumulate in the soil and remain there for years. The results show that there is a linear relationship between the amount of phosphorus in the surface water and the content of phosphorus in the soil. As a result, most of the nutrients in the soil end up in water (Sharpley, 1996).

- Runoff to surface water and leaching to groundwater.

Nutrients from human activity tend to move from land to surface or groundwater. Nutrient loss in runoff and leachate is often associated with agriculture. Modern agriculture often involves the use of nutrients in fields to maximize yields. Regulations aimed at reducing nutrient exports from agriculture are often far stricter than those of sewage treatment plants and other point source polluters. It should also be noted that forest land is affected by surface runoff. Runoff can remove mineral nitrogen and phosphorus from debris, leading to slow and natural eutrophication of water (Klimaszyk, 2010).

- Atmospheric deposition.

Nitrogen is released into the air due to ammonia volatilization and nitrous oxide production. Burning fossil fuels makes a great contribution to the pollution of atmosphere by nitrogen compounds. Atmospheric nitrogen reaches the ground through two different processes. The first is wet precipitation, such as rain or snow, and the second is dry deposition (gaseous nitric acid, particulate ammonium and nitrate found in the air). Atmospheric precipitation (in the form of acid rain, for example) can also affect nutrient concentrations in water, especially in highly industrialized areas (Paerl, 1997).

2.5 Phosphorus in the aquatic environment.

Phosphorus in the aquatic environment exists as different phosphoric acid salts (orthophosphate PO_4^{3-}), polyphosphates $(\text{PO}_3)_n$ or is bounded to organic compounds. Ortho-phosphates together with metal ions (e.g. aluminium and iron) form poorly soluble phosphates.

Phosphate is the primary factor of eutrophication process in the natural environment (Ullman Encyclopedia). The availability of phosphorus generally promotes excessive plant growth and decay, favouring simple algae and plankton over other more complicated plants. Phosphorus is a necessary nutrient for plants to live and is the limiting factor for plant growth in many freshwater ecosystems. Phosphate adheres tightly to soil, thus is mainly transported by erosion. Once translocated to lakes, the extraction of phosphate into water is slow, hence the difficulty of reversing the effects of eutrophication.

Phosphate stimulates the growth of plankton and aquatic plants that feed large organisms, including plankton, fish, humans and other mammals. Plankton is the basis of the food chain. Initially, increased productivity will lead to increased fish stocks and increased biodiversity throughout the system. However, as the phosphate load continues, the accumulation of phosphate in the lake or other surface water will accelerate the aging process of aquatic ecosystem. Excessive production of lakes or reservoirs can lead to the imbalance in the circulation of nutrients (Ricklefs, 1993). The aging process can lead to large fluctuations in lake water quality and nutritional status, sometimes leading to periodic outbreaks of cyanobacteria.

In aerobic conditions, the natural cycle can be more or less balanced until excess nitrate (nitrogen) and/or phosphate enter the system. At this point, aquatic plants and algae begin to grow faster than in stable conditions. When this happens, plants and algae also decay in excess, because sunlight is

not able to reach the lower levels of water. Bacteria try to break down organic waste, consume oxygen, and release more phosphate, known as "circulation or internal circulation." Some phosphate can be deposited as iron phosphate and stored in the sediment, and next released under anoxic conditions. Under anaerobic conditions, with the deterioration of conditions, as more phosphates and nitrates enter the water bodies, all the oxygen may be broken down by bacteria, leading to its complete depletion.

2.6 Methods of removing phosphorus from water.

One of the most popular methods of phosphorus removal from water or wastewater is chemical precipitation with use of Fe, Al and Ca salts. The resulting metal salts simultaneously precipitate suspended organic matter and the concentration of organically bound phosphorus decreases. In Finland, the most commonly used chemicals for phosphorus precipitation are Fe(II) (ferrous) or Fe(III) (ferric) compounds, mostly ferrous sulphate. The chemical phosphorus removal process is simple and stable, but treatment costs are high due to the large amount of needed chemicals, and a large amount of sludge is generated as well (Chaochun, 2015).

Phosphorus can also be removed biologically with the help of polyphosphate-accumulating organisms (PAO). In that case, the phosphorus-rich biomass can be separated from wastewater as excess sludge. This excess sludge can be used either as fertilizer in fields or transform further into minerals. Biological phosphorus removal under alternate anaerobic and aerobic conditions (activated sludge plants) is not widely used in Finland but is popular in central Europe.

Biological treatment methods alone (excluding the PAO process) are not efficient enough as regards phosphorus removal and requires strict and stable operation. The average phosphorus reduction in a conventional activated sludge plant is 30%. Better results can be reached by combining both biological and chemical purification methods. Chemical precipitation together with biochemical reactions occur simultaneously when suitable aluminium and iron salts are added to the aeration basin and then the phosphorus removal rate increases up to 90%. This method is known as simultaneous or parallel precipitation.

Among available treatment methods (more or less efficient), adsorption technique may be also applied to reduce phosphorus concentration in water or wastewater. Various porous materials, known as low-cost (natural) or advanced (synthesized) adsorbents, can be successfully utilized for treatment process. Natural adsorbents include fly ash, steel slag, zeolite, bentonite, montmorillonite, attapulgite, sepiolite, active alumina, sea cotton etc. Synthetic adsorbents include various metal (hydro)oxides, i.e. Al, Mg, Fe, Ca, Ti, Zr and La. Depends on the type of adsorptive material and process conditions, the removal of phosphorus may happen via different mechanism, like physical adsorption or chemical adsorption; however, co-precipitation may be also observed in some treatment systems. The efficiency of adsorption process depends mainly on the properties of adsorbent, for example porosity and specific surface area (the larger the better) and chemical surface activity (Yunfeng, 2009).

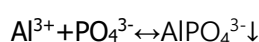
2.7 Aluminium sludge.

2.7.1 Advantages of aluminium sludge.

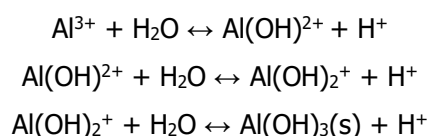
Effective treatment of water or wastewater contain excessive amount of phosphorus in an urgent subject and many research activities in this matter can be recently observed. The key issue is to have a cheap adsorptive material with high selectivity towards phosphorus. Therefore, many low-cost natural or waste adsorbents are investigated, for example red mud, fly ash, calcite or steel slag. Aluminium sludge is a by-product of water treatment process where aluminium, iron and calcium-based flocculation agents are used. However, most of the aluminium sludge is regarded as waste and is abandoned. Studies have shown that the aluminium sludge can be utilized for adsorptive removal of phosphorous from water and its adsorptive properties are closely related to the content of calcium, aluminium and iron. Apart from such advantages of this material like low costs and high efficiency, additionally management of aluminium sludge as a waste may be beneficial for water treatment utilities (Jing Hu, 2009).

2.7.2 Chemical background.

Chemical coagulation followed by sedimentation is the basic and most widely used approach for phosphorus removal from water. The principle of phosphorus removal by chemical coagulation is to form insoluble phosphate precipitate by adding chemical agents (flocculants), and removal precipitate by solid-liquid separation (sedimentation). The coagulation process is carried out in mixing tanks where the rapid mixing in followed by the slow mixing (flocculation) during the floc formation is observed. The chemistry of aluminium is complex. The principle of phosphorus removal by aluminium sludge is generally believed that when aluminium sludge is dispersed in water Al^{3+} reacts with PO_4^{3-} , and the reaction is as follows:



On the other hand, first, Al is hydrolysed to form mononuclear complexes, such as $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^+$ etc., and then the mononuclear complexes condense further to form a series of polynuclear complexes, $\text{Al}(\text{OH})_3$:



$\text{Al}(\text{OH})_3$ is a visible precipitate which transform into larger particles known as flocs. Most commonly, flocs are removed from water by gravity separation within one-two hours of sedimentation process. The aluminium polynuclear complexes often have high positive charge and the specific surface area which can quickly adsorb negatively charged impurities from water, neutralize colloidal charge, compress double layer and reduce colloidal potential, promote the rapid destabilization, coagulation and precipitation of colloids and suspended solids.

The pH value of the solution determines which aluminium hydrolysis products are dominant, and their solubility is shown in Figure 8. The optimal pH range for phosphorus removal process is between 5.0 and 8.0.

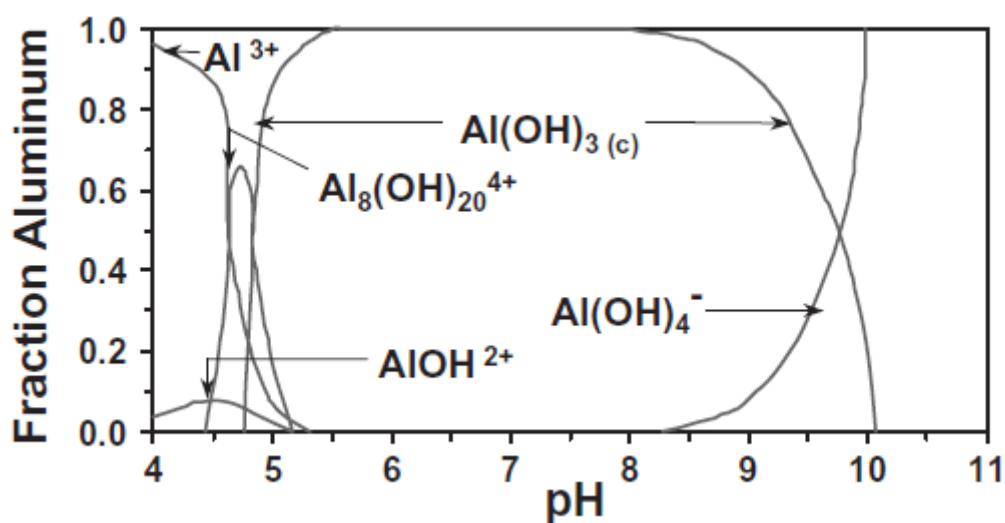


Figure 8. Fractional distribution of aluminium species as a function of pH (concentration of 5.0×10^{-4} M).

2.7.3 Water treatment residue.

The water treatment residues (WTR), sometimes referred to as hydrosols, "alum sludge" or "iron sludge", are managed in a variety of ways, including discharge to wastewater treatment facilities, landfill treatment or land application. In the production of drinking water, coagulants such as $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ and FeCl_3 or $\text{Fe}_2(\text{SO}_4)_3$ are usually used to remove particulate matter and dissolved components from water. The resulting waste, called water treatment residue, contains precipitated aluminium or iron hydroxides, which have a strong affinity for anionic species, but also may contain various trace metals, suspended solids, organic chemicals and biological particles.

Recent studies have focused on the use of WTR as a cost-effective material to reduce soluble phosphorus in organic waste (manure and biological solids) in the soil, runoff and land use. The study shows that the adsorption of phosphorus by WTR is fast and almost irreversible, which indicates the long-term stable immobilization of WTR binding phosphorus (Ippolito, 2016).

WTR removal of other potential environmental pollutants (ClO_4^- , $\text{Se}(\text{IV})$, $\text{Se}(\text{VI})$, $\text{As}(\text{III})$, $\text{As}(\text{V})$, Hg) have been investigated as well, indicating the potential use of WTR in environmental restoration (Ippolito, 2016). While researchers are concerned about the toxicity of aluminium plants and enhanced aluminium leaching, these effects are minimal at ambient neutral soil pH. Radioactive, micronutrient levels and strong manganese leaching are also considered as potential problems when WTR is applied as a soil supplement. However, these issues can be managed in such a way as to not limit the beneficial use of WTR in controlling off-site phosphorus loss in sensitive waters or reducing soil available phosphorus concentrations.

Based on the final WTR characteristics, the material can be used as a soil conditioner or a soil substitute. However, the material generally has a strong affinity for anionic species. Therefore, soil conditions, plant growth and nutrient uptake (at least related to aluminium or iron) and anionic species should be closely monitored when used as soil amendments.

Previous studies have shown that plant phosphorus decreases with the application of WTR soil, with symptoms of phosphorus deficiency, and plant yield decreases (Ippolito, 2016). After the application of Al-WTR, the activity of soil phosphodiesterase and pyrophosphatase decreased and the activity of acid phosphatase and phytase increased. The decreased activity of phosphodiesterase indicates less phosphorylation of biomass sources (nucleic acids and phospholipids), while the increased activity of acidic phosphatase and phytase indicates that esters P and inositol P may be important plant active phosphorus sources in the soil. Plant community composition and coverage were not affected by aluminium WTR.

3 MATERIALS AND METHODS

3.1 Materials.

The water sample from lake (natural water) was spiked with phosphorus (stock solution of K_2HPO_4 contains 1000 mg/L PO_4^{3-}) and nitrogen (stock solution of NH_4Cl contains 1000 mg/L N). The Al-based sludge (Al-WTR) was collected from flocculation process (from Kuopion Vesi Oy). Cuvette tests LCK349 and LCK350 (Hach-Lange) were used for phosphorus measurement. The solution of HCl and NaOH were used for pH adjustment.



Figure 9. The Al-based sludge from flocculation process (from Kuopion Vesi Oy) (Xinyue Wang)

3.2 Experimental methods.

Kinetics studies include three types of tests:

- Test 1A: Effect of adsorbent dose
 - 1) 5 g/L Al, 2 mg/L P, 2 mg/L N
 - 2) 10 g/L Al, 2 mg/L P, 2 mg/L N
 - 3) 20 g/L Al, 2 mg/L P, 2 mg/L N
- Test 1B: Effect of initial concentration of phosphorous
 - 1) 10 g/L Al, 2 mg/L P, 2 mg/L N
 - 2) 10 g/L Al, 5 mg/L P, 2 mg/L N
 - 3) 10 g/L Al, 10 mg/L P, 2 mg/L N
- Test 1C: Effect of solution pH
 - 1) 10 g/L Al, 2 mg/L P, 2 mg/L N, pH=4
 - 2) 10 g/L Al, 2 mg/L P, 2 mg/L N, pH=5
 - 3) 10 g/L Al, 2 mg/L P, 2 mg/L N, pH=6

Kinetics tests were performed using the jar-test. All experiments were conducted in the laboratory and included several steps:

- 1) Fill the jar-test beakers with 800 mL of well-mixed lake water using the graduated cylinder.
- 2) Place the filled jars on the stirrer, with the paddles positioned identically in each beaker.
- 3) Mix the content of beakers at 150 rpm for 3 hours. In 5, 10, 20, 30, 60, 120 and 180 minutes of the process, collect from the jar-test 15 mL of water sample to test the phosphorus content using LCK349 and LCK350 cuvette tests.
- 4) The remaining amount of collected samples were acidified with HCl solution before the nitrogen and DOC measurement.
- 5) After 3-hour-mixing remove the jars from the stirrer, empty the contents and thoroughly clean the beakers.

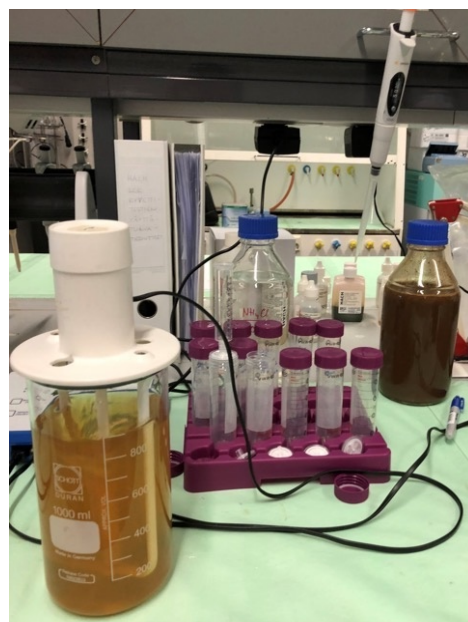


Figure 10. Experiment step
(Xinyue Wang)

3.3 Laboratory equipment.

- 1) Jar-test apparatus (Kemira Flocculator 2000)
- 2) Spectrophotometer (Hach-Lange DR 6000)
- 3) TOC analyser (Analytikjena multi N/C 2100s)
- 4) High Temperature Thermostat (Hach-Lange)
- 5) Shaker (New Brunswick Innova 40R)
- 6) pH-meter and conductivity-meter (Hach-Lange)
- 7) Other equipment:
 - Electronic scale
 - Conical flasks
 - Beakers
 - Pipettes
 - Volumetric flasks

4 DISCUSSION OF RESULTS

4.1 Test 1A: Effect of adsorbent dose.

In the first set of experiments, phosphorus and nitrogen were both fixed on 2 mg/L and aluminum sludge was added in 3 different doses - 5 g/L, 10 g/L and 20 g/L. Obtained results are listed in Table 3-5 and presented in Figure 11 and 12.

Table 3. Results from kinetic test with adsorbent dose1 of 5 g/L.

1A: Effect of adsorbent dose				
Dose1 (5 g/L) = 3.99 g/800 mL = 4.9875 g/L; PO_4^{3-} =2.2 mg/L				
Time(min)	pH	T _{pH} (°C)	Cond. (μS/cm)	T _{cond} (°C)
initial test	7.05	20.6	85.0	20.7
5	7.73	21.7	/	/
10	8.00	21.5		
20	7.67	21.8		
30	7.65	21.5		
60	7.62	21.1		
120	8.98	21.6		
180	8.45	21.9		
final test	8.17	21.4		

Table 4. Results from kinetic test with adsorbent dose2 of 10 g/L.

1A: Effect of adsorbent dose				
Dose2 (10 g/L) = 8.07 g/800 mL = 10.0875 g/L; PO_4^{3-} =2.3 mg/L				
Time(min)	pH	T _{pH} (°C)	Cond. (μS/cm)	T _{cond} (°C)
initial test	7.14	19.2	84.0	19.2
5	7.36	20.8	/	/
10	7.25	20.9		
20	7.26	20.7		
30	7.30	20.6		
60	7.98	21.7		
120	7.78	21.3		
180	7.70	21.8		
final test	7.60	21.5		

Table 5. Results from kinetic test with adsorbent dose3 of 20 g/L.

1A: Effect of adsorbent dose				
Dose3 (20 g/L) = 16.08 g/800 mL = 20.1 g/L; PO_4^{3-} =2.5 mg/L				
Time (min)	pH	T_{pH} (°C)	Cond. (μ S/cm)	T_{cond} (°C)
initial test	7.16	19.4	93.3	20.0
5	8.29	21.4	/	/
10	9.01	21.1		
20	7.71	21.2		
30	7.73	21.0		
60	7.62	22.1		
120	7.57	22.2		
180	7.51	22.4		
final test	7.49	22.1	85.1	22.0

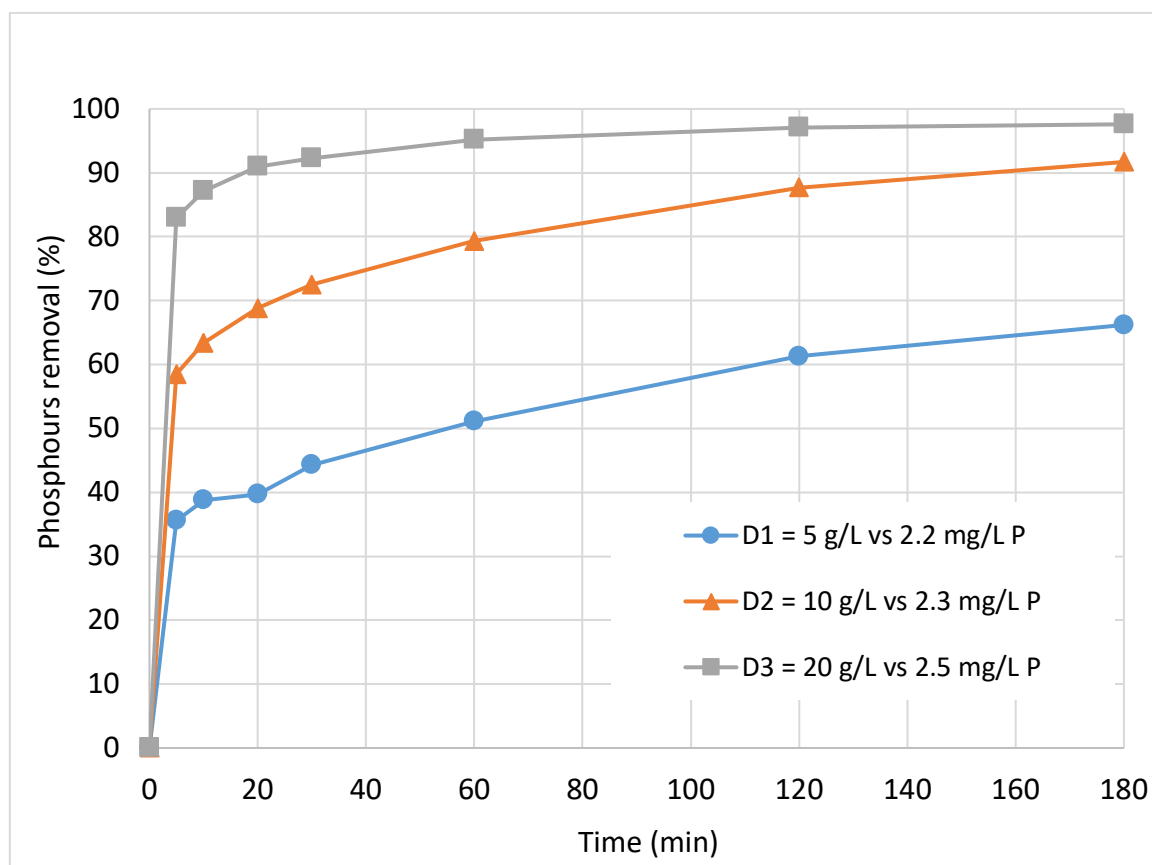


Figure 11. Effect of Al-WTR dose on process efficiency (test 1A).

As shown in Figure 11, all tested adsorbent doses (5, 10, 20 g/L) effectively removed phosphorus from lake water. It was observed that higher amount of Al-based material gives better treatment results. The phosphorus was removed in 98% within 180 minutes of the process when 20 g/L of Al-WTR was dosed into the water sample. The lowest removal efficiency was recorded in the test with 5 g/L of adsorbent, where only 66% of phosphorous was adsorbed.

In case of all tested doses of Al-WTR, the most significant rise in phosphorus removal occurred in first 5 minutes. After this time the removal rate of phosphorus slow down but gradual increase in process efficiency was observed until 120-180 min. For 20 g/L of Al-WTR the plateau is visible, but smaller amount of adsorbent, like 5 or 10 g/L, needs longer time to reach equilibrium.

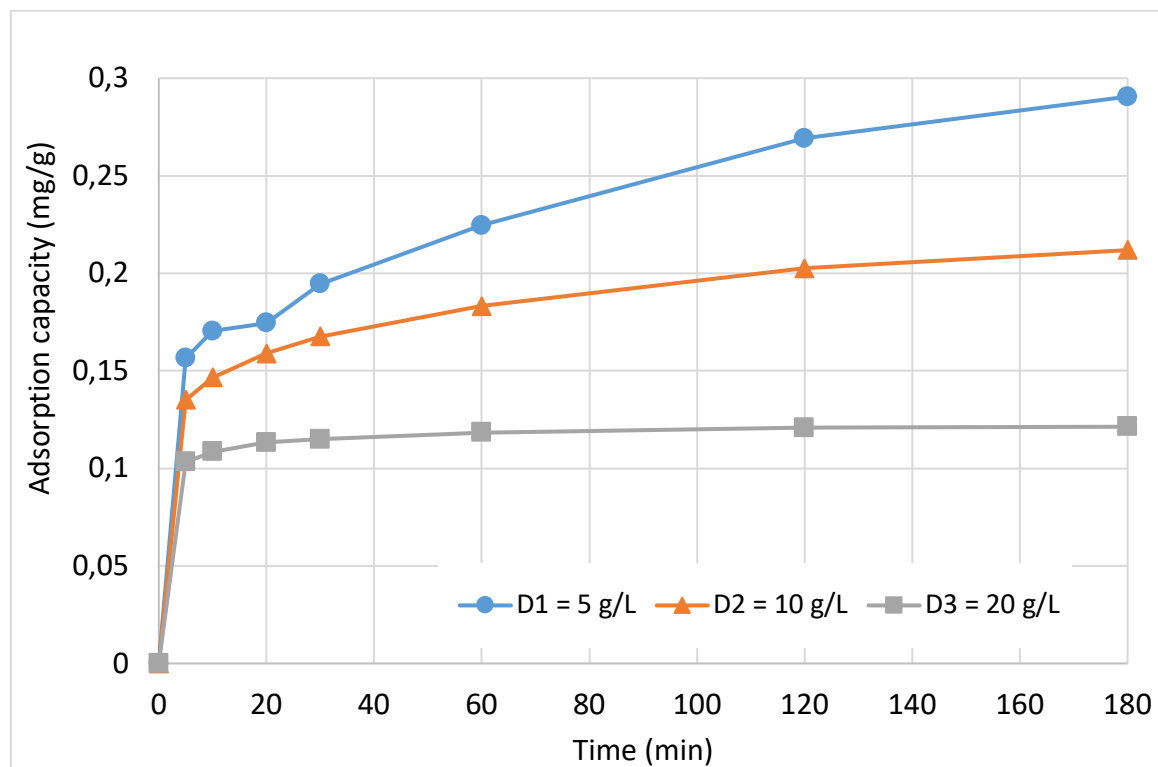


Figure 12. Adsorption capacity of Al-WTR for phosphorus (test 1A).

Figure 12 shows the phosphorus adsorption capacity of tested material for three various doses. By evaluation of adsorption capacity, it is possible to assess the potential efficacy of Al-WTR for the removal of phosphorous from contaminated water or wastewater. Among three tested doses, the highest phosphorus adsorption capacity was obtained for 5 g/L of adsorbent and it reached 0.291 mg/g within 180 minutes of the process. The lowest phosphorus adsorption capacity (0.121 mg/g), was recorded in the test with 20 g/L of adsorbent. The similar pattern was observed as mentioned previously, i.e. fast adsorption within 5 minutes resulting in sudden increase in adsorption capacity followed by the slower process.

4.2 Test 1B: effect of initial phosphorus concentration.

The second set of experiments was performed with the constant adsorbent dose of 10 g/L and nitrogen concentration of 2 mg/L. The initial concentration of phosphorus varied among 2 g/L, 5 g/L and 10 g/L. Obtained experimental results are listed in Table 6-9 and presented in Figure 13-17.

Table 6. Results from kinetic test with initial phosphorous concentration Co1 of 2.3 mg/L.

1B: Effect of initial concentration of phosphorous				
Initial Co1 = 2.3 mg/L; Adsorbent dose: 8.07 g/800 mL = 10.0875 g/L				
Time(min)	pH	T _{pH} (°C)	Cond. (μS/cm)	T _{cond} (°C)
initial test	7.14	19.2	84.0	19.2
5	7.36	20.8	/	/
10	7.25	20.9		
20	7.26	20.7		
30	7.30	20.6		
60	7.98	21.7		
120	7.78	21.3		
180	7.70	21.8		
final test	7.60	21.5	83.2	21.6

Table 7. Results from kinetic test with initial phosphorous concentration Co2 of 5.5 mg/L (first test).

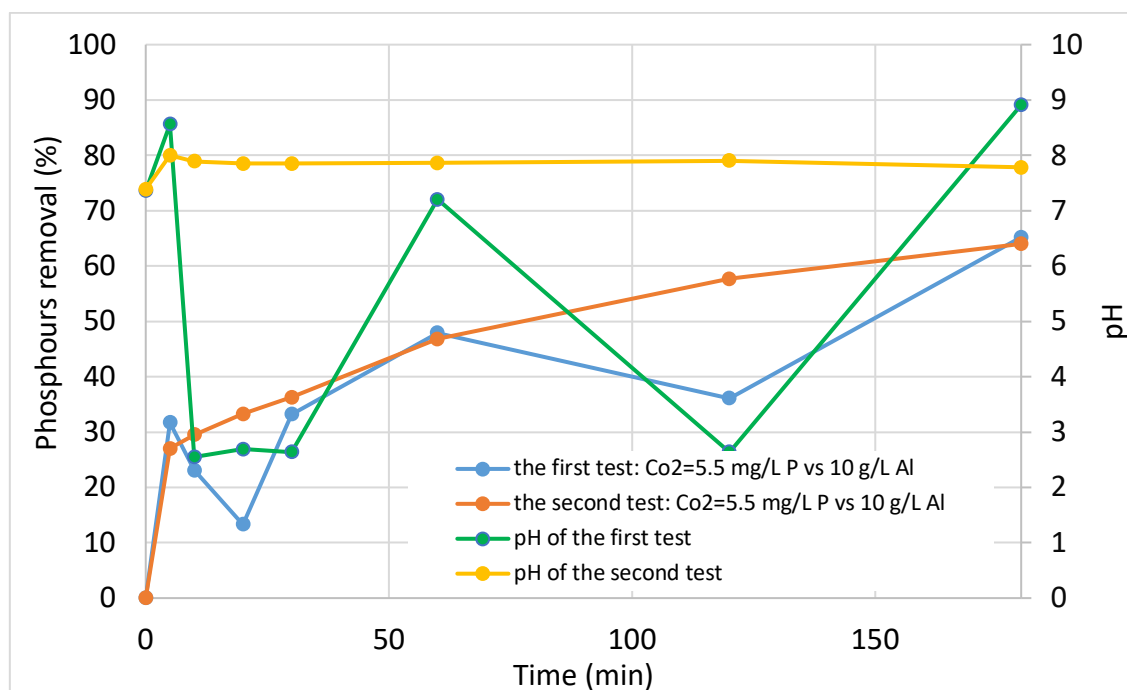
1B: Effect of initial concentration of phosphorous				
Initial Co2 = 5.5 mg/L; Adsorbent dose: 7.96 g/800 mL = 9.95 g/L				
Time(min)	pH	T _{pH} (°C)	Cond. (μS/cm)	T _{cond} (°C)
initial test	7.36	20.7	106.9	21.1
5	8.56	21.7	/	/
10	2.55	22.0		
20	2.69	21.9		
30	2.64	22.1		
60	7.20	21.9		
120	2.64	21.9		
180	8.91	22.7		
final test	8.60	22.2	104.5	22.1

Table 8. Results from kinetic test with initial phosphorous concentration Co2 of 5.5 mg/L (second test).

1B: Effect of initial concentration of phosphorous				
Initial Co2 = 5.5 mg/L; Adsorbent dose: 8.04 g/800 mL = 10.05 g/L				
Time(min)	pH	T _{pH} (°C)	Cond. (μS/cm)	T _{cond} (°C)
initial test	7.39	21	113.7	22.1
5	8.00	21.7	/	/
10	7.89	21.5		
20	7.85	21.4		
30	7.85	21.4		
60	7.86	21.7		
120	7.90	21.6		
180	7.78	22.1		
final test	7.90	21.4	113.5	21.7

Table 9. Results from kinetic test with initial phosphorous concentration Co_3 of 10.4 mg/L.

1B: Effect of initial concentration of phosphorous				
Initial Co_3 = 10.4 mg/L; Adsorbent dose: 7.99 g/800 mL = 9.9875 g/L				
Time (min)	pH	T_{pH} (°C)	Cond. (μ S/cm)	T_{cond} (°C)
initial test	9.06	20.8	140.1	20.7
5	8.62	21.5	/	/
10	8.27	21.5		
20	8.14	21.3		
30	7.95	21.3		
60	7.32	21.7		
120	7.47	20.9		
180	7.51	21.1		
final test	7.55	21.4	131.1	21.5

Figure 13. Comparison of two kinetic tests with initial phosphorous concentration Co_2 of 5.5 mg/L.

The first test has been abandoned because of the lack of logical trend in changes of phosphorous concentration and pH with time. The second attempt was consistent with other experiments, so it was taken as a correct experimental run.

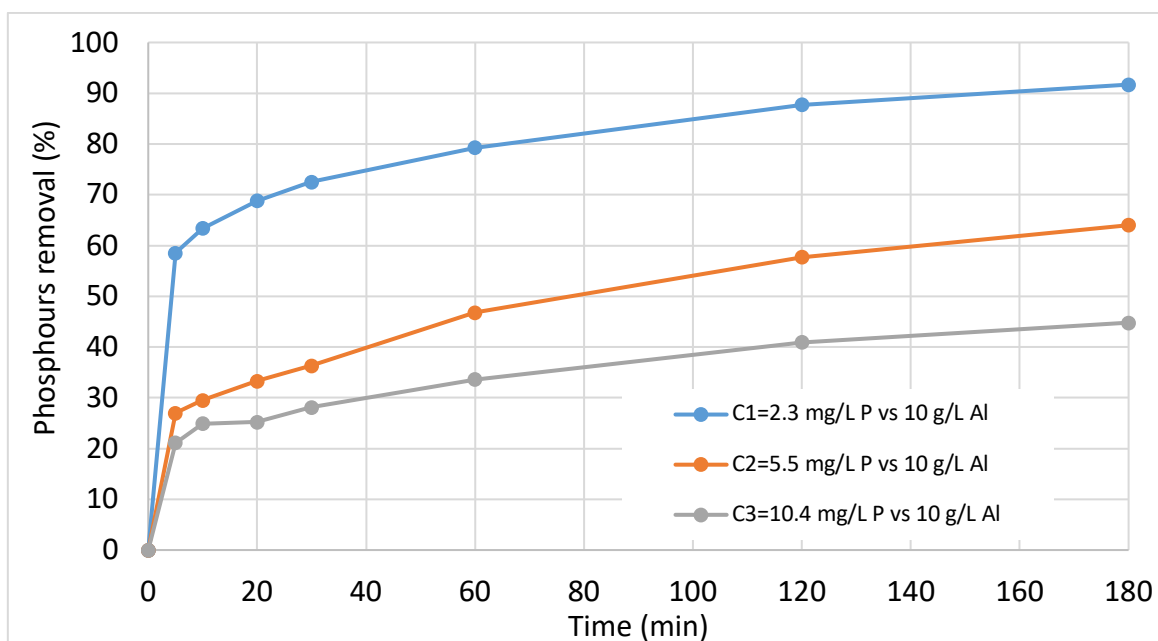


Figure 14. Effect of initial phosphorus concentration on process efficiency (test 1B).

As can be seen in Figure 14, the influence of initial phosphorous concentration on Al-WTR performance was significant. Based on results obtained for three different concentrations (2, 5 and 10 mg/L), it was found that more difficult was to remove phosphorous present in treated water sample in higher concentration comparing to its lower amount. The phosphorous was removed in about 91.7% and 44.8% for initial phosphorus concentration of 2.3 mg/L and 10.4 mg/L, respectively. The most considerable rise in phosphorus removal by Al-based material occurred in first 5 minutes of the process, for all tested scenarios. Next the removal of phosphorus continued to increase over the remaining time.

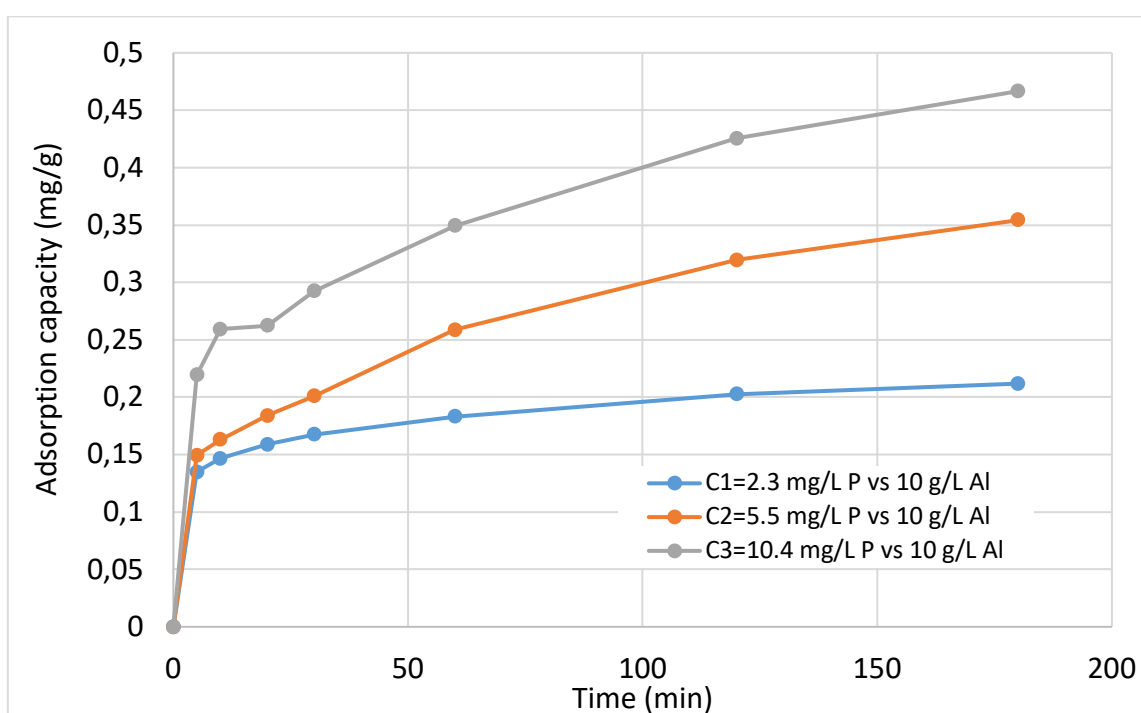


Figure 15. Adsorption capacity of Al-WTR for phosphorus (test 1B).

Figure 15 showed the influence of initial concentration of phosphorous on adsorption capacity of tested Al-based adsorbent. Generally, the higher phosphorus concentration, the higher value of calculated adsorption capacity of Al-WTR was recorded. For the 2.3 mg/L, 5.5 mg/L and 10.4 mg/L of phosphorous present in the treated solution the maximal adsorption capacity was 0.212 mg/g, 0.354 mg/g and 0.467 mg/g, respectively. As previously, the fastest adsorption was observed in the first 5 minutes, regardless the initial concentration of phosphorous. However, the largest increment in adsorption capacity between 5th and 180th minutes of the process was recorded in case of highest tested concentration of phosphorous.

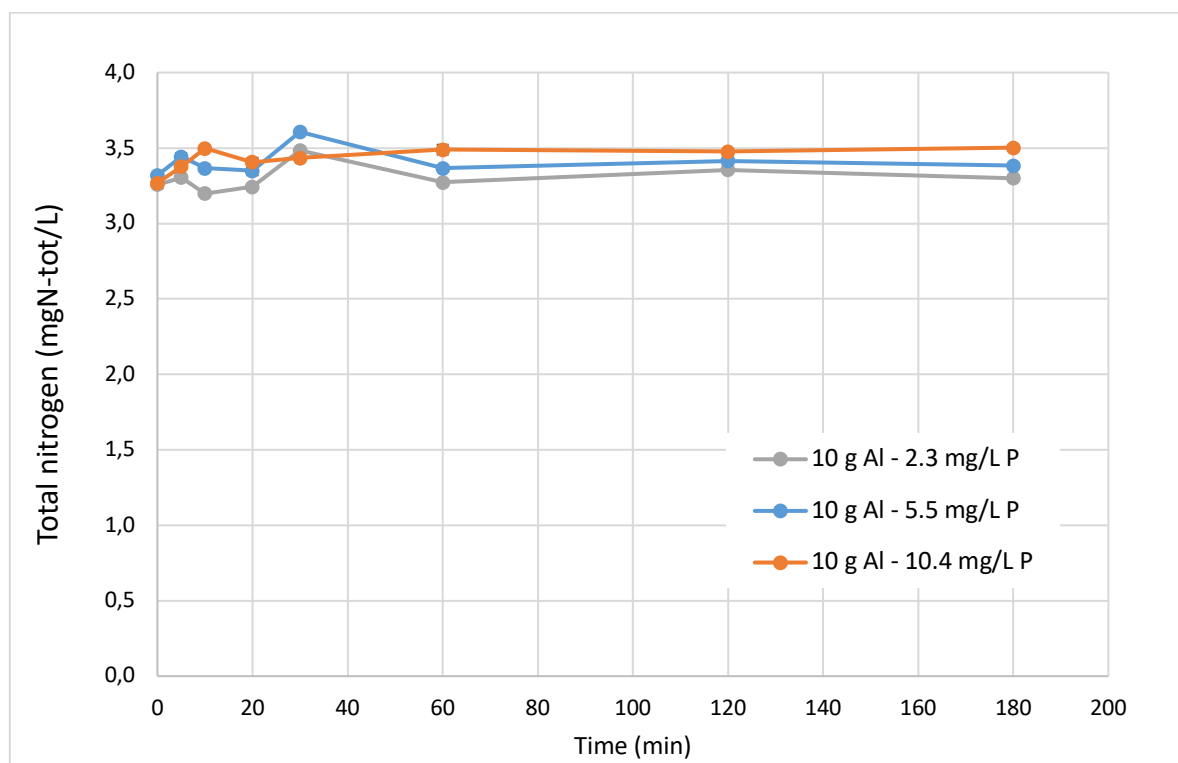


Figure 16. Efficiency of total nitrogen removal (test 1B).

As shown in Figure 16, all tested doses (2, 5, 10 mg/L initial phosphorus concentration) had no effect on nitrogen removal from simulated lake water. At the beginning of the process (0-60 min), the process efficiency varied significantly and then remained stable within 60-180 minutes. For the 2.3 mg/L, 5.5 mg/L and 10.4 mg/L of phosphorous present in the treated solution, the final increase in nitrogen was 0.03 mg/L, 0.11 mg/L and 0.18 mg/L. So in the presence of various amount of phosphorous in treated water observed changes of total nitrogen concentration within the 180 mins of the process were similar.

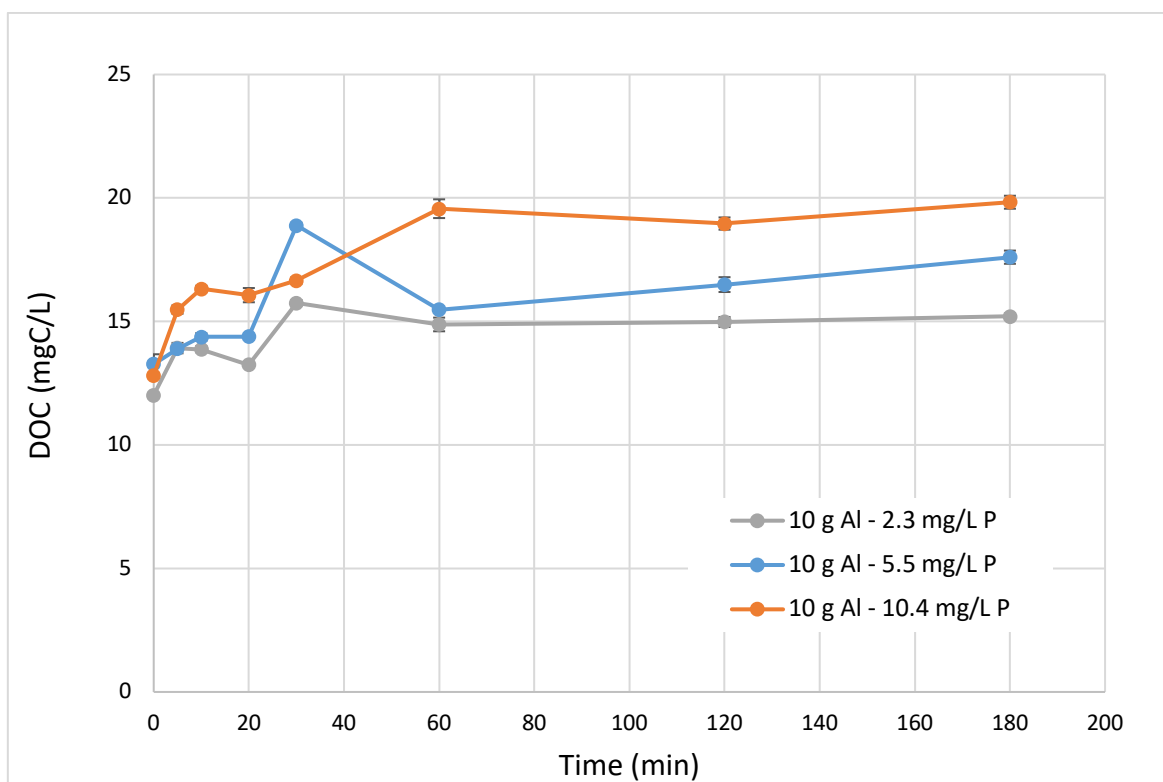


Figure 17. Efficiency of dissolved organic carbon removal (test 1B).

As shown in Figure 17, the amount of organic matter in treated water varied depending on initial concentration of phosphorus. It was found that the DOC increased during the process and after 3 hours of contact time its concentration was significantly higher than at the beginning. Most probably a certain amount of organic matter was in the composition of tested adsorbent and was released into the solution.

4.3 Changes of pH and conductivity (test 1A & 1B).

In both Test 1A and 1B, in all collected samples, apart from phosphorus, pH was also measured and obtained results are presented in Figure 18.

In general, all tests had similar stable pH, which was between 7 and 8 (with some minor fluctuations), which indicates no influence of aluminum sludge adsorbent on the pH value of treated water sample.

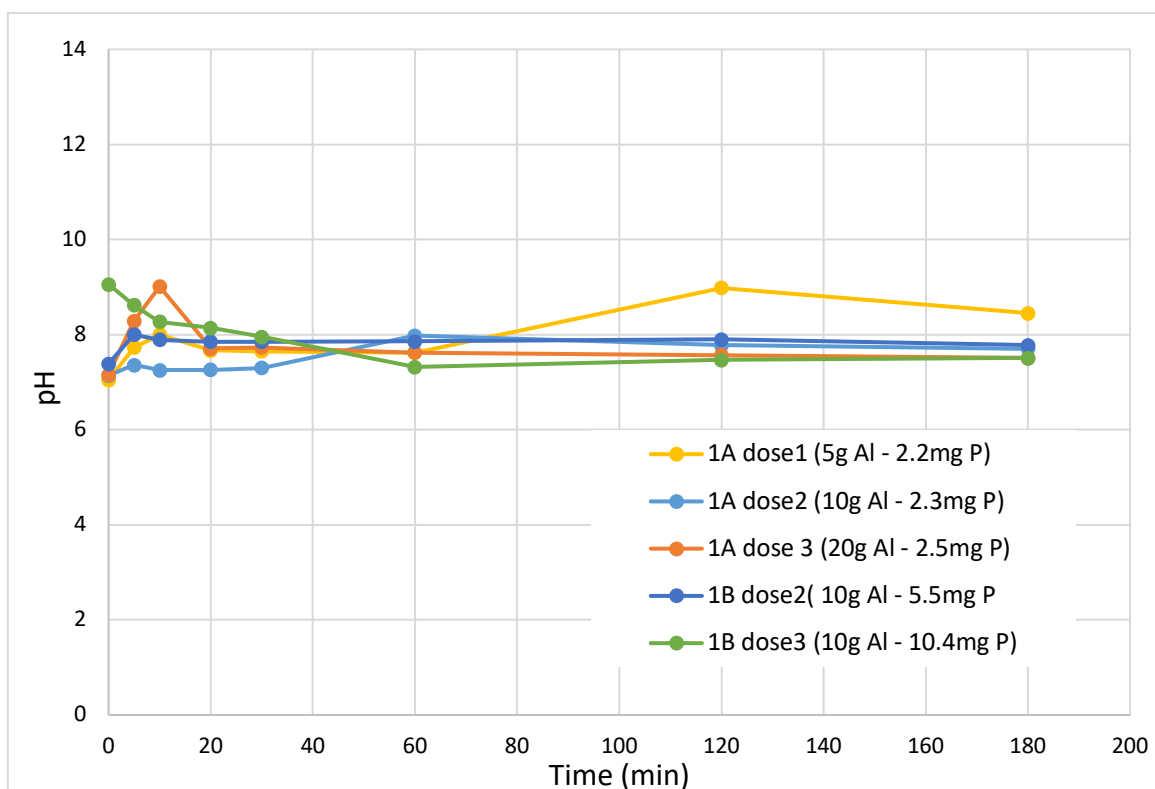


Figure 18. Time-related changes in pH (test 1A and 1B).

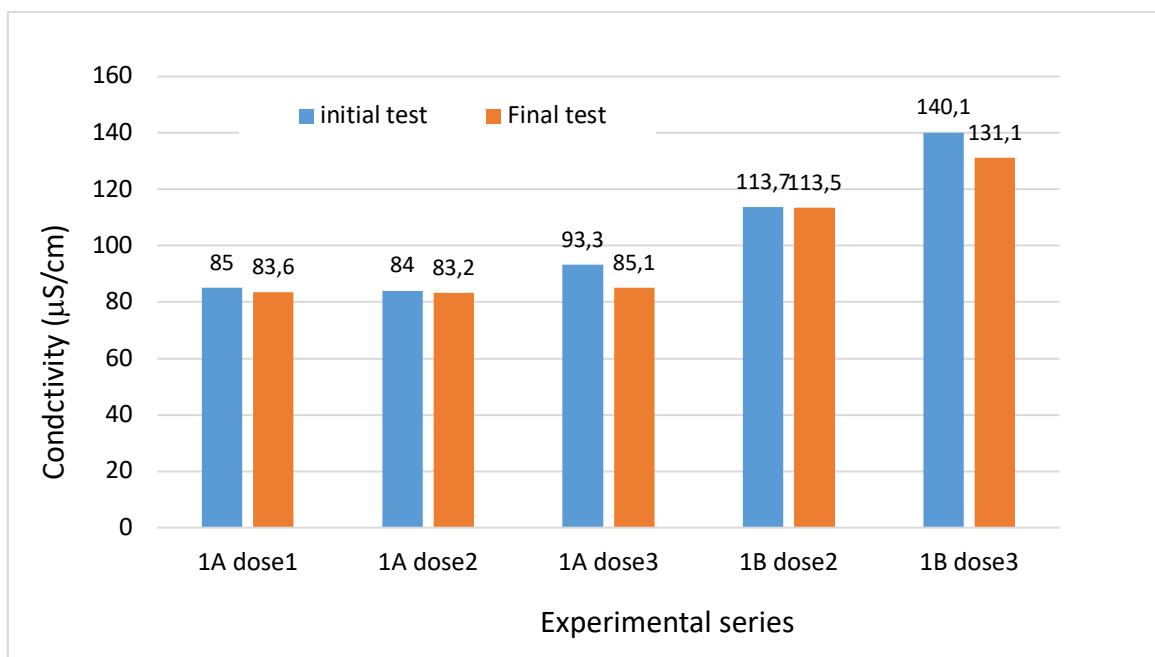


Figure 19. Changes in conductivity (test 1A and 1B).

In both Test 1A and 1B, the conductivity before and after the process was measured as well. As can be seen in Figure 19, the initial conductivity of simulated lake water samples was between 84 and 140 $\mu\text{S}/\text{cm}$. It was observed that the final conductivity of treated samples was comparable to its initial value, in all performed five experiments.

4.4 Test 1C: effect of solution pH.

The third set of experiments was performed with the constant adsorbent dose of 10 g/L and nitrogen and phosphorous concentration of 2 mg/L. The initial pH was adjusted to 4, 5 and 6 and kept constant during the 3 hours of the process.

Obtained experimental results are listed in Table 10-12 and presented in Figure 20 and 21.

Table 10. Results from kinetic test with pH1 = 4.

1C: Effect of solution pH				
pH1 = 4; Adsorbent dose: 7.97 g/800 mL = 9.9625 g/L; PO_4^{3-} = 2.4 mg/L				
Time (min)	pH	T_{pH} (°C)	Cond. (μ S/cm)	T_{cond} (°C)
initial test	7.20	20.8	91.4	22.3
5	/	/	/	/
10				
20				
30				
60				
120				
180				
final test	4.23	21.8	162.5	22
HCl amount	13 drops			

Table 11. Results from kinetic test with pH2 = 5.

1C: Effect of solution pH				
pH2 = 5; Adsorbent dose: 8.02 g/800mL = 10.025g/L; PO_4^{3-} = 2.3 mg/L				
Time (min)	pH	T_{pH} (°C)	Cond. (μ S/cm)	T_{cond} (°C)
initial test	7.09	20.7	85.9	21.6
5	/	/	/	/
10				
20				
30				
60				
120				
180				
final test	5.11	22.8	146.9	22.7
HCl amount	11 drops			

Table 12. Results from kinetic test with pH3 = 6.

1C: Effect of solution pH				
pH3 = 6; Adsorbent dose: 8.01 g/800mL = 10.0125 g/L; PO ₄ ³⁻ = 2.3 mg/L				
Time (min)	pH	T _{pH} (°C)	Cond. (μS/cm)	T _{cond} (°C)
initial test	6.99	21.3	103.7	21.9
5	/	/	/	/
10				
20				
30				
60				
120				
180				
final test	6.28	22.8	137.2	22.8
HCl amount	9 drops			

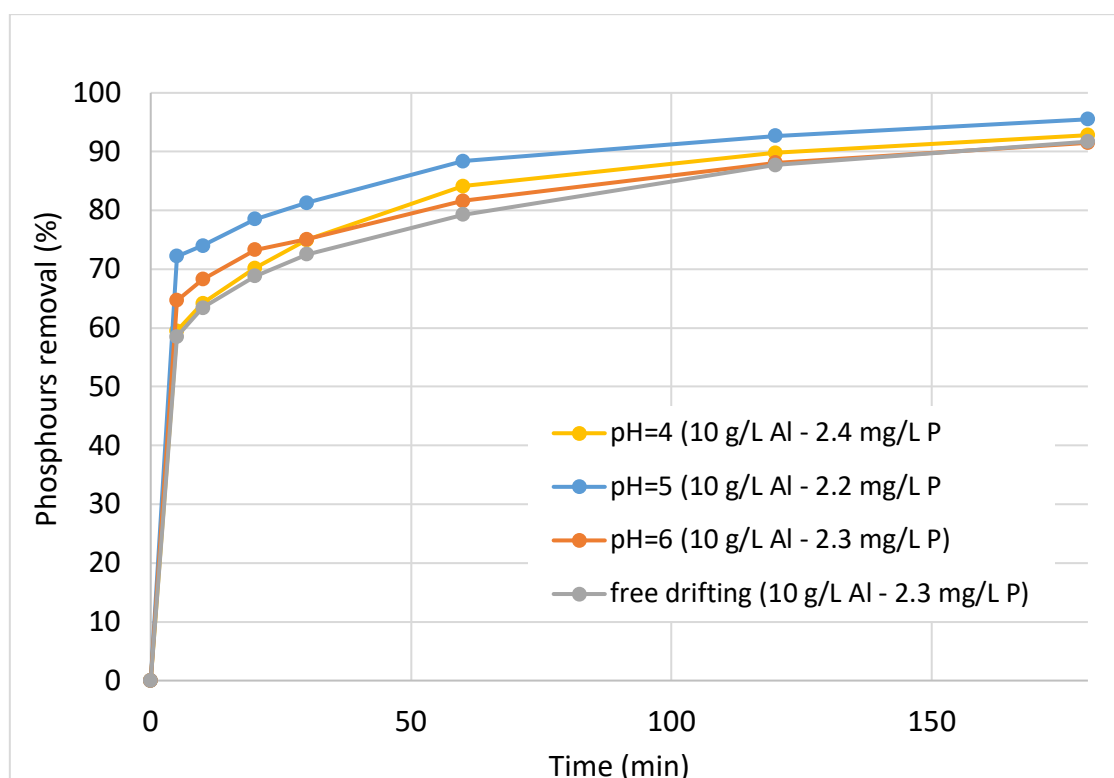


Figure 20. Effect of solution pH on process efficiency (test 1C).

It was shown in Figure 20 that solution pH (4, 5, 6) have a little effect on adsorption of phosphorus from lake water. No significant differences were observed in terms of percentage removal of phosphorus under experimental conditions with controlled pH and free-drifted pH (without control). It was observed that the highest removal rate of phosphorus was obtained for pH 5 (95.5 %), while the lowest efficiency of the process was recorded for pH 6 (91.5 %) after 3 hours of contact time. The most significant rise in phosphorus removal of Al-based material occurred in 5 minutes, for all pH values. After this time the gradual increase was observed until 120- 180 min of the process.

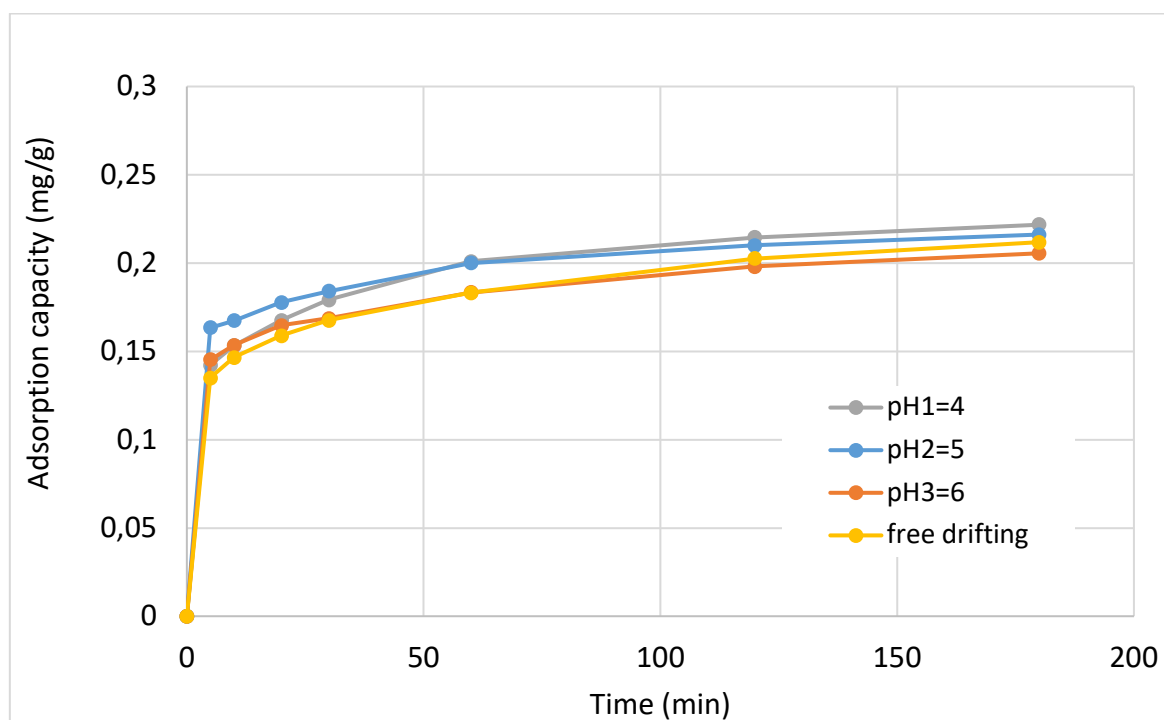


Figure 21. Adsorption capacity of Al-WTR for phosphorus (test 1C).

Figure 21 showed the phosphorus adsorption capacity of Al-WTR under various pH conditions (4, 5, 6). It has been found that adsorbent performance does not depend on solution pH. Among three tested pH values, the highest phosphorus adsorption capacity was obtained at pH 4 and it reached 0.222 mg/g. The lowest adsorption capacity recorded in the test performed at pH 6 reached 0.202 mg/g within 180 minutes of the process. The similar pattern was observed, i.e. the fastest process was within 5 minutes and after this time the adsorption capacities of phosphorus for all tested pH constantly increase to maximal values at the 180th minute of the process.

5 CONCLUSIONS

- Aluminium based water treatment residues (Al-WTR) were used in the study as a low-cost adsorbent for phosphorous removal from water. Tested Al-WTR is a by-product of water treatment process (coagulation) where aluminium sulphate as a coagulant is used. Its ability for phosphorous removal from water was assessed based on adsorption kinetic experiments where various process parameters, including adsorbent dose (test 1A), initial phosphorus concentration (test 1B) and solution pH (tests 1C), were analysed.
- In all conducted kinetic tests, the longer contact time of treated water with adsorbent gives the better results in terms of percentage removal of phosphorous and adsorption capacity of Al-WTR.
- It was confirmed that the efficiency of the process depends on the amount of applied adsorbent. All tested doses (5, 10, 20 g/L) effectively removed phosphorus from simulated lake water, however the higher amount of Al-based material gives better treatment effect comparing to the smaller dose of Al-WTR.
- The influence of initial phosphorous concentration on process efficiency was analysed based on tests with three different concentrations (2.3, 5.5 and 10.4 mg/L). It was observed that more difficult was to remove phosphorous present in the treated water sample in higher concentration comparing to its lower amount.
- In the experiments where the effect of solution pH on Al-WTR performance was determined, it was found that pH (4, 5, 6) has a little effect on adsorption of phosphorus from lake water. No significant differences were observed in terms of percentage removal of phosphorous under experimental conditions with controlled pH and free-drifted pH (without control).
- In the presence of various concentration of phosphorous in treated water observed changes of total nitrogen concentration within the 180 mins of the process were similar. All tested doses (2, 5, 10 mg/L initial phosphorus concentration) had no effect on nitrogen removal from simulated lake water.
- The amount of organic matter in treated water varied depending on initial concentration of phosphorus. It was found that the DOC increased during the process and after 3 hours of contact time its concentration was significantly higher than at the beginning. Most probably a certain amount of organic matter was in the composition of tested adsorbent and was released into the solution.
- In general, comparing results obtained in the adsorption tests with use of Al-WTR with the efficiency of other low-cost materials like for example fly ashes, it can be concluded that aluminium sludge shows the superior stability in terms of pH, conductivity and is effective in phosphorus removal.
- Al-based WTR adsorbent is a promising material and due to the fact that the water in Finland is faintly acidic, the application of aluminium sludge can be a useful method to decrease eutrophication in lakes.
- It is recommended to do further experiments to explore the optimum temperature for the adsorption of phosphorus on aluminium sludge. Then it would be possible to correctly assess whether tested aluminium-based water treatment residues can be applied in real conditions.

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