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REMOVAL OF PHOSPHO-RUS FROM AQUATIC ENVI-RONMENT ONTO WOOD-BASED FLY ASH

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THESIS
Abstract

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Abstract

Lake eutrophication is a water pollution phenomenon caused by the excessive content of nitrogen and phosphorus and is a serious environmental problem, both in Finland and China. Therefore, fundamental aspects related to eutrophication of natural waters are addressed in the presented work.
In this thesis, the efficiency of phosphorus removal from natural lake water was analysed. As an adsorbent, the wood-based fly ash was utilised. Laboratory experiments were performed with various process parameters to determine the optimum conditions of phosphorus removal and to verify the adsorbent suitability for treatment nutrient-rich waters and wastewaters. Specifically, tests with different fly ash dose, the initial concentration of phosphorus and various solution pH were conducted using the jar-test method. Removal of nitrogen and DOC by fly ash was also examined.

Keywords: Lake eutrophication, Phosphorus, Nitrogen, Fly ash

CONTENTS

1   LITERATURE REVIEW

1.1   Eutrophication – stages and environmental impact.

Lake eutrophication is a water pollution phenomenon caused by excessive nutrient content, including nitrogen and phosphorus.
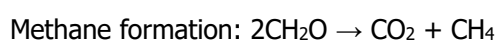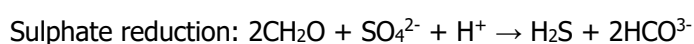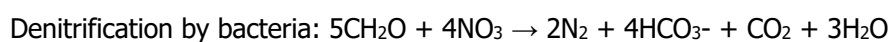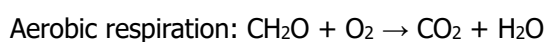
Eutrophication is a dynamic process and is an indication of the functions and structures of aquatic biological life and their adaptation to new changes arising in the water environment. Four main stages of eutrophication are briefly described below (Browne, 2011).

The first process is triggered by the increase of excessive nutrients level above regular concentrations in the ecosystem. In the second stage, an escalation of biological productivity, leads to the production and overgrowth of aquatic plants and algae. A thick layer of floating algae is formed.

The third phase corresponds to the death and decomposition of algae and aquatic plants at the bottom of the water body. During this phase, the oxygen content is depleted and eventually, is used up as decomposition of biomass accelerates. Anaerobic conditions appear in the water, leading to denitrification, followed by sulphate reduction. Hydrogen sulphide (H_2S) is formed as waste by sulphate-reducing bacteria.

The fourth stage is manifested by the continuous supply of water with nutrients and further degradation of water quality. The release of H_2S and ammonia contributes to the process because nutrients are prevented from settling down.

Several chemical reactions brought about by anoxic conditions in waters are as follows (CH_2O signifies decomposing of organic matter):

Aerobic respiration: $CH_2O + O_2 \rightarrow CO_2 + H_2O$

Denitrification by bacteria: $5CH_2O + 4NO_3 \rightarrow 2N_2 + 4HCO_3- + CO_2 + 3H_2O$

Sulphate reduction: $2CH_2O + SO_4^{2-} + H^+ \rightarrow H_2S + 2HCO^{3-}$

Methane formation: $2CH_2O \rightarrow CO_2 + CH_4$

Iron reduction: $CH_2O + 7CO_2 + 4Fe(OH)_3 \rightarrow 4Fe^{2+} + 8HCO^{3-} + 3H_2O$

The negative influence of eutrophication on lakes condition is a serious environmental problem around the world. The transparency of water is reduced, thus the sunlight penetrating the water layer is limited, what affects the plants' photosynthesis under the water and the release of oxygen. At the same time, plankton blooms rapidly and consumes a large amount of oxygen, causing a serious shortage of dissolved oxygen in the water and harmful conditions for aquatic animals (mainly fish). The organic materials piled up at the bottom of eutrophic water bodies will decompose and emerge harmful gases in anaerobic condition. Some of the plankton will produce biological toxins as well.

Additionally, nitrite and nitrate may occur in eutrophic water bodies which are problematic at concentrations above accepted standards.

1.2   The present situation of eutrophication of Chinese lakes.

In Finland, the main way for phosphorus to enter the water environment is the agriculture. Finland is a country of cold weather with short growing season. Some north-west European countries such as Norway, Sweden, United Kingdom and Ireland also have deal with unfavourable weather. Therefore, in Finland plenty of fertilizers of many kinds contains phosphorus are wildly used to enhance the growth of crops. Losses of total phosphorus (P) vary from 0.1 to 2.0 kg ha^{-1} year^{-1} and are largest in catchments with clay soils. This may lead to the overgrowth of algae in receiving lakes and their eutrophication.

The issues leading to destruction of aquatic ecological balance are different in China than in European countries. The total amount of fresh water resources in China is about $28000*10^8$ m^3, which accounts for 6% of the global water resources. However, due to the large population, China's per capita water resource is only 2300 m^3 - it is ¼ of the world's per capita and 121st in the world ranking, which positions China as one of the countries with the lowest per capita water resource in the world.

China is also a country of numerous lakes. There are more than 2700 lakes, covering an area of more than 91,000 km^2. One third of Chinses lakes are shallow and are located mainly on the east coast (middle and lower reaches Yangtze river). According to the survey data and evaluation of lake eutrophication indexes, among the 37 major lakes in China, mesotrophic and rich in nutrient lakes are accounting for 55.8%, eutrophic lakes are accounting for 14.7% and serious eutrophic lakes are accounting for 8.8%. Among them, the Dian lake (in Yunnan Province) is severely eutrophic lake and its water quality belongs to class V or inferior V. Besides, the Taihu lake (in Jiangsu Province) and the Chaohu lake (in Anhui Province) are eutrophic lakes. Therefore, the problem of eutrophication of urban lakes in China is a serious problem need to be solved.

Nitrogen and phosphorus are the main elements which in excessive amounts may lead to eutrophication. Therefore, the removal of these contaminants has an important role in controlling eutrophication process.

1.2.1 Case-study - Taihu Lake, China.

Taihu Lake is located on the south edge of the Yangtze river delta and is one of the five largest freshwater lakes in China. Taihu Lake covers an area of 2427.8 km^2, with a water area of 2338.1 km^2. The coastline of the lake is 393.2 km and its west and south-west sides are the hilly mountains, and the east side is dominated by plain and water network. Taihu Lake is in the subtropical zone where the climate is mild and humid. It is a monsoon climate with many estuaries. There are more than 50 rivers flowing in and out. The water of Taihu Lake is flowing from west to east, with an average annual runoff of 7500 m^3 and a storage capacity of 4400 m^3.

Taihu Lake is presented in Figure 1.

Figure 1. Picture of Taihu Lake (Baidu picture).

The Water Environment Monitoring Centre of Taihu Lake conducted water resource quality monitoring for the lake and the water body of the south-eastern river basin from January 2 to 12, 2018. In January 2018, the value of average total nitrogen index of Taihu Lake indicated V class of water quality, total phosphorus index was for class IV, the other indexes were typical for class III or better than class III. The nutritional status was moderate eutrophication. According to the Surface Water Environmental Quality Standard (GB3838-2002), the water quality of the whole Taihu Lake belongs to class V according to the worst index.

According to the representative area, 0.3% of the Taihu waters are class III, 18.8% are type IV, 27.8% are class V, 53.1% are worse than class V, 31.4% waters exhibit slight eutrophication, 68.6% waters exhibit moderate eutrophication. Values of Taihu Lake main water quality index are: the average concentration of permanganate index of 4.57 mg/L and ammonia nitrogen of 0.17 mg/L.

Values of Taihu Lake nutritional status evaluation index are: the average concentration of total nitrogen of 0.091 mg/L, total phosphorus of 1.87 mg/L and chlorophyll of 21.1.mg/L (Bulletin of Taihu Lake basin and water resources of River southeast of provincial quality status, 2018).

Comparison of Taihu Lake water quality with the same period in 2017, reveals similar water quality. In 2018, the total phosphorus and permanganate index increased, concentration of ammonia nitrogen and chlorophyll decreased, total nitrogen concentration remained the same, slight eutrophication area decreased, and moderate eutrophication area increased.

The main factors affecting water quality of Taihu Lake are:

- Agricultural pollution. The amount of chemical fertilizers and pesticides used in agriculture, year by year is increasing gradually, leading to increase of nitrogen and phosphorus content in the water body.
- Pollution of the aquaculture industry and livestock. After the large-scale industrial development in the 1990s, many aquaculture farms were settle in this area as well as livestock farms were built around Taihu Lake. However, these farms discharged directly their wastewater into the lake without any treatment, contributing to the contamination of Taihu Lake.
- Pollution of industrial and urban sewage. Because of the geographical location of Taihu Lake, many businesses decide to build factories on the bank of the Taihu Lake. Additionally, Taihu area

is densely populated, therefore apart from industrial effluents also domestic sewage is a reason of eutrophication problem.

- Tourism. The booming tourism industry is also one of the factors that lead to eutrophication of Taihu Lake. The beautiful scenery of Taihu Lake attracts tourism and therefore, a lot of resorts, restaurants, hotels and other facilities have been built around the lake. The discharge of domestic wastewater, without proper treatment, caused that the degree of eutrophication in Taihu Lake has increased.

- Secondary pollution. The secondary pollution by sediment is the source of internal pollution in Taihu Lake. According to a comprehensive investigation, the sediment of Taihu Lake has reached 1.9 billion m^3, an average thickness is 0.28 m and covering 68%. The release of sediment nutrient can cause eutrophication of water body of Taihu Lake.

1.3   Phosphorus – forms and sources.

In natural waters, phosphorus is present in different forms which can be transformed into one another. Most of the suspended phosphorus (including organic and inorganic states) can be found in the remains of bacteria, animal, and plants. The dissolved phosphorus is present in various forms of orthophosphate such as PO_4^{3-}, HPO_4^{2-} and $H_2PO_4^-$ which can be absorbed by algae as nutrients. Researchers also shown that the compound and organophosphorus in soluble orthophosphates and sediments are easily absorbed by algae.

The phosphorus in water bodies can be divided into exogenous and endogenous phosphorus. The source of exogenous phosphorus includes precipitation, runoff, anthropogenic emissions and so on. Endogenous phosphorus refers to the phosphorus from the interior of the water, which is caused by surface runoff aggregation, sewage discharge and the deposition of aquatic organisms in water bodies.

Phosphorus has different forms in the lake water. There are two main forms: suspended phosphorus (including organic and inorganic states) and dissolved phosphorus (orthophosphate such as PO_4^{3-}, HPO_4^{2-} and $H_2PO_4^-$).

Table 1. General properties of phosphorus (Wikipedia, Phosphorus).

Phosphorus, ^{15}P	
Appearance	Colourless, waxy white, yellow, scarlet, red, violet, black
Standard atomic weight ($A_{r,standard}$)	30.973 761 998(5)
Abundance (in the Earth's crust)	5.2 (taking silicon as 100)
Atomic number	15
Phase (at STP)	Solid
Crystal structure	Body-centred cubic (bcc)

Phosphorus in water bodies comes from:

- Rainwater. The concentration of phosphorus in rainwater is in the range of 0.01 mg/L to unde-tectable which has little effect on lake water pollution.
- Agricultural drainage. Due to the use of agricultural phosphorus fertilizer, quite large amount of nutrients is accumulated in the soil and enter the natural waters with runoff from farmland. Be-sides, the waste produced by livestock also contains a considerable amount of nutrients which can be drained into the adjacent water.
- Municipal sewage. The main sources of phosphorus are faecal, food residues, and synthetic de-tergents.
- Other sources. These include runoff from towns and villages, industrial wastewater, and so on.

1.4 Phosphorus removal methods.

There are several treatment techniques available for phosphorus removal from water or wastewater:

- chemical precipitation - the basic principle of this method is to add chemicals into water to pre-cipitate phosphate in an insoluble form and then remove it from water by solid-liquid separation,
- biological treatment - this method is used to remove phosphorus from organic wastewater,
- adsorption - the removal of soluble form of phosphorus is possible due to usage of porous adsor-bents, additionally ion exchange or surface precipitation of the surface of the adsorbent may occure.
- other methods, including electrolytic process, membrane separation, spray drying process (Jiang, et al. 2011).

There are also many different phosphorus removal methods utilized when non-point nutrient source is considered and they have been described below.

1.4.1 Constructed wetland method.

Constructed wetland manmade system characterized by emergent aquatic vegetation (reed is most popular used plant), which aimed at stimulating the wastewater treatment in a form of lake (non-point pollution water).

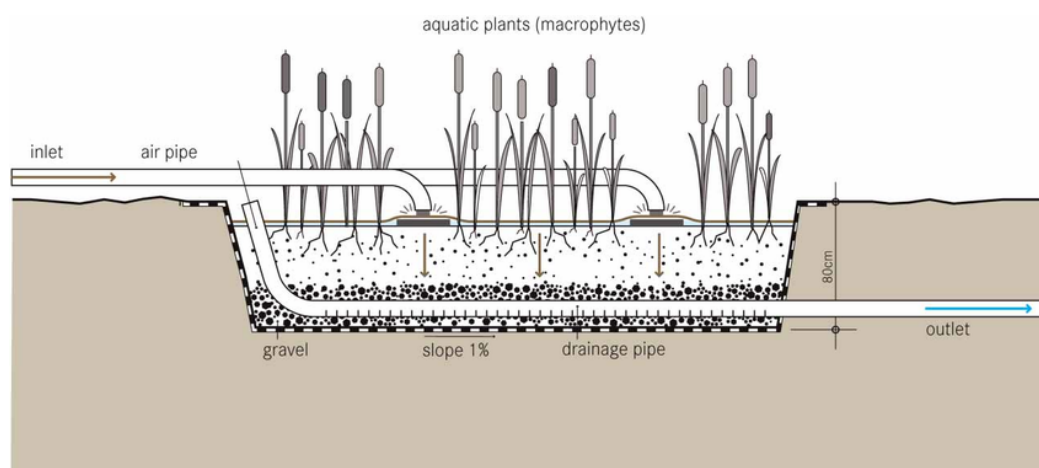Figure 2 shows an example of the vertical flow constructed wetland system.

Figure 2. The vertical flow constructed wetland system (Tilley, et al. 2008).

This process gives a good results in terms of phosphorus removal in both wastewater treatment and non-point nutrient source. In theory, constructed wetland method is a combination of plant absorption, adsorption, filtration and microbial transformation. All microorganisms which are attached growth and suspended forms can absorb and in the process of growth, they make use of inorganic phosphate present in wastewater.

Some studies have shown that the phosphorus of wetland ecosystem is mainly trapped in the soil, rarely in plants and leaves and only a handful of aquatic plants can absorb phosphorus. The abilities of phosphorus absorption by plant roots of most species is very weak and not effective. Thus, the most important process is the phosphorus adsorption and precipitation of the substrate.

The phosphorus removal rate in wetland is generally low, between 40-60%. Therefore, the filter matrix selection plays an important role in improving the efficiency of phosphorus removal. Currently, the common matrix is pumice, sand, active porous media, silica fume, industrial waste, high slag, lime, etc. (Cooke, et al. 2005). Constructed wetland is one of the most promising technologies which can be implemented in developing countries, due to their properties like utilization of natural processes, simple construction, simple operation and maintenance, process stability, cost effectiveness, etc. (Zhen 2002).

1.4.2 Pre-dams method.

Pre-dams are commonly used in North America, especially in United States, to protect downstream reservoirs from nutrients and silt. Pre-dams may also protect water supplies from accidental or purposeful spills of toxic or radioactive materials. Figure 3 shows the Lake Shasta behind Shasta Dam in Northern California.

Figure 3. The Lake Shasta behind Shasta Dam in Northern California (Photo copyright Lee Foster).

Pre-dams normally have a surface overflow plus a deep gate to allow remove water and sediment. They function primarily through sedimentation of particulates, and nutrient removal occurs by maximizing diatom growth and sedimentation while minimizing blooms of buoyant cyanobacteria and algae-grazing Daphnia (to prevent remineralization). Effectiveness depends upon retention time, with short times preventing significant settling of particulate phosphorus. The optimum design of a pre-dam for nutrient retention includes a mean depth that is not significantly greater than euphotic zone depth to prevent internal phosphorus loading common in dimictic lakes.

A primary problem of the pre-dam is that unless it is constructed at the same time as the main reservoir, a retro-fit may be impossible because land may be unavailable or may be too small in area (Cooke, et al. 2005).

1.4.3 Riparian zone rehabilitation method.

The riparian zone is the "gradient-dominated" community between stream or lake and the land, and it has major influences on water quality. The riparian zone has these functions: (1) reduce surface and sub-surface runoff volume, (2) protect banks from erosion, and (3) lower pollutant concentrations in runoff.

Figure 4 shows the example of the vegetated buffer zone between land development and the stream.

Figure 4. The vegetated buffer zone (Flowing Water and Riparian Habitats).

Creating a vegetated buffer zone between land development and the stream provides stream protection by intercepting nutrients and sediments and assists in restoring lost biodiversity. The effectiveness of a buffer zone can be reduced when there are irregular contours that concentrate runoff area and lower buffer zone area in contact with most of the runoff. While buffer zone width is important, the amount of impervious area, human and livestock impacts, slope, and inspection and maintenance, also determine effectiveness (Cooke, et al. 2005).

1.5 Nitrogen.

In addition to phosphorus, nitrogen is also a very important nutrient in water. There are different forms of nitrogen in the aquatic environment such as a molecular nitrogen, organic nitrogen, ammonia nitrogen, nitrate nitrogen, sulphur cyanide, cyanide, etc. Among all mentioned above, the ammonia nitrogen is one of the most important form of nitrogen. Ammonia nitrogen is present in industrial wastewater and when entering water, especially the lake or gulf of relatively slow flow, can cause the mass reproduction of algae and other microorganisms leading to water eutrophication. Some general properties of nitrogen are shown in table 2.

Table 2. General properties of nitrogen (Wikipedia, Nitrogen).

Nitrogen,$_7$N	
Appearance	Colourless gas, liquid or solid
Standard atomic weight ($A_{r,standard}$)	[14.006 43, 14.007 28] conventional: 14.007
Atomic number	7
Phase (at STP)	Gas
Density (at STP)	1.2504 g/L at 0 °C, 1013 mbar
Crystal structure	Hexagonal

Nitrogen deposited in aquatic ecosystems from the atmosphere has several origins, including releasing gases from agriculture and burning of fossil fuels. Combustion releases significant quantities of fixed nitrogen into the atmosphere, both from the oxidation of organic nitrogen stored in the fossil fuels and from the fixation of molecular N_2 during high-temperature, high-pressure combustion.

1.6 Nitrogen removal methods.

In wastewater treatment, there are many methods which are used for nitrogen removals such as biological nitrification and denitrification, zeolite selective exchange adsorption, air stripping and breakpoint chlorination (Xu, 2009).

There are also many different nitrogen removal methods utilized when non-point nutrient source is considered. They include landscape management, agricultural nitrogen management and atmospheric deposition.

1.6.1 Landscape management.

Riparian (shoreline) vegetation can significantly reduce non-point nutrient flows to surface waters. This vegetation also makes important contributions to fish and wildlife habitat and regional biodiversity. Wetlands, lakes and rivers are sites of denitrification (conversion of NO_3 to atmospheric N_2) that decrease the flow of nitrogen to downstream ecosystems. Restoration of wetlands and floodplains is likely to increase denitrification at a landscape scale, thereby reducing nitrogen pollution of aquatic

systems to some extent. Wetland restoration may be the most cost-effective method of decreasing non-point nitrogen pollution (Carpenter, et al. 1998).

1.6.2 Agricultural nitrogen management.

The ultimate causes of non-point pollution from agricultural lands are excessive fertilizer use and high-density livestock operations. There are direct solutions. Fertilizer application can be reduced to match crop needs. Wastes from high-density livestock operations can be managed as a point source of pollution. Nutrients in manure can be used as fertilizer, or nutrients can be removed (as in sewage treatment) before wastes are discharged to surface waters. Nitrogen runoff can be greatly reduced if nutrients are applied at rates that match their uptake by crops and if fertilizers are applied when crops are growing rapidly. Also, transport of nitrogen to surface waters by erosion and runoff may be reduced by riparian zones, buffer strips, conservation tillage, terracing, contour tillage, cover crops, and retention ponds (Carpenter, et al. 1998).

1.6.3 Atmospheric deposition.

Atmospheric deposition of nitrogen can be reduced by more efficient use of fertilizers and improved handling of animal wastes. Thus, steps needed to reduce surface transport of agricultural nitrogen will also reduce atmospheric transport. Reductions in fossil fuel combustion and improved interception of NO_3 from fossil fuel combustion will also decrease atmospheric deposition of nitrogen (Carpenter, et al. 1998).

1.7 Fly ash.

Fly ash, also known as "pulverized fuel ash", is a coal combustion product that is composed of the particulates (fine particles of fuel) that are driven out of coal-fired boilers together with the flue gases. Fly ash is a by-product of power generation in coal-fired power stations. Within a power station, coal is fed to a series of mills that pulverize the coal to a very fine powder. This powder is then fed into a boiler which combusts the coal to produce heat, that is then used to produce steam required for power generation. During the coal combustion process, minerals in the coal fuse form glassy aluminosilicate spheres. These spheres remain in suspension within the flue gas from the boiler and are ultimately collected downstream by either electrostatic or mechanical precipitation.

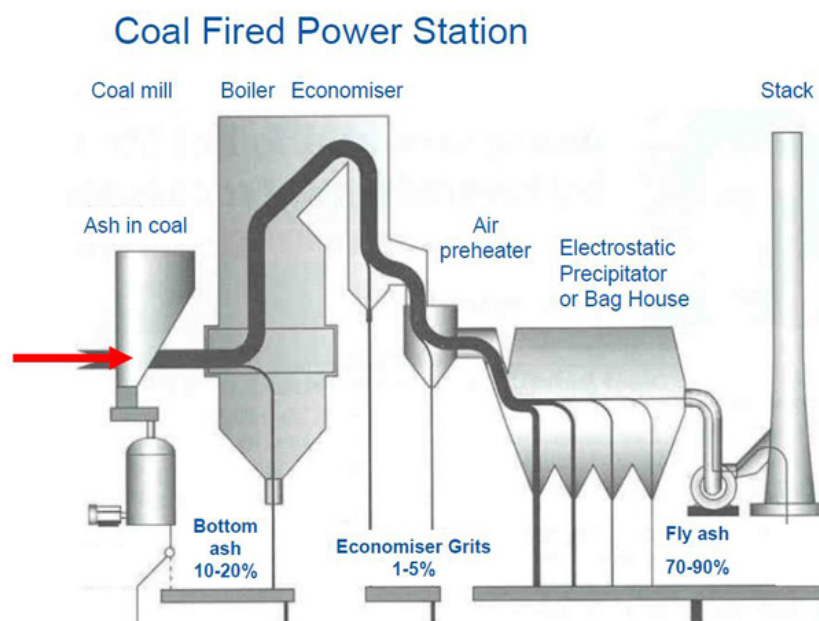Figure 5 shows the process of producing fly ash at a power station.

Figure 5. The production process of fly ash at a power station (fly ash Australia).

Depending upon the source and makeup of the coal being burned, the components of fly ash vary significantly but all fly ash includes substantial amounts of silicon dioxide (SiO_2) (both amorphous and crystalline), aluminium oxide (Al_2O_3) and calcium oxide (CaO).

Figure 6 shows fly ash particles at magnification 2000x (photomicrograph made with a Scanning Electron Microscope.
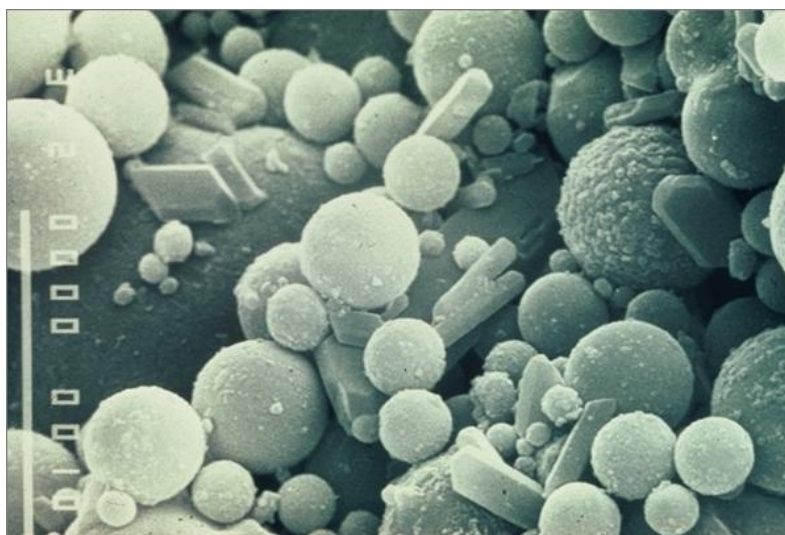
Figure 6. Fly ash particles at 2000x magnification (fly ash Australia).

The usage of fly ash has many advantages in different area, i.e. economy, environment, etc. Around one third of EU municipal waste was sent to landfill in 2012. To turn waste into a resource, waste management objectives must be aligned with the goals of a circular economy transition. However, fly ash is an economic material. It comes from one of the biggest sources of air pollution and carbon dioxide emissions on Earth, and yet it's considered to be a green material. However, regulation labelling fly ash as hazardous waste are currently under discussion between the EPA and the power industry.

According to statistics, with the completion the operation of large coal-fired power plants, the output of fly ash has increased by an average of 15% per year, and the proportion of industrial solid waste has reached 60%. At present, China's fly ash is mainly used for building materials, construction and road engineering. Fly ash, being a waste by-product, is of no or negligible cost. Thus, replacing a portion of cement with fly ash in cement concrete saves the cost. It's utilisation in concrete is its indirect input to the environment.

Production of ordinary Portland cement (OPC) contributes to greenhouse effect due to substantial emission of carbon dioxide. The greater the use of fly ash in concrete, the lesser the production of OPC is, thus the smaller the carbon emission is observed. So, this ensures reduced contribution to the serious greenhouse problem. The comprehensive utilization rate of fly ash in China has increased from 35% in 1994 to 68% in 2011. The remaining fly ash is stacked and abandoned, causing environmental pollution and occupying large number of cultivated lands (Jiang, et al. 2011). The utilization rate of fly ash in Finland, Denmark, Japan and other countries has reached over 80%.

1.8 Fly ash – properties and application.

The physical and chemical properties of fly ash are related to the mineral composition, combustion mode and dust collecting way of fuel.

The composition of fly ash from different power plants differs significantly, depending on the composition and combination of various particles.

SiO_2 and Al_2O_3 mainly exist in the Al-rich vitreous body of fly ash. Besides, fly ash contains a small amount of Fe_2O_3, CuO, MgO, Na_2O and other compounds. Sometimes, it also has relatively high amount of CaO, unburned carbon, no altered minerals (such as quartz) and other debris. In addition, a small number of particles, such as zeolite and activated carbon, can be also found in the composition of fly ash. The fly ash surface is porous structure due to the glass particles which contain many irregular shapes and different numbers of small bubbles. The density of fly ash is 1.9~2.9 g/cm^3. The bulk density is 0.531~1.261 g/cm^3. The void ratio is 60~75%. The specific surface area of fly ash measured by nitrogen adsorption method is 800~19500 cm^2/g (particle sizes range from a few hundred microns to a few microns). Fly ash has certain surface energy because the surface atomic force of fly ash is unsaturated. Fly ash particles of very small size are mostly made up of clear glass spheres. Spongy particles formed either by fusion of many fine particles or from ore particles (common in most fly ashes). The clear glass spheres are smaller than other particles and have a high specific surface area while the spongy particles are larger and generally of a low specific surface area. About 60% of the particles in the ash have diameter less than 3 microns. However, these particles constitute less than 10% of the total weight.

Fly ash can be successfully applied to the treatment of wastewater, especially organic wastewater, ammonia nitrogen wastewater, dye wastewater, domestic sewage and wastewater contains heavy metals.

The arbitrary emission of nitrogen and phosphorus wastewater will lead to great number of algae and other plants in the water and finally to the eutrophication of the water body. The eutrophic water contains a large amount of nitrate and nitrite, which seriously endangers human health for a long time.

When the fly ash is introduced into water at pH value is between 10- 3, then in such alkaline conditions it has a negatively charged surface, what enhanced the removal of some toxic metal anions by precipitation or electrostatic adsorption.

Fly ash can also be used as agricultural fertilizer and soil amendment. Fly ash has good physical and chemical properties which can be widely used in the transformation of heavy clay, soil, acidic soil and saline soil. It can make up the defects of the thin acid sticky board. Fly ash contains large amounts of water-soluble calcium, magnesium, and phosphorus which are necessary nutrient elements for crops. It can be used as agricultural fertilizer.

Fly ash can be also used as a raw material for papermaking, for example it is used in Germany and Denmark (Jiang, et al. 2011).

2 MATERIALS AND METHODS

2.1 Materials.

2.1.1 Chemicals and adsorbents.

1. Phosphorous stock solution of 1000 mg/L; used chemical K_2HPO_4
2. Nitrogen stock solution of 1000 mg/L; used chemical NH_4Cl
3. 1 mol/L solution of HCl (for pH control & total nitrogen determination)
4. 1 mol/L solution of NaOH (for pH control)
5. Biochar (Mikkeli RKP Hiili Oy)
6. Fly ash - sample 3 (Wood fuel; Pielavesi, LK106)
7. Lake water

2.1.2 Equipment.

1. Laboratory scale
2. HQ11D Digital pH-meter with pH gel electrode (Hach Lange)
3. HQ14D Digital conductivity-meter with conductivity cell (Hach Lange)
4. Jar test apparatus
5. Spectrophotometer DR6000 Benchtop (Hach Lange)
6. Digital Thermostats HT200S (Hach Lange)
7. TOC analyser: multi N/C® 2100/2100S (analytik jena)
8. Shaker: New Brunswick™ Innova® 40, Innova® 40/40R, 230 V/50 Hz, orbit diameter 1.9 cm (3/4 in)
9. LCK Cuvette Tests for phosphorus (Hach Lange):

    LCK 349 test (0.05–1.50 mg/L PO_4-P)

    LCK 348 test (0.5–5.0 mg/L PO_4-P)

    LCK 350 test (2.0–20.0 mg/L PO_4-P)
10. Other lab equipment (syringes, syringe-driven filters (0.45 μm), probes, beakers, conical flasks, pipette, volumetric flasks)

2.2 Methods.

2.2.1 Jar Testing.

Jar testing is a method of simulating a full-scale water treatment process, providing system operators an idea how applied chemical will behave and perform. Because it mimics full-scale operation, system operators can use jar testing to determine which treatment chemical will give best treatment results. Jar test device used during the laboratory work is shown in Figure 7.
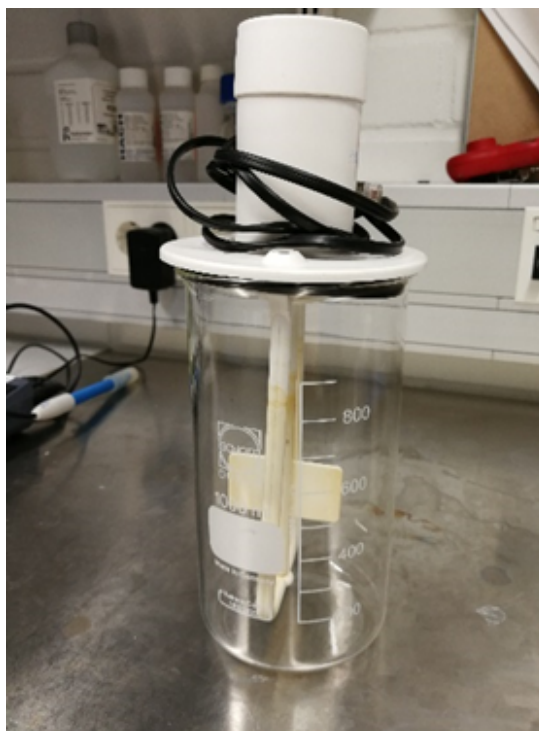
Figure 7. Jar test unit used in the study

The general procedure of laboratory experiments with jar test was as following:

1. Filling the transparent jars with the 850 mLl of lake water using a 1000 mL graduate cylinder.
2. Spike the prepared lake water sample with required amount of P-stock solution and N-stock solution.
3. Close the jar with lid (the lid had a stirrer with the paddles) and connect the jar to the controller.
4. Mix the prepared water sample for 30 seconds.
5. Stop mixing and collect 50 mL of the water sample for determination of initial water quality parameters.
6. Add the accurate amount of fly ash (0.5 g – 2 g) into jars contain 800 mL of prepared water.
7. Fix the filled jars on the gang stirrer with the paddles positioned identically in each beaker.
8. Start mixing and run the process for 180 minutes.
9. During the test collect the samples in various time intervals.
10. After 180 mins stop mixing. Wait for a while until particles have settled down in jars and determine the final pH and conductivity.
11. Remove the jars from the gang stirrer, empty the contents and thoroughly clean the beakers.

2.2.2 Analysing the variable conditions.

The efficiency of tested fly ash was analysed under different operating conditions. The kinetic tests were performed with various adsorbent dose, initial concentration of phosphorous and solution pH. The tests conditions were as followed:

1. 1A kinetic tests – to determine the effect of adsorbent dose on process efficiency: initial phosphorus concentration of 1 mg/L, initial nitrogen concentration of 2 mg/L and different doses of fly ash (0.5 g/L, 1 g/L, 2 g/L).

2. 1B kinetic tests – to determine the influence of different initial concentration of phosphorous on process efficiency: the fly ash dose of 1 g/L, initial nitrogen concentration of 2 mg/L and different initial phosphorus concentration (1 mg/L, 2 mg/L, 5 mg/L).

3. 1C kinetic tests – to determine the influence of different pH on phosphorus removal: fly ash dose of 1 g/L, initial phosphorus concentration of 2 mg/L, initial nitrogen concentration of 2 mg/L and different pH (5, 6, 8) maintained constant during the process.

3   EXPERIMENTAL RESULTS AND DATA ANALYSIS

3.1   Testing of biochar – preliminary results.

The 12.5 g/L of biochar (added 10.0104 g biochar into 800 mL water) was used for treatment the lake water sample contains 2 mg/L of P. The test was conducted for 3 hours and samples were collected after 5, 10, 20, 30, 60, 120 and 180 mins. In collected samples the phosphorus concentration was measured using the LCK350 test.

The following figures showed the percentage removal of phosphorus by fly ash and its adsorption capacity.
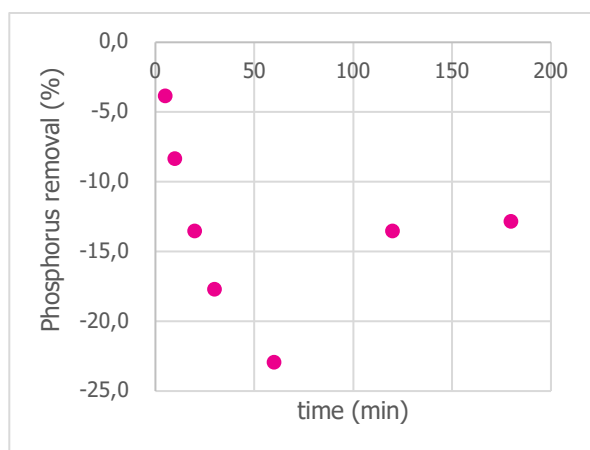

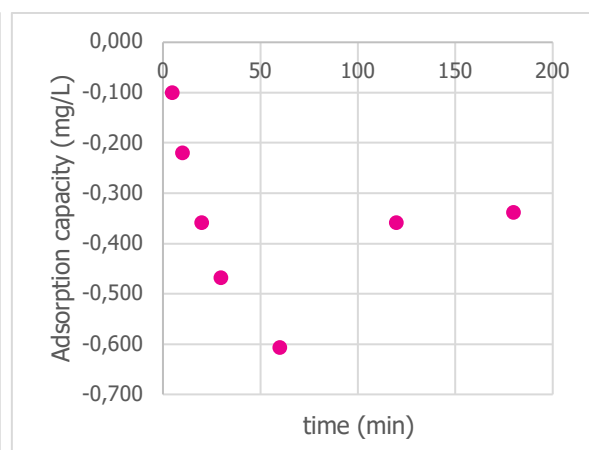Figure 8. Effect of phosphorus removal by biochar.   Figure 9. Adsorption capacity of biochar.

It was observed that the percent of phosphorus removal and the calculated adsorption capacity are below 0. This indicate that the tested biochar didn't adsorb phosphorus from treated water but it released some amount into the water sample. The initial phosphorus concentration was 2.66 mg/L, but after 180 mins of contact time, the final phosphorus concentration increased to 3.00 mg/L. It was observed that during the first 60 mins the release was increasing constantly and reached the maximum value of 3.27 mg/L. After one hour of contact time the amount of phosphorous in solution decreased what can suggest that after intense releasing the slow removal process takes place. The conclusion is that the biochar was not a suitable material for phosphorus removal. Probably, this type of biochar was very fresh and not cleaned, so it released phosphorus during the contact with the solution. Therefore, the laboratory experiments with biochar as an adsorbent were terminated.

3.2   Testing the fly ash.

Different series of kinetics tests with fly ash were performed. Briefly, experiments included tests with 3 different amount of fly ash (test 1A), 3 different initial phosphorus concentration (1B) and 3 different solution pH (1C). Detail information on analysed variable condition are given at point 2.2.2. Chapter 6 showed obtained experimental results.

3.2.1 Test 1A – effect of adsorbent dose.

The experimental data obtained within the test 1A are listed in tables 3-6 and presented on figures 10 and 11.

Table 3. Results from kinetic tests with fly ash dose1 of 0.5 g/L.

1A Adsorbent dose1 (0.5 g/L): 0.4070 g/800 mL; initial phosphorus: 1.07 mg/L				
Time(min)	pH	$T_{pH}(°C)$	cond(μs/cm)	$T_{cond}(°C)$
Initial test	7.00	19.6	77	19.6
5	11.29	19.8	/	
10	11.39	19.6		
20	11.43	19.6		
30	11.43	20.8		
60	11.44	20.5		
120	11.27	21.7		
180	11.06	21.6		
Final test	11.09	21.3	503	21.3

Table 4. Results from kinetic tests with fly ash dose2 of 1 g/L.

1A Adsorbent dose2 (1g/L): 0.8057 g/800 mL; initial phosphorus: 1.12 mg/L				
Time(min)	pH	$T_{pH}(°C)$	cond(μs/cm)	$T_{cond}(°C)$
Initial test	6.92	20.7	77.6	20.6
5	11.66	20.8	/	
10	11.74	20.0		
20	11.76	20.0		
30	11.77	20.1		
60	11.80	20.7		
120	11.60	21.0		
180	11.65	21.5		
Final test	11.68	21.5	1131	21.5

Table 5. Results from kinetic tests with fly ash dose3 of 2 g/L.

1A Adsorbent dose3 (2 g/L): 1.6060 g/800 mL; initial phosphorus: 1.13 mg/L				
Time(min)	pH	$T_{pH}(°C)$	cond(μs/cm)	$T_{cond}(°C)$
Initial test	7.11	20.5	80.3	20.5
5	12.00	20.8	/	
10	12.11	20.8		
20	12.13	20.8		
30	12.13	20.7		
60	12.10	22.0		
120	12.08	22.1		
180	12.05	22.1		
Final test	12.07	21.7	2550	21.8

Dose4 of fly ash is the same as dose2, but to find out the optimum amount of adsorbent for the 1B test, test with dose4 was conducted to verify the correctness of results.

Table 6. Results from kinetic tests with fly ash dose4 of 1 g/L.

1A Adsorbent dose4 (1g/L): 0.8030 g/800 mL; initial phosphorus: 1.13 mg/L				
Time(min)	pH	$T_{pH}(°C)$	cond(μs/cm)	$T_{cond}(°C)$
Initial test	7.84	21.3	77.7	21.5
5	11.68	21.2		
10	11.79	21.3		
20	11.83	21.3		
30	11.84	21.3	/	
60	11.86	21.3		
120	11.83	21.6		
180	11.78	21.7		
Final test	11.78	21.5	1222	21.6

Figure 10 showed the comparison of phosphorus removal by various amount of applied fly ash (dose 1, 2, 3, 4).
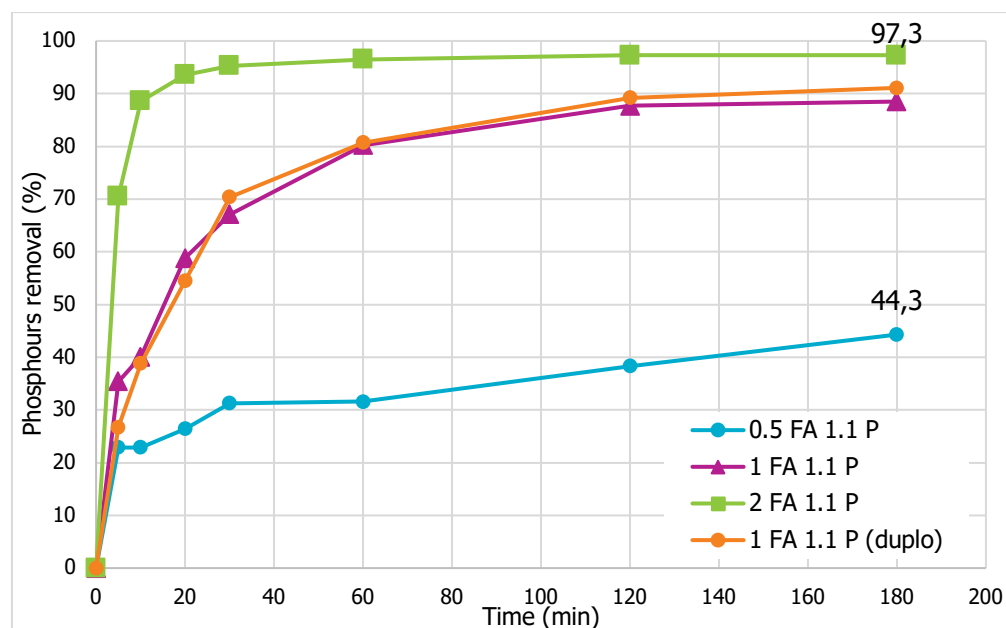

Figure 10. Comparison of phosphorus removal by fly ash – effect of adsorbent dose.

In Figure 10, the green curve (2 FA 1.1 P) represents the highest phosphorus removal (97.3%) and the blue one (0.5 FA 1.1 P) is the lowest (44.3%). According to the data, the difference between the process efficiency performed with smaller amount of fly ash (0.5 g/L) and the higher dose (2 g/L) is 53%. Hence it is not difficult to conclude that with the fixed phosphorus concentration (1.1 mg/L P), the more fly ash is added, the higher phosphorus removal is obtained. Besides, the fastest removal (green curve; dose 2 g/L) is in the first 20 minutes. After this time, the process slow down and no significant changes in phosphorous removal are observed. In case of 1 g/L of adsorbent (purple curve;

1 FA 1.1 P and the orange curve; 1 FA 1.1 P duplo) the adsorption is much slower and after one hour of contact time curves become stable. But generally, the longer contact time gives better results and the concentration of phosphorous decreases to a greater or lesser extent in case of all tested doses of fly ash.

Figure 11 showed the comparison of calculated adsorption capacity of fly ash for phosphorus - dose 1, 2, 3 & 4.
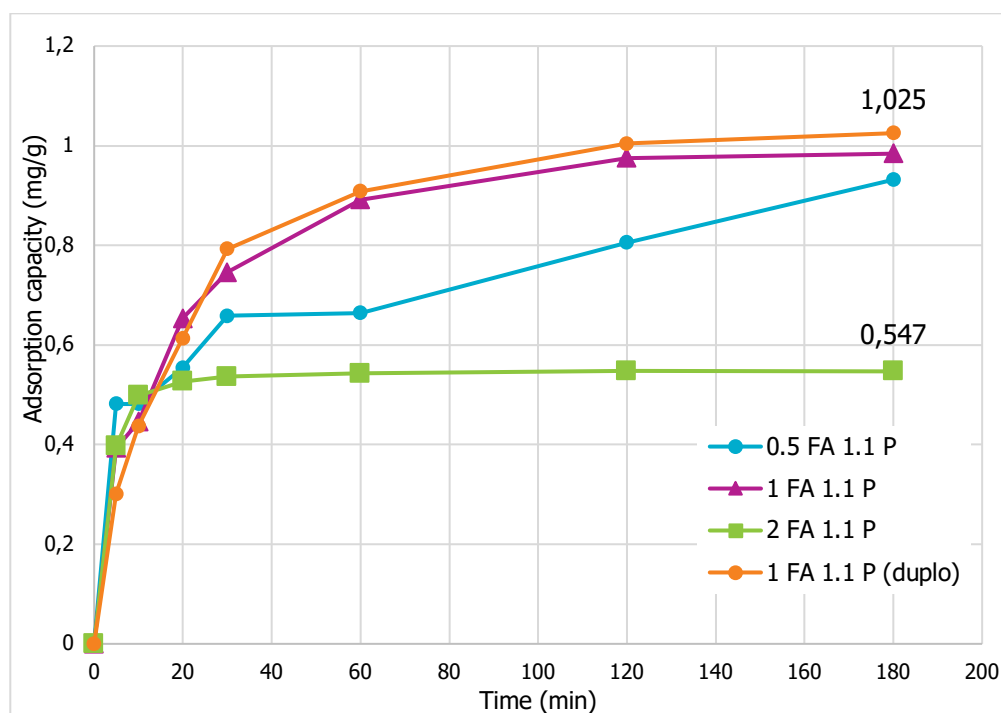

Figure 11. Comparison of adsorption capacity of fly ash for phosphorus – effect of adsorbent dose.

In Figure 11, the calculated adsorption capacities for tested 1 g/L of adsorbent (orange curve; 1 FA 1.1 P duplo and purple curve; 1 FA 1.1 P) are quite similar and give the highest value. In case of the largest amount of fly ash dosed into the treated water (2 g/L), the adsorption capacity for phosphorous was 0.547 mg/g. The difference between the adsorption capacity of these two doses was 0.478 mg/g. Generally, for all tested doses, the most significant changes in adsorption capacity occurred in the first 30 minutes of the process. After that, process slow down and curves gradually going to the plateau. However, for the 2 g/L (green curve; 2 FA 1.1 P), the fastest adsorption was observed in the first 10 minutes; after that adsorbent has been almost completely saturated and no significant changes were recorded. Comparing the results obtained in the test 1A (Figure 10 & 11), it has been decided that the 1 g/L of fly ash will be the most suitable dose for the further experiments (1B, 1C) where other variables of the process are examined.

3.2.2 Test 1B – effect of initial phosphorous concentration.

The experimental data obtained within the test 1B are listed in tables 7-9 and presented on figures 12-13.

Table 7. Results from kinetic tests with initial phosphorous concentration C1 of 1.13 mg/L.

1B Initial concentration of phosphorus C1 = 1.13 mg/L; 0.8030 g fly ash/800 mL				
Time(min)	pH	T_{pH}(°C)	cond(μs/cm)	T_{cond}(°C)
Initial test	7.84	21.3	77.7	21.5
5	11.68	21.2		
10	11.79	21.3		
20	11.83	21.3		
30	11.84	21.3	/	
60	11.86	21.3		
120	11.83	21.6		
180	11.78	21.7		
Final test	11.78	21.5	1222	21.6

Table 8. Results from kinetic tests with initial phosphorous concentration C2 of 5.53 mg/L.

1B Initial concentration of phosphorus C2 = 5.53 mg/L; 0.8034 g fly ash/800 mL				
Time(min)	pH	T_{pH}(°C)	cond(μs/cm)	T_{cond}(°C)
Initial test	7.83	21.1	114.0	21.2
5	11.69	21.3		
10	11.71	21.3		
20	11.78	21.4		
30	11.81	21.3	/	
60	11.74	21.6		
120	11.72	21.8		
180	11.52	23.7		
Final test	11.63	22.6	1091	22.0

Table 9. Results from kinetic tests with initial phosphorous concentration C3 of 2.30 mg/L.

1B Initial concentration of phosphorus C3 = 2.30 mg/L; 0.8066 g fly ash/800 mL				
Time(min)	pH	T_{pH}(°C)	cond(µs/cm)	T_{cond}(°C)
Initial test	7.37	21.2	93.6	21.4
5	11.41	21,3	/	
10	11.60	21.6		
20	11.70	21.8		
30	11.73	21.9		
60	11.73	21.9		
120	12.23	22.6		
180	12.20	22.5		
Final test	12.21	22.3	1215	22.6

Figure 12 showed the comparison of phosphorus removal by fly ash – initial concentration C1, C2 and C3.
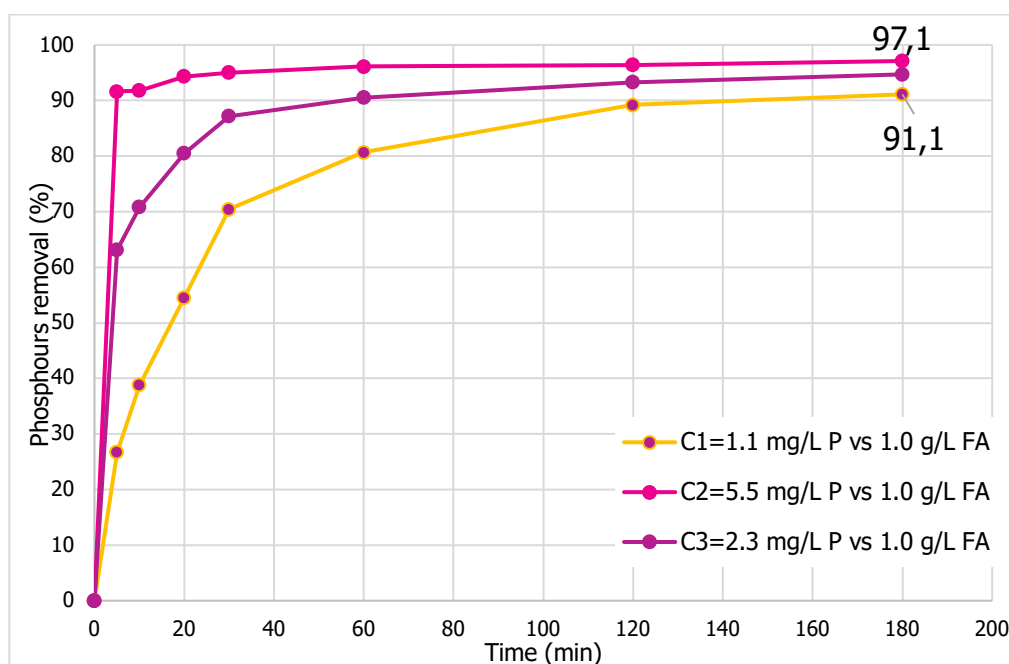

Figure 12. Comparison of phosphorus removal by fly ash – effect of initial P concentration.

In Figure 12, it can be seen, that the tested fly ash successfully removed phosphorus from simulated lake water with the efficiency of over 90%. The highest removal rate of phosphorous (97.1%) was obtained for its initial concentration of 5.5 mg/L (pink curve, 5.5 P vs 1 FA) while worst results (91.1%) were observed for its lowest concentration (yellow curve, 1.1 P vs 1 FA). After 180 minutes of contact time, for the same added amount of fly ash, difference between process efficiency for 1 mg/L and 5 mg/L of phosphorous was only 6%. The fastest removal rate of phosphorous was observed in the test with the highest initial concentration. In the first 5 minutes 91.6% of phosphorous was removed from treated water and after that the removal was significantly slower. In case of 2.3 mg/L (purple curve) and 1.1 mg/L (yellow curve) of phosphorus, the fastest changes were recorded in the first 30 minutes and after that gradual increase in the effectiveness of the process was observed.

Calculated adsorption capacity of fly ash for various phosphorus concentrations (C1, C2, C3) is shown in Figure 13.
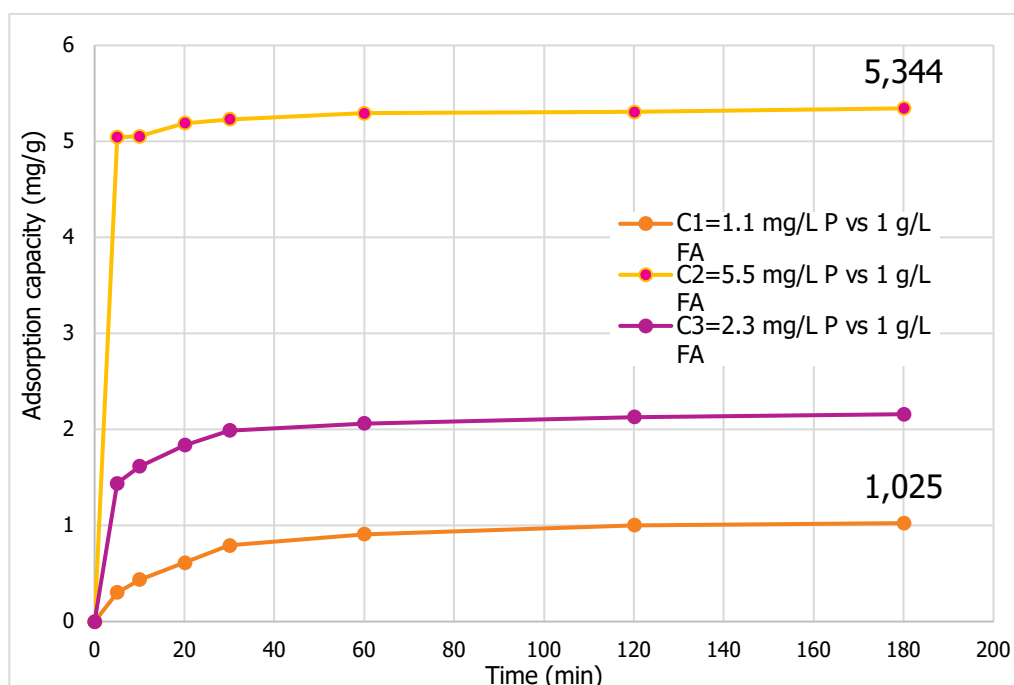

Figure 13. Comparison of adsorption capacity of fly ash for phosphorus – effect of initial phospho-rous concentration.

In Figure 13, it can be found that the adsorption capacity of fly ash depends on the initial concentration of phosphorous. For the same amount of adsorbent, the higher initial concentration of phosphorus resulted in higher value of calculated adsorption capacity, expressed as milligrams of phosphors ad-sorbed per gram of fly ash. Adsorption capacity of fly ash after 180 minutes of the process was 1.025 mg/g, 2.159 mg/g and 5.344 mg/g for initial amount of phosphorous of 1.1 mg/L, 2.3 mg/L and 5.5 mg/L, respectively. It was observed that for all initial phosphorous concentrations, fast removal was up to first 30 minutes of the process and then became almost constant, resulting in small changes in adsorption capacity of fly ash.

It has to be pointed out, that the adsorption capacity of fly ash was calculated in order to assess the usefulness of this material for treatment phosphorous-rich waters or wastewaters. However, the re-moval mechanism of phosphorus was not analyzed in this study. According to the available literature,

phosphate may be removed from water using fly ash due to adsorption and/or precipitation, but that which mechanism is dominant depends on solution pH and composition of fly ash (Lu et. all. 2009).

3.2.3 pH and conductivity – test 1A and 1B.

In Test 1A and 1B, the initial and final pH and conductivity were controlled and additionally changes of pH during the process were monitored. The specific data has been shown in Table 3-9.
Figure 14 shows the pH changes over time for Test 1A and 1B while Figure 15 shows the initial and final conductivity.
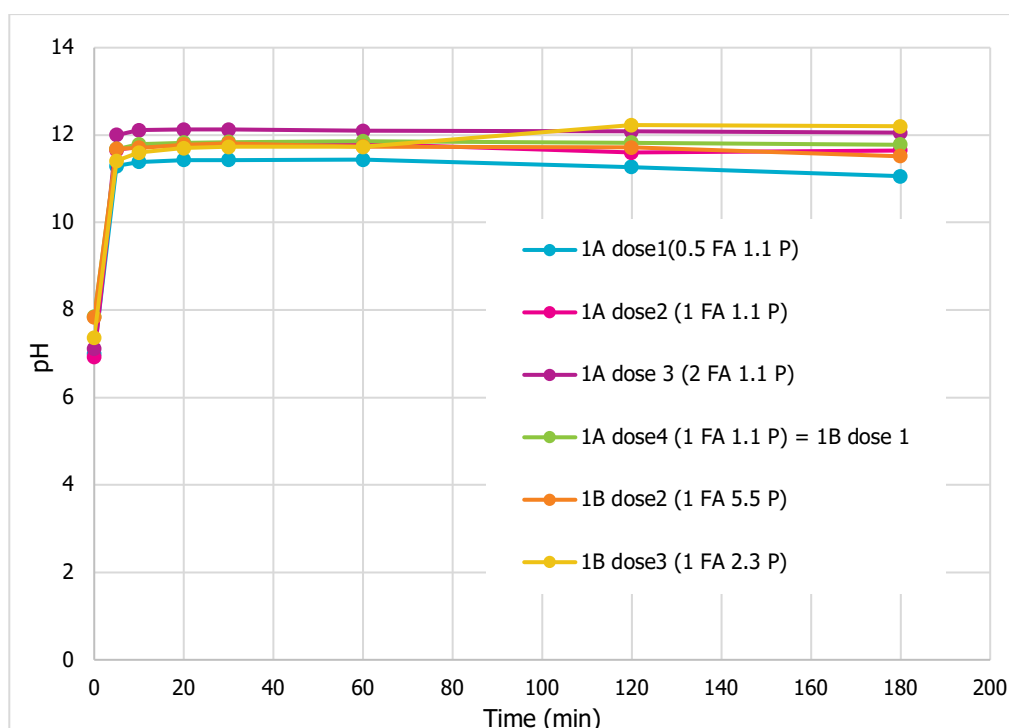

Figure 14. Changes of pH vs time for Test 1A and 1B.

From the Figure 14, it is evident that the changes of pH for all seven performed tests have similar pattern. Generally, within the first 5 minutes of the process the pH significantly jumped from its initial value of about 7-7.8 to above 12. The highest pH values were obtained for 2 g/L (purple curve) of fly ash which was the largest amount among the all tested adsorbent doses. Accordingly, for the smallest dose of adsorbent (0.5 g/L, blue curve) the lowest pH values were obtained. Observed changes of pH were mainly due to the various amount of fly ash used for treatment lake water. Thus, for three tests of experiment 1B where the same dose of adsorbent was added into the solution, only slight changes in pH were recording during the 180 minutes of the process. Obtained results indicate that the tested fly ash has a significant impact on solution pH. Moreover, the adsorbent is alkaline and may release a large amount of OH^- ions into the solution when it starts to adsorb phosphorus.

However, in the real situation (especially in Finland), farmland and streams are weakly acidic under natural conditions (pH 4.61 in 1973, pH 4.50 in 1978 and pH 4.66 in 1996). Therefore, this needs further analysis to confirm whether this fly ash will acceptably perform in real conditions.
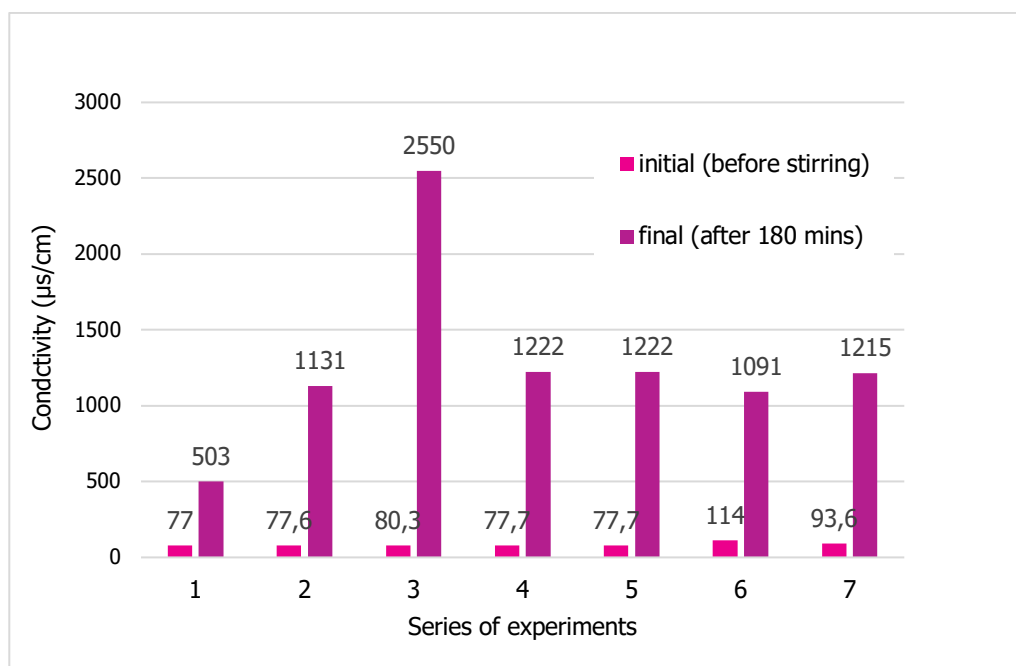
Figure 15. Initial conductivity (before stirring) and final (after 180 mins) for Test 1A and 1B.

From the Figure 15, the initial conductivity all simulated lake water sample was between 77 and 114 µS/cm. The final conductivity value varies from each other and the changes are related to the amount of adsorbent used in the experiment. Conductivity followed the similar pattern as observed in case of pH, i.e. the highest increased in conductivity was obtained for the highest tested dose of fly ash and for the smallest dose the lowest value of conductivity was recorded. Considering series 5-7 (Test 1B dose1, 2, 3), the final conductivity values were comparable, since the amount of fly ash used in the Test 1B was the same.

In the mixed water sample the fly ash is in the state of solid which can release various ions (impurities) into the solution and of course OH- ions (confirmed in tests which pH) what explained significant changes of conductivity.

3.2.4 Test 1C - effect of solution pH.

The pH is one of the most important factors influencing the efficiency of adsorption of various anions. Therefore, the effect of different initial pH on the phosphorous removal was studied. In Test 1C, the pH of treated water sample was adjusted to 5, 6 and 8 and the experimental data obtained within the test 1C are listed in tables 10-12 and presented on Figure 16-17.

Table 10. Results from kinetic tests with solution pH 6.0.

1C pH1 = 6; 2.73 mg/L phosphorus; 0.8085 g fly ash/800 mL				
Time(min)	pH	T_{pH}(°C)	cond(µs/cm)	T_{cond}(°C)
Initial test	6.80	20.6	87.7	21.2
5	6	/	/	
10				
20				
30				
60				
120				
180				
Final test	6.11	22.4	1597	22.5
Estimated HCl amount: 11 mL				

Table 11. Results from kinetic tests with solution pH 5.0.

1C pH2 = 5; 2.35 mg/L phosphorus; 0.8051 g fly ash/800 mL				
Time(min)	pH	T_{pH}(°C)	cond(µs/cm)	T_{cond}(°C)
Initial test	7.43	22.2	90.0	22.3
5	5	/	/	
10				
20				
30				
60				
120				
180				
Final test	4.90	22.9	1970	22.8
Estimated HCl amount: 15 mL				

Table 12. Results from kinetic tests with solution pH 8.0.

Time(min)	pH	$T_{pH}(°C)$	cond(μs/cm)	$T_{cond}(°C)$
1C pH3 = 8; 2.17 mg/L phosphorus; 0.8033 g fly ash/800 mL				
Initial test	7.04	21.3	93.1	22.0
5	8	/	/	
10				
20				
30				
60				
120				
180				
Final test	8.06	23.0	1245	23.0
Estimated HCl amount: 6.5 mL				

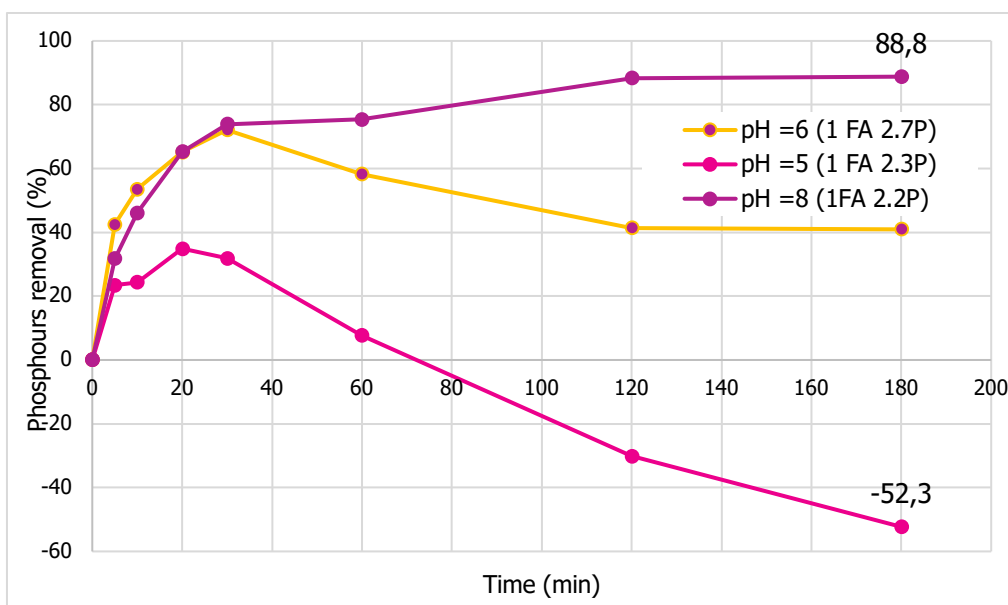Figure 16 shows the comparison of phosphorus removal in test 1C at pH=5, 6 and 8.

Figure 16. Comparison of phosphorus removal by fly ash – effect of pH.

Figure 16 presents data from the experiment where pH was adjusted at the beginning of the test and controlled during 180 minutes. It can be seen, that fixed dose of fly ash can efficiently remove phosphorus (up to 89%) under weakly alkaline conditions (pH 8). At pH 6 and 5 the fly ash was able to remove phosphorous in about 65% and 35%, respectively within first 20 minutes, but after this time the efficiency gradually decreased. However, the observed drop in percentage removal resulted in negative values in test with pH 5. At the (weakly)acidic conditions, the most probably fly ash released a certain amount of phosphorous into the water sample increasing concentration above its initial value. Considering that in Finland almost all of the farmlands and streams are weakly acidic (pH about 4-5), the tested fly ash is not suitable to apply in real natural conditions.

Calculated adsorption capacity of fly ash for various pH values (5, 6, 8) is shown in Figure 17.
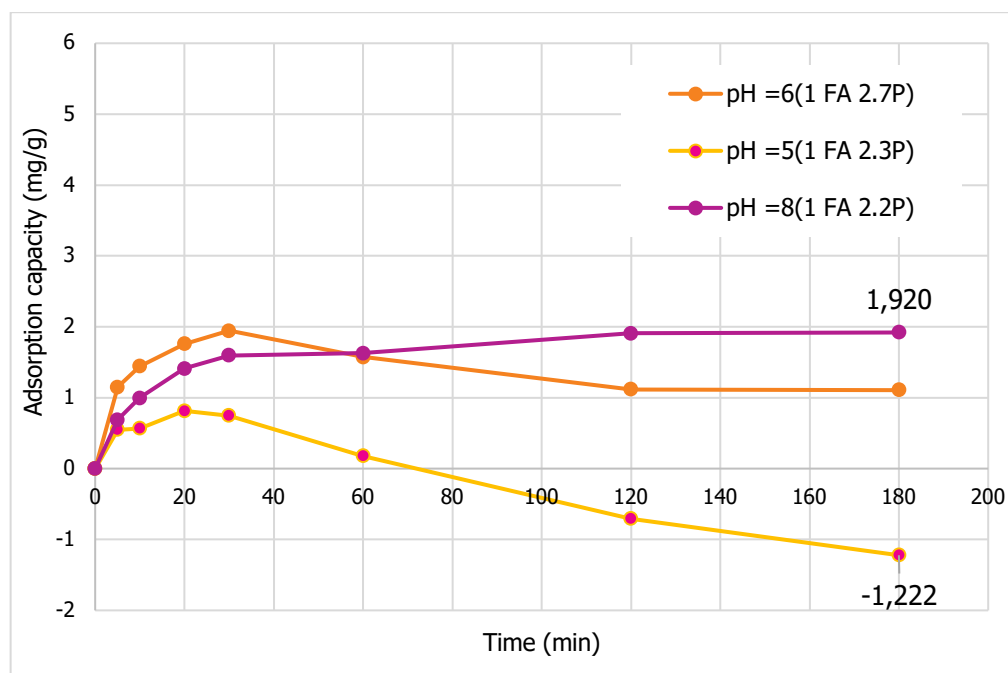

Figure 17. Comparison of adsorption capacity of fly ash for phosphorus – effect of pH.

It has been confirmed that the pH affects the adsorption capacity of tested fly ash, as shown in Figure 17. For the fixed amount of adsorbent and the same initial concentration of phosphorus, the maximal adsorption capacity varied from the negative value (for pH 5) to nearly 2 mg/g (for pH 8). The adsorption capacity of fly ash calculated with the use of results from experiments with pH 5 and 6 is initially increasing with time and then is showing a declining trend. For the test performed under weakly acidic conditions, after one hour of the process the adsorption capacity of fly ash for phosphorous was negative. Therefore, in order to correctly discuss the observed tendency, the composition of fly ash as well as the removal mechanism of phosphorous from aqueous solutions should be studied (but it is not an aim of this work).

3.3   Nitrogen adsorption results and analysis.

Knowing from the literature that the fly ash has a potential to remove nitrogen and organic matter from water, the additional studies were performed to verify its ability. The samples collected in Test 1B were analysed in terms of

dissolved organic carbon (DOC) and total nitrogen (Tot-N).

Dissolved organic carbon, sometimes known as dissolved organic matter, is a broad classification for organic molecules of varied origin and composition within aquatic systems. Quite often the term "dissolved" is used for compounds below 0.45 micro meters. In case of nitrogen, there are three forms commonly measured in water or wastewater samples: ammonia, nitrates and nitrites, but in the present study only total nitrogen was analysed.

Figure 18 shows the DOC results obtained from test 1B (1.1 FA 1.1P/ 5.5P/ 2.3P) while Figure 19 presents the changes in Tot-N (1.1 FA 1.1P/ 5.5P/ 2.3P).
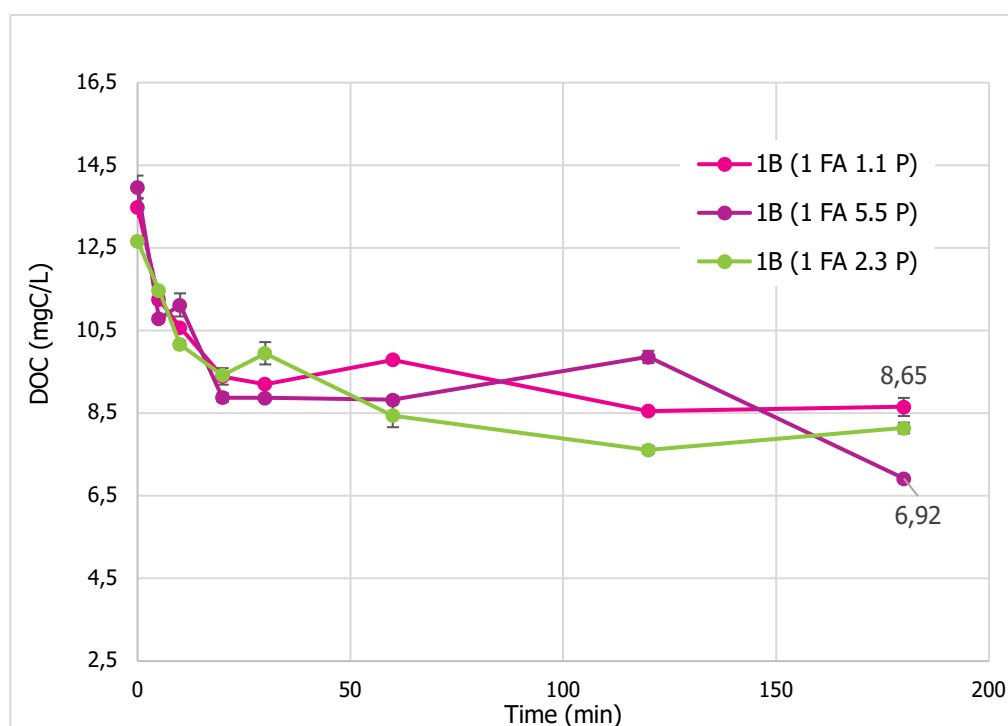

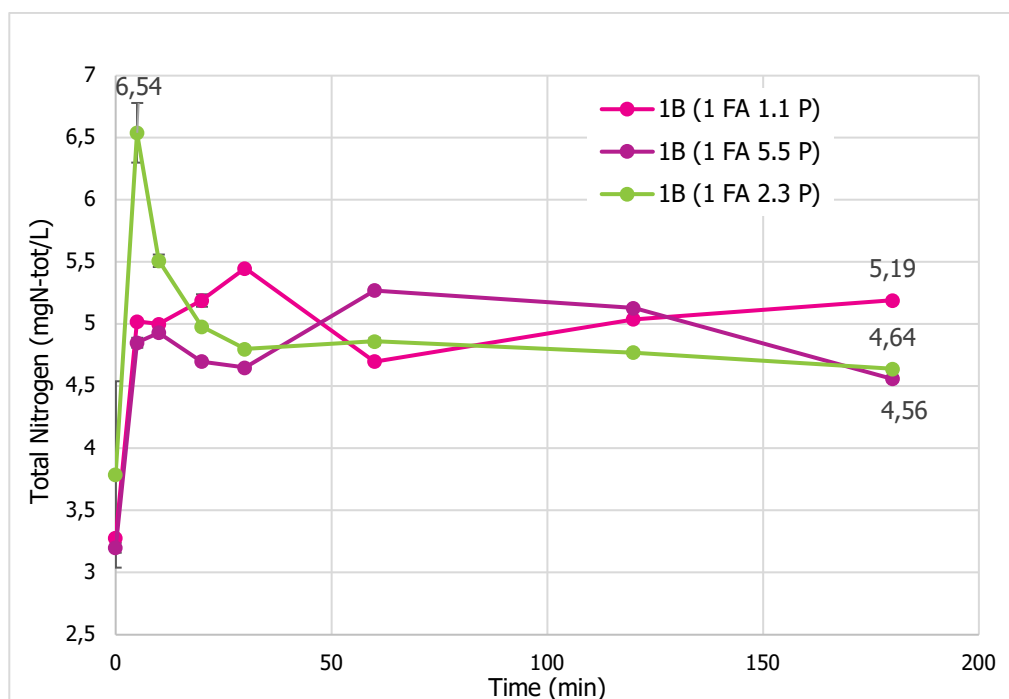Figure 18. Effect of DOC removal by fly ash - Test 1B.

Figure 19. Effect of total nitrogen removal by fly ash - Test 1B.

From Figure 19, it can be found that fly ash has a good performance in removal of DOC from treated lake water, regardless the initial concentration of phosphorous. The content of dissolved organic matter was significantly reduced from its initial concentration of 12.66-13.97 mgC/L to 6.92-8.65 mgC/L within the 3 hours of treatment process. Based on obtained results it may be concluded that the tested fly ash has a great potential and can be also successfully used for organic matter removal from water or wastewater.

In case of nitrogen, it can be noticed that its concentration in treated water samples increased with time. In general, the similar trend is observed for all tested initial concentrations of phosphorous, i.e. the sudden jump of total nitrogen is observed in the first 5 minutes of the process and then the changes in nitrogen concentration are quite stable. In the presence of 1.1, 2.3 and 5.5 mg/L of phosphorous in treated water, the nitrogen content increased from about 3.2-3.8 mg/L to 5.19 mg/L, 4.56 mg/L and 4.56 mg/L, respectively.

In contrast to DOC, the tested fly ash hasn't shown good nitrogen removal ability under applied experimental conditions. Therefore, to correctly assess the potential of fly ash in nitrogen removal different process conditions should be explored as well.

4   CONCLUSIONS

1. From Test 1A, it can be concluded that with the fixed initial phosphorus concentration (1.1 mg/L P), its higher removal is obtained when the higher adsorbent dose is applied. Fly ash shows fast phosphorus removal in the first 30 minutes. After this time, the process slow down and no significant changes in phosphorus removal are observed. As the process continue, the concentration of phosphorus in the solution began to decrease and the reaction rate gradually slowed down. After 2h of contact time, most of the phosphorus was adsorbed by fly ash, and the adsorption equilibrium was basically reached within 3h of the process. Fly ash dose of 1 g/L was the most suitable dose for Test 1B and 1C.

2. From Test 1B, with the fixed amount of fly ash, the adsorption capacity increases with the increase of initial phosphorus concentration. Among them, the final removal rate of 5.5 mg/L of phosphorus reached 97.1%. Consequently, the best phosphorus adsorption capacity was recorded and one gram of fly ash was able to adsorbed 5.344 mg of phosphorus under given experimental conditions. It can be found that the tested fly ash successfully removed phosphorus from simulated lake water with the efficiency of over 90%. It was observed that for all initial phosphorous concentrations, fast removal was up to first 30 minutes of the process and then became almost constant, resulting in small changes in adsorption capacity of tested fly ash. In this experiment, the adsorption capacity of fly ash was calculated in order to assess the usefulness of this material for treatment phosphorous-rich waters or wastewaters (the removal mechanism of phosphorus was not analysed).

3. From Test 1C, in the weakly acid environment, the removal effect of phosphorus decreased with the decrease of solution pH (at pH=5, adsorbent begins to release phosphorus into the solution). In the weakly alkaline environment, fly ash has a better adsorption capacity for phosphorus. The tested fly ash shows a good phosphorus removal ability (up to 98%) and a high phosphorus adsorption capacity under pH value of about 11-12. In order to correctly discuss the observed trend, the composition of fly ash as well as the removal mechanism of phosphorous from aqueous solutions should be studied in the future.

4. The nitrogen adsorption test indicates that tested fly ash wasn't a good adsorbent for removal of nitrogen from the solution under experimental conditions and further research should be conducted to optimise the process efficiency. However, better performance in terms of organic matter was recorded.

8. REFERENCES

Benefits of fly ash; Available from: http://civilconstructionresourcez.word-press.com/2012/09/25/benefits-of-fly-ash/ [Accessed on April 2018]

Boqiang Qin (2007), The Causes of the Occurrence of Eutrophication in Taihu Lake and the Counter-measures, China Forum on environment and development, 2007; Available from: Cnki http://www.cnki.net [Accessed on April 2018]

Dissolved organic carbon (DOC), Wikipedia, Available from: https://en.wikipedia.org/wiki/Dissolved_organic_carbon [Accessed on March 2018]

Encyclopaedia; Taihu Lake (Jiangsu lake). Available from: https://baike.baidu.com/item/%E5%A4%AA%E6%B9%96/112298?fr=aladdin [Accessed on March 2018]

Finnish Environment Institute, Water quality of lakes, rivers and sea areas in Finland in 2000-2003, Available from: http://www.environment.fi/waterquality. [Accessed on March 2018]

G. Dennis Cooke, Eugene B. Welch, Spencer A. Peterson, Stanley A. Nichols (2005), Restoration and Management of Lakes and Reservoirs [Accessed on May 2018]

Guangxi Eia Technology Development co. LTD; The Application of Biochar- ozone Combined Treatment Process in Reclaimed Water Treatment, Frontiers of Architectural Research, No.8, 2017; Available from: https://www.chinaking.com [Accessed on March 2018]

He Xu; Adviser: Zhou Lei, Huang Zhi Ping, An Overview of Ammonia Removal Methods in Water(2009), Chinese People's Liberation Army Anti-chemical Command Engineering College, Available from: https://mr.baidu.com/ylgxfmv [Accessed on March 2018]

Hot Topic Hour Mcllvaine Presentation; (2012), Presentation: FLY ASH PONDS AND WASTE WATER TREATMEN, T, Time: 03.05.2012, Available from: http://www.mcilvainecompany.com/Decision_Tree/subscriber/Tree/DescriptionTextLinks/Naomi%20Levy%20-%20Infilco%20Degremont%20-%205-3-12.pdf [Accessed on April 2018]

Hu Xiao Zhen (2002), Ecological Engineering Techniques Ffor Lake Restoration Iin Japan (Oct. 29th, 2001—Apr. 27th, 2002) [Accessed on April 2018]

Jiang L, Chen J Y, Li X M, et al. (2011), Adsorption pf phosphate from wastewater by fly ash ceramsite. Acta Scientiae Circumstantiae, 31(7): 1413-1420 [Accessed on March 2018]

Jiang Xutao; Adviser: Chi Jie(2013), Study on the Ad-sorption of Ammonia and Phosphate by Biochar,Department of Environmental Science and Engineering, Tianjin University [Accessed on March 2018]

K. Kyllmar , L. Stjernman Forsberg, S. Andersson, K. Mårtensson(2014), Small agricultural monitoring catchments in Sweden repre-senting environmental impact, Department of Soil and Environment, Swedish University of Agricultural Sciences, P.O. Box 7014, Uppsala SE-750 07, Sweden, Available from: www.elsevier.com/locate/ag [Accessed on April 2018]

Li Wei (2011), The Application of Biomass Char-coal in the Environment, Available from: https://mr.baidu.com/i8h7mbp [Accessed on March 2018]

Liang Ming; (2007), Research on Principle and Control of Eutrophication for City Lakes Polluted by Outer Source, Journal of Wuhan University Of Technology. Vol 29, No.8, Aug. 2007, Available from: https://mr.baidu.com/axvmoms [Accessed on April 2018]

Lu, S.G., Bai, S.Q., Zhu, L., Shan, H.D. (2009). Removal mechanism of phosphate from aqueous solution by fly ash, Journal of Hazardous Materials, 161, 95-101.
Mats Åström, Robert Sundström, Maria Holmberg, Karl-Erik Storberg (2005), pH of streams in western Finland – a perspective from the Middle Ages into the mid -21st century, Available from: https://www.researchgate.net/publication/242730819_pH_of_streams_in_western_Finland_-_A_perspective_from_the_Middle_Ages_into_the_mid_21st_century [Accessed on March 2018]

Nhat Trung Nguyen; (2015), Adsorption of Phosphorus from Wastewater onto Biochar: Batch and Fixed-bed Column Studies, Helsinki Metropolia University of Applied Sciences [Accessed on March 2018]

Obemah D. Nartey and Baowei Zhao; Biochar Preparation, Characterization, and Adsorptive Capacity and Its Effect on Bioavailability of Contaminants: An Overview [Accessed on March 2018]

S. R. Carpenter N. F. Caraco D. L. Correll R. W. Howarth A. N. Sharpley V. H. Smith; (1998), Non-point Pollution of Surface Waters with Phosphorus and Nitrogen, Available from: https://doi.org/10.1890/1051-0761(1998)008[0559:NPOSWW]2.0.CO;2 [Accessed on May 2018]

SNF Holding Company, Procedure for Laboratory Jar Test. Available from: http://www.snf.us. [Accessed on April 2018]

Swedish University of Agricultural Sciences (2007), Division of Water Quality Management, Box 7014, SE 750 07 Uppsala, Sweden [Accessed on March 2018],

Tang Chaochun, Liu Ming, Chen Huimin, Shao Penghui and Jian Meipeng (2014), Research Progress in Adsorbing Phosphorus Removal Technology, Vol.40 No.9, September, 2014, TECHNOLOGY OF WATER TREATMENT,East China Jiaotong University Civil Architecture College, Nanchang of Jiangxi Province, Available from: http://www.cnki.net [Accessed on April 2018]

The effect of fly ash in water treatment, Available from: http://www.xzbu.com/8/view-4409710.htm [Accessed on April 2018]

Total nitrogen, Available from: https://www.epa.gov/sites/production/files/2015-09/documents/totalnitrogen.pdf [Accessed on May 2018]

Ville Mattika (2017) - Finland is a country of thou-sands of lakes — (Utilising social media in project work 2017-09-18 – 2018-01-15). Background information for Project work [Accessed on March 2018]

Wei Suo (2018), Bulletin of Taihu Lake basin and water resources of River southeast of provincial quality status,Economic Daily, 28.02.2018, Available from: http://www.xinhuanet.com/energy/2018-02/28/c_1122463555.htm [Accessed on April 2018]

Wikipedia - Fly ash. Available from: https://en.wikipedia.org/wiki/Fly_ash [Accessed on March 2018]

Zheng Guanghong, Qiao Junlian, Gu Guowei, Xu Yifei and Shen Yang (2003), Treatment of Dyeing Wastewater by Hydrolysis-contact oxidation- biocar-bon Technology, Vol.23, No.10, October 2003, Industrial Water Treatment [Accessed on March 2018]

ZHU Guangwei, JIN Yingwei, REN Jie, XIA Mingfang, XU Hai, ZHU Mengyuan, FEI Guosong& CHEN Weimin; J. (2016), Characteristics of diatom blooms in a reservoir-water supply area and the countermeasures in Taihu Basin，China; Lake Sci. 2016，28(1): 9-21, DOI 10. 18307 /2016. 0102; 2016 by Journal of Lake Sciences [Accessed on April 2018]