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TECHNOLOGY, COMMUNICATION AND TRANSPORT

TREATMENT OF PHOSPHORUS-RICH WATER BY FLY-ASH MATERIAL

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Abstract The excessive amount of nutrients – nitrogen and phosphorus, in the aquatic environment can lead to the rapid growth of plants and algae. As a consequence, the eutrophication of the water body can occur, which is an ageing phenomenon and is usually observed in lakes, reservoirs and some rivers. The eutrophication of water is a serious environmental problem and may affect various industrial sectors, agriculture as well as tourism. In the study, the treatment efficiency of phosphorus-rich water by fly ash was examined. The wood fly ash was collected from Kiuruvesi in Finland (the outdoor stack of district heating plant) and utilized in jar-test experiments. To determine the ability of fly ash for phosphorus removal, various process conditions were tested, including fly ash dose, initial concentration of phosphorus and solution pH. Additionally, the efficiency of nitrogen and DOC removal was analysed.			
Keywords Phosphorus, Nitrogen, Fly ash, Eutrophication			

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1. LITERATURE REVIEW

1.1. Eutrophication phenomenon and potential hazards.

The abnormal reproduction and growth of various aquatic organisms and plants are caused by the discharge of excess nutrients (i.e. nitrogen and phosphorus) in natural water bodies. This phenomenon is called water eutrophication [1]. These excess nutrients are derived from farmland fertilization, agricultural waste, municipal sewage and some industrial wastewater. Nitrogen is divided into two kinds: organic nitrogen and inorganic nitrogen. Organic nitrogen compounds include such as protein, polypeptide, amino acid and urea, while ammonia nitrogen and nitrate nitrogen refer to inorganic nitrogen. Most of these compounds come directly from sewage, but some are formed by the decomposition and transformation of organic nitrogen by the microorganism [2]. The use of phosphorus detergents as well as the excessive usage of fertilizers, is the source of nitrogen, phosphorus and other nutrients into the water body. It is considered that the water body is in the state of eutrophication, when total phosphorus and inorganic nitrogen is 20 mg/ m^3 and 300 mg/m^3 , respectively. The key of eutrophication is not the concentration of nutrients, but continuous load of the nutrients into the water body. Therefore, the eutrophication level of water cannot be determined entirely according to the concentration of nutrients in the water. The critical load between the poor nutrient lake and the eutrophic lake is: the total phosphorus of 0.05 g/m^2 every year and total nitrogen of $5\text{-}10 \text{ g/m}^2$ every year [3].

The role of phosphorus is far greater than the effect of nitrogen, which can cause eutrophication when the phosphorus content is not very high [4]. In the normal circulation of natural substances, lakes will develop from poor nutrient lakes to eutrophic lakes, and further into swamps and dry lands; but this process needs to be developed. In natural conditions, it takes tens of thousands of years or even hundreds of thousands of years, while the eutrophication caused by water pollution will significantly speed up this process. If plant nutrients such as nitrogen and phosphorus enter a large and continuous stream of water in lakes, reservoirs or bay, it promotes the activity of various aquatic organisms leading to serious consequences [3].

Eutrophication phenomenon may severely affect the quality of the water body. Then, it can be observed that the reduction of the water transparency makes sunlight difficult to penetrate the water layer, affecting the photosynthesis of plants in the water. As well, it may be a reason of the supersaturated state of dissolved oxygen, and as a consequence of extinction of aquatic animals.

At the same time, algae with cyanobacteria and green algae, as the dominant species, grow on the surface of eutrophic water bodies and form a layer of "green scum", resulting in decomposition of harmful gases and some of the organic matter that accumulates under the anaerobic conditions.

Eutrophic water also contains nitrates and nitrites, which in a high concentrations and long-term consumption are dangerous for livestock and human health [5].

The eutrophication of water will accelerate the shrinking of lakes and convert them into swamps. If a large number of plant nutrients such as nitrogen and phosphorus enter the lakes, reservoirs, bays, etc., they will enhance the activity of various aquatic organisms and stimulate their abnormal reproduction (mainly algae). Then, algae start occupying more and more space in the water and reducing the free space for fish movement [6].

Overgrowth and growth of algae will cause drastic changes in dissolved oxygen as well. The respiration of algae and the decomposition of dead algae consume large amounts of oxygen, which may cause the water to be in a state of severe hypoxia within a certain period of time, seriously affecting the survival of fish. In the absence of oxygen, they are decomposed by some microorganisms and produce harmful gases such as methane and hydrogen sulphide. Already mentioned, nitrites and nitrates will occur in such conditions as well [7].

Once water eutrophication occurs, water cannot be used directly by humans and animals. The eutrophication not only affects utilization of water bodies and causes the financial losses in fisheries but also is troublesome because of restoration [1].

1.2. Nutrients – phosphorus and nitrogen.

Phosphorus is an essential element for many biological processes. Phosphorus is the main component of nucleic acid, cell membrane and bone. High energy phosphoric acid is transferred reversibly between adenosine two phosphoric acid (ADP) and adenosine three phosphoric acid (ATP). It is the energy of all biochemical functions in the cells. Phosphorus does not exist in any form of gas compounds, so phosphorus is a typical sedimentary cycle material [8].

Nitrogen is an element in variable valence state (from positive five to negative trivalent). In the polluted surface water and underground water body, there are mainly ionic states of NH_4^+ -N, NO_3^- -N, NO_2^- -N, gaseous NH_3 , N_2 , N_2O , and one organic nitrogen in organic matter. In ionic nitrogen compounds, although the NO_2^- -N content is always less than the highest concentration of NO_3^- -N or NH_4^+ -N, however, from the chemical and environmental toxicity of NO_2^- -N, the presence of micro amounts of NO_2^- -N is usually considered as an important nitrogen pollution sign [9].

The factors related to nitrogen pollution in water environment are extensive and complex. Sources of nitrogen pollution include urban domestic sewage, nitrogen-containing industrial wastewater, and farmland nitrogen fertilizer. The effects of urban sewage and nitrogen-containing industrial wastewater on the nitrogen contamination of water environment (especially the nitrogen pollution in the surface water) are obvious, but the extent of the impact is mainly determined by [9]:

- (1) the form and content of nitrogen compounds in nitrogen containing sewage,
- (2) the emission intensity of nitrogen-containing sewage,
- (3) the purity of the water.

1.3. Point sources of pollution.

Excessive amount of nutrients, including phosphorous and nitrogen, in the lake can lead to the rapid growth of plants and algae in the water resulting in oxygen depletion. This is one of the reasons why the eutrophication phenomenon in the lake environment may occur.

In Finland, there are thousands of lakes which are shallow with small amount of water. Because of that, Finnish lakes to be easily affected by eutrophication.

Phosphorus is the so-called limiting factor in Finnish lakes. This means that there is enough nitrogen for the plants available and phosphorous is limiting their growth. So, all "extra" load of phosphorous

can cause problems in water. There are three main sources of phosphorus in water - agricultural pollution, domestic sewage and industrial wastewater.

In Finland majority of the catchment area is forestry land, about 75 % of the surface area. The amount of the agricultural land is only 8% but the most significant source of external loading of phosphorous is agriculture (60%). Other minor loading source is amount of scattered settlements (13%) and also forestry (8%). Agricultural production in most places is intensive as result of favourable conditions. Typically, these conditions are close to lakes where the soil can be cultivated.

Point sources of pollution are when pollution is discharged at one point where the concentration is highest than in wastewater from municipal and industrial facilities. Significant point sources of pollution are discovered within the catchment area of the Baltic Sea, despite the fact that pollution control has for some time focused on non-point sources rather than point sources. The most famous cases of recent years are the phosphorus leaches from waste phosphogypsum stacks adjacent to fertilizer factories in Kingisepp in Russia, Gdansk and Polica in Poland, investigated not only by researchers but also by the Finnish Helsingin Sanomat and the Russian security service. The discovery of an unexpected pollution source may be a politically and economically sensitive subject, but for the health of the Baltic Sea, it is really important. It is fairly easy to stop phosphorus leaching from such stacks, and far less costly than reducing diffuse pollution [10].



Figure 1. Phosphogypsum stacks in Polica, Poland

1.4. Non-point source pollution.

Finland accounts for around 10% of the nutrient loading in the Baltic Sea. For example, in the 2000s, Finnish rivers have carried an annual average of 3,400 tonnes of phosphorus and 74,000 tonnes of nitrogen into the Baltic Sea, which accounts for approximately one-tenth of the Baltic Sea's overall load. The Baltic Sea nutrient loading must be reduced because the sea is suffering from eutrophication.

Generally, annual variation of nutrient level in reservoirs is high because the time and amount of rain affect run-off from forests and fields. Regarding rivers, the quantities of river-borne nutrients have remained almost unchanged from the 1970s to the present day, despite the substantial reduction in pollution from point sources. High levels of nutrients in rivers are mainly related to agricultural activity. Despite significant reduction in amounts of used fertilizers, there has been no substantial reduction in nutrient run-off from croplands.

According to the ecological classification of surface waters dated to 2008, more than half of Finland's coastal waters are in moderate ecological condition or worse. The EU aims to achieve at least a good status for all surface waters by 2015. To reach this target is very difficult in Finland's coastal waters, since survey of the ecological condition of surface waters dated to 2013 indicates that the status of coastal waters remained much the same since 2008 [10].

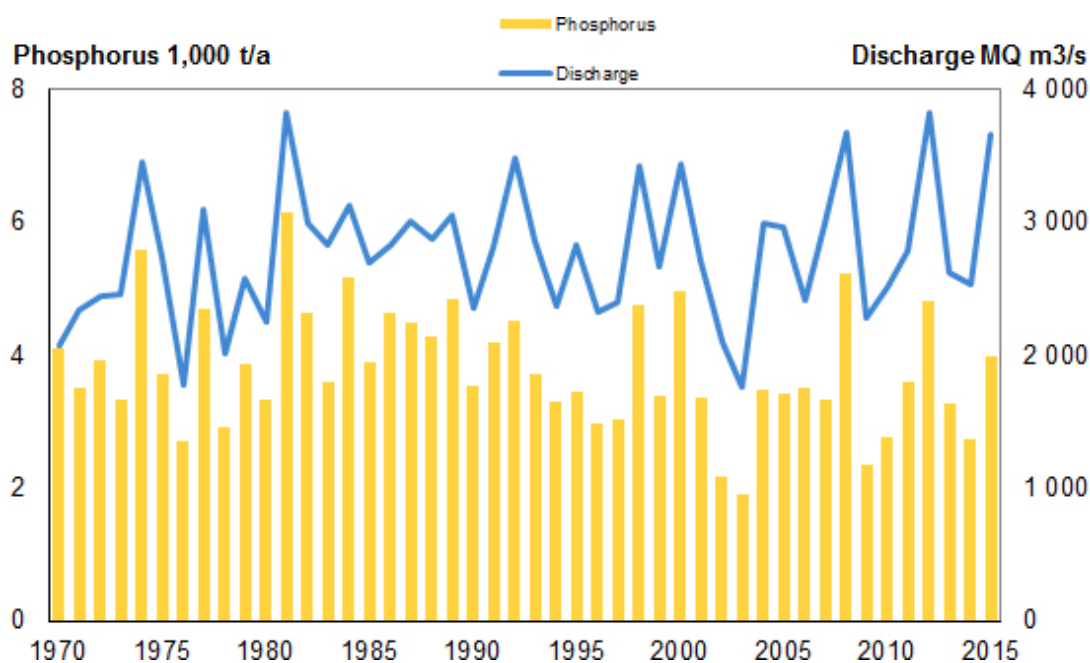


Figure 2. Phosphorus discharge from Finnish rivers into the Baltic Sea in 1970-2015 [10].

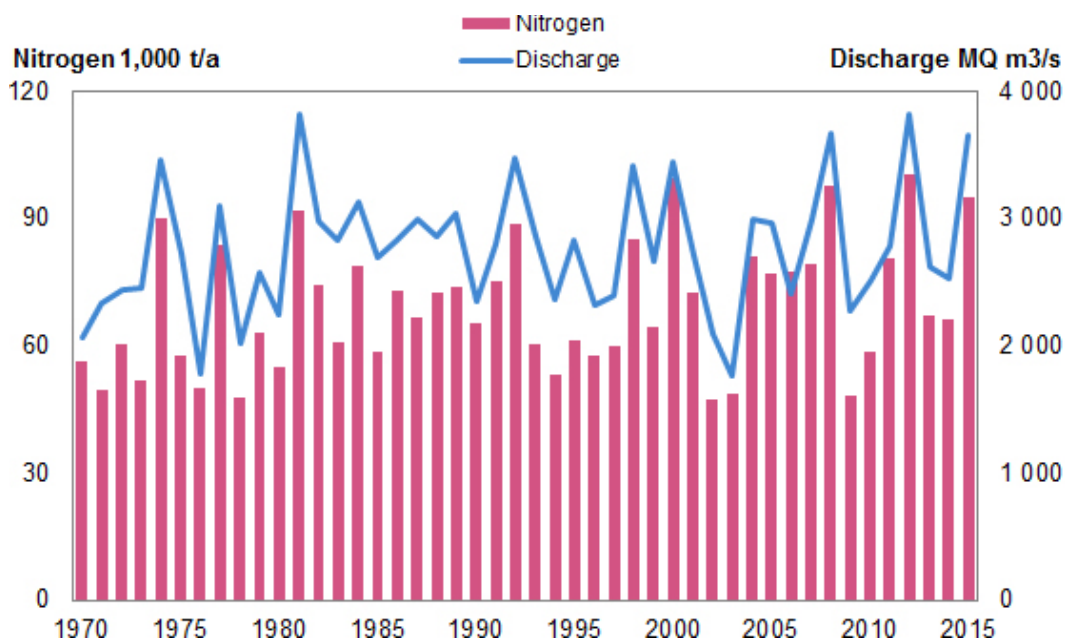


Figure 3. Nitrogen discharge from Finnish rivers into the Baltic Sea in 1970-2015 [10].

Non-point sources of pollution are related to many diffuse sources are generally from the usage of fertilizers in bigger areas such as crops, lawns, golf courses and also from livestock and pet waste, precipitation and natural sources from rocks and soil. Non-point source of pollution is caused by

rainfall or snowmelt moving over and through the ground. As the runoff moves, it collects and carries away natural and human-made pollutants, finally depositing them into lakes, rivers, wetlands, coastal waters and ground waters. The effects of non-point source pollutants on specific waters vary and may not always be fully assessed. However, it is known that these pollutants have harmful effect on drinking water supplies, recreation, fisheries, and wildlife.

Non-point source pollution may include (US EPA) [11]:

1. Excess fertilizers, herbicides, and insecticides from agricultural lands and residential areas, oil, grease and toxic chemicals from urban runoff and energy production, sediment from improperly managed construction sites, crop, forest lands, and eroding streambanks.
2. Salt from irrigation practices and acid drainage from abandoned mines, nutrients from livestock, pet wastes, and faulty septic systems.
3. Atmospheric deposition and hydromodification.

1.5. Eutrophication as a worldwide problem.

More and more attention has been paid to the eutrophication of water body. Water eutrophication survey of lakes and reservoirs from the United Nations Environment Programme (UNEP) shows that 30% to 40% of lakes and reservoirs are affected in different degrees, and there is a great disparity in eutrophication process in affected areas [13].

Most of the large lakes in the world are unaffected and have good water quality, such as Big Bear Lake, Baer Lake and Spirit Lake in USA, Lake Malawi and Tanganyika in Africa or Great Slave Lake in Canada. In the dry climate areas, the eutrophication of water is a serious problem, for example, in 800 reservoirs in Spain, at least 1/3 is in a state of heavy eutrophication. In South America, South Africa, Mexico and some other places, there are reports on the occurrence of eutrophication in the reservoirs, mainly concentrated in the densely populated area. In Europe, the most problematic factors related to lakes is eutrophication. About 80% of the lakes are contaminated by nitrogen and phosphorus in different degrees, showing eutrophication. Among the five most popular lakes in North America, the water quality of Lake Michigan is in the middle nutrition state, while Lake Ontario has relatively poor quality and belongs to eutrophic lakes. The water quality of lakes in Asia is quite different, the water quality of the northern lakes is better, but the water quality of the southern lakes is poor. The main characteristic of the water quality in the Asia lakes is the high nitrogen and phosphorus content in the water (the majority of the pollution sharing rate is 30%) [13].

1.5.1. Eutrophication in China.

Chaohu is a part of the Yangtse River system and is located in the central part of Anhui province. It is wide 54.5 km east-west, 15.1 km north-south, and 181 km long. The largest water area is about 825 km², with a maximum volume of 4 billion 810 million m³, with a maximum depth from 0.98 to 7.98 m [13]. It is one of the five largest freshwater lakes in China. The lake water is mainly recharged by the ground runoff. The main famous aquatic animals in Chaohu are silvery fish, beautiful white shrimp and lake crab. The three are known as "Chaohu three fresh" [13].

The Chaohu Lake Basin is located between the two major rivers, the Yangtze River and the Huaihe River. There are numerous rivers entering the lake. Chaohu Lake plays an extremely important role in the socio-economic development of the basin. In recent years, with the rapid development of industrialization and urbanization in the Chaohu Lake Basin, Chaohu Lake has experienced a serious eutrophication situation [13]. The deterioration of water quality caused by the blue-green algae outbreak and the decline of the lake ecosystem has caused a series of ecological problems in the country [14].

The situation surrounding Chaohu [15]:

1. Industrial situation: There are more than 3,000 industrial and mining enterprises in the Chaohu Basin, and the annual discharge of wastewater is 140 million m³.
2. Agricultural situation: The basin is the main grain-producing area in Anhui Province. The area of agricultural arable land is 6479 km², accounting for about 62% of the total area of the basin and is distributed around the lake.
3. Living conditions: In recent years, the population in the river basin has increased dramatically, and domestic sewage has been directly discharged.

The eutrophication status of Chaohu Lake began in the 1980s. With the rapid growth of population and industrial and agricultural production in the river basin and the acceleration of urbanization, the loads of N, P and other nutrients in the Chaohu Lake increased, and the lake became eutrophic. Most of industrial and mining enterprises are large sewage users in the river basin. Most of the sewage is discharged directly to Chaohu without any treatment. Moreover, agricultural pollution also contributes to this ecological disaster, since the application of nitrogen-phosphorus fertilizers is too large.

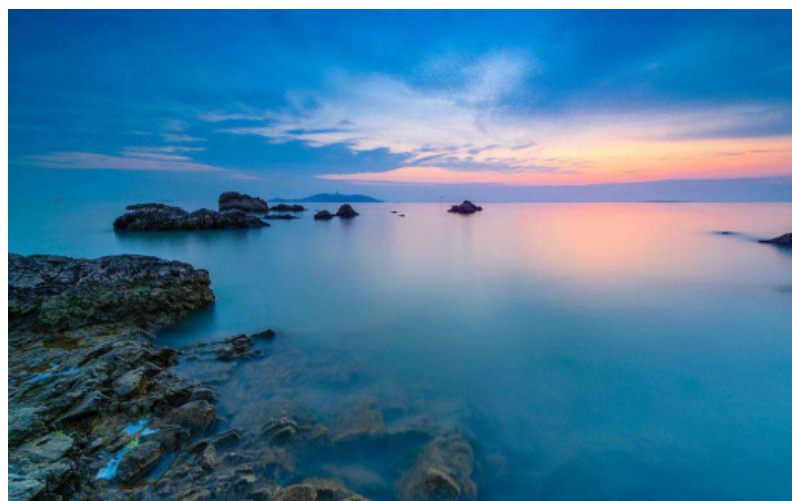


Figure 4. Chaohu lake basin before damage [13].



Figure 5. Destroyed Chaohu lake basin [13].

1.5.2. Eutrophication in Finland.

The Baltic is a shallow sea and has a slow exchange of water with the open seas. In its catchment area live 5.2 million Finns and about 80 million citizens of other countries. A large part of the pollution, especially from homes, workplaces and farms, ends up in the sea. Symptoms of the Baltic's serious ecological problems include mass algal blooms, declining fish stocks and extensive lifeless areas on the seabed.

The depletion of oxygen from large areas of the seafloor is a consequence of the high inputs of nutrients entering the Baltic. Oxygen is used when algae and other organic matter sink to the seabed and decompose. In the absence of oxygen, large quantities of phosphorus can be released from seafloor sediments into the water body. This internal nutrient loading can prolong the eutrophication process even where new inputs of nutrients from the land are kept under control.

The condition of the Baltic Sea troubles communities and politicians from all the countries around its shores. One of the first ever international environmental agreements - the Helsinki Convention, on the protection of the Baltic marine environment was signed by the coastal states in 1974. The Helsinki Commission (HELCOM) was set up to co-ordinate both the implementation of the convention and related improvements in environmental protection around the Baltic Sea.

Thanks to national and international actions, the amounts of toxic chemicals entering the Baltic Sea have been radically reduced. Many of the coastal states have also limited nutrient inputs. More than half of the most problematic pollution sources around the Baltic has already been handled, enabling them to be removed from HELCOM's Hot Spots List. Only one from the ten of the originally listed Finnish hot spots remains: farmland in southwest Finland close to the Archipelago Sea [16].



Figure 6. Helsinki sea area [16].

1.6. Methods of phosphorus removal.

Common methods used for phosphorus removal are as follows:

1. Chemical precipitation method. The method is to form a precipitate by adding a chemical precipitant into wastewater contains phosphorus. The flocs formed, and phosphorus can be easily separated from treated wastewater [17]. Additionally, phosphorous may adsorbed on the flocs what enhance its removal. Commonly used precipitating agents include lime, alum, ferric chloride, and mixtures of lime and ferric chloride. In order to reduce the cost of wastewater treatment and improve the treatment efficiency, a lot of work has been done to develop new, cheap and efficient chemical precipitating agents. It is found that when the raw water contains phosphorous of 10 mg/L, the addition of 300 mg/L of $\text{Al}_2(\text{SO}_4)_3$ or 90 mg/L FeCl_3 can remove about 70% of the phosphorus. When the initial precipitation is added then the total phosphorus can be removed up to 80%. According to the chemical coagulation, the sedimentation rate of the precipitable material can be increased and the new alkaline aluminum chloride is added to the new water purifying agent. The settlement effect is from 80% to 85%. This method is simple and easy to handle and has good treatment effect. But the long-term operation results show that the addition of chemical precipitant will cause the increase of pH value in the wastewater, the formation of scale in pipes, and will generate a certain amount of sludge [9].
2. Biological method. In 1970s, the US Spector discovered that microbes could absorb phosphorus under aerobic condition, and that phosphorus was released in the anaerobic state of organic matter. Since that time, the biological treatment of phosphorus-containing wastewater was gradually developed. At present, there are three main types of biological dephosphorization technologies commonly used. First is the addition of dephosphorizing coagulant to the aeration tank, second is usage of soil for wastewater treatment (the orthophosphate ion will react with the oxides of Fe and Al in the soil or replace the OH^- or Si_3O_2 in clay to produce phosphoric acid compounds) and finally third method is activated sludge process which is the most widely used biological treatment technology. Biological phosphorus removal method has good treatment effect, it is not difficult to deal with sludge, does not require addition of precipitator, but the management of the process is quite demanding [9].
3. Ion exchange method. To remove phosphates from wastewater a strong alkali anion exchange resin is required. However, in the presence of other anions in treated wastewater the capacity of

resin can be limited. The exchange capacity of P_4O_3 removal by ion exchange resin after regeneration is relatively stable. However, the costs of ion exchange technique are high, due to the high price of the resin and chemical reagents required for its regeneration [18].

4. Adsorption method. In 1980s, porous materials were used as adsorbents for water purification and pollution control. Huang Wei et al studied the dephosphorization characteristics of simulated wastewater containing phosphorus from 50 to 120 mg/L by using fly ash as an adsorbent. The research shows that the fly ash contains more active alumina and silicon oxide and can effectively adsorb phosphorous. The fly ash is not only capable to adsorb the inorganic phosphate, but due to the presence of calcium in its composition, precipitation of phosphates can take place, especially in alkaline conditions. Therefore, precipitation along with adsorption are the main mechanisms of phosphates removal by fly ash. Adsorption has attracted much attention due to its small footprint, simplicity, convenient operation and no sludge production, especially for low concentration of phosphorous in wastewater [18].

5. Membrane separation methods. Liquid membrane separation is a new type of membrane separation technology similar to the solvent extraction. A liquid membrane is formed by a thin layer of organic solvents (organic phase) between two aqueous phases of different compositions. This thin layer of liquid film ($1 \sim 10 \mu\text{m}$) is formed on the surface of the micro drop, and the internal phase reagent is in the membrane. In the mixed column, the emulsion microdroplets of this surface area are exposed to the wastewater, and the metal ions to be removed through the liquid membrane through selective infiltration, extraction and adsorption. Therefore, the metal ions in the wastewater are separated and removed [19].

1.7. Fly Ash - production and feedstock.

Fly ash is included to the group of low-cost adsorbents, because it is a waste material from high-temperature combustion of wood and coal [20]. Fly ash is an alkaline material, exhibits good sorption capacity and non-toxicity, and is also susceptible to biodegradation. The utilization of fly ash for treatment wastewater, including phosphorous-rich wastewaters, is gaining popularity around the world [21].

The fly ash used in the study is wood-based combustion material from heating plant [22].

The wood bark is the outermost layers of stems and roots of woody plants. It overlays the wood and consists of the inner bark and the outer bark. The inner bark, which in older stems is living tissue, includes the innermost area of the periderm. The outer bark in older stems includes the dead tissue on the surface of the stems, along with parts of the innermost periderm and all the tissues on the outer side of the periderm. Products derived from bark include bark shingle siding and wall coverings, spices and other flavourings, tanbark for tannin, resin, latex, medicines, poisons, various hallucinogenic chemicals, and cork. Bark has been used to make cloth, canoes, and ropes and used as a surface for paintings and map making. A number of plants are also grown for their attractive or interesting bark colorations and surface textures or their bark is used as landscape mulch [20].

Sawdust is a by-product or waste product of woodworking operations such as sawing, milling, planing, routing, drilling, and sanding. It is composed of fine particles of wood. These operations can be performed by woodworking machinery, portable power tools or by use of hand tools [23]. Wood

dust is also the by-product of certain animals, birds, and insects which live in wood, such as the woodpecker and carpenter ant. A major use of sawdust is for particleboard; coarse sawdust may be used for wood pulp. Sawdust has a variety of other practical uses, including serving as a mulch, as an alternative to clay cat litter, or as a fuel [24]. Until the advent of refrigeration, it was often used in icehouses to keep ice frozen during the summer. It has been used in artistic displays, and as scatter in miniature railroad and other models. It is also sometimes used to soak up liquid spills, allowing the spill to be easily collected or swept aside. As such, it was formerly common on barroom floors [20].



Figure 7. Wood bark [20].



Figure 8. Sawdust [20].

1.8. Fly ash utilization.

In China, fly ash can be used as the admixture of cement, mortar and concrete [25]. It became a component of clinker, sintered brick, autoclaved aerated concrete, foam concrete, hollow brick or paved road. Fly ash is used in the construction of dams or ports, for farmland potholes, coal mine subsidence areas and mine backfill. It can also be selected from the materials such as bleaching, microbeads, iron powder, carbon, aluminum and other useful substances, which can be used as insulating materials, refractory materials, plastics and rubber fillers [21].

Forests have a significant role in Finnish energy supplies. The predominant part of the energy from forests originates from industrial residues of stem woods but the extraction of branches and tops for energy purposes has also become common in many places.

In Finland, large amounts of wood ash are generated annually in the forest industry and energy plants. Previously, these generated ashes have mainly been deposited in industrial landfills, but ash from waste incineration can be utilized in landfill construction and mine back-filling. Fly ash can be used in many types of earthworks including public roads, streets, bicycle lanes, and pavements. In Finland, fly ash can be also utilized as a stabilizing agent for forest roads construction and renovation. Moreover, it can be used for fertilizing forest. The aim of wood ash fertilization is to compensate the nutrients removed with the harvested timber, balance nutrient status of the tree stand, counteract soil acidification and improve tree growth [13].

2. RESEARCH OBJECTIVES

The aim of the study was to investigate the efficiency of phosphorous removal from water using fly ash and analyse the material suitability for use in water/wastewater treatment sector. Jar-test experiments with various process conditions were conducted to determine the performance of fly ash in phosphorus removal, including tests with fly ash dose, initial concentration of phosphorous and solution pH. The adsorption capacity of fly ash for phosphorous was calculated to assess its potential as a low-cost adsorbent. Additionally, the efficiency of nitrogen removal was analysed.

The specific experiments were performed:

- Test 1A to determine the effect of fly ash dose on phosphorous removal from simulated water sample.
- Test 1B to determine the effect of initial concentration of phosphorous on fly ash performance.
- Test 1C to determine the influence of various solution pH on the efficiency of phosphorous removal by fly ash.

3. MATERIALS AND METHODS

In this section, the materials and methods used in experiments are listed. The tested adsorbent is fly ash number 2 which is wood-based combustion fly ash from Savon Voima Oy's district heating plants. The wood material is a wood bark and sawdust, collected from Kiuruvesi, outdoor stack of district heating plant, dated 1.8.2017. The experiments were divided into three parts (1A, 1B and 1C). The experiments were performed under controlled conditions and in each test various factors were analysed. The water used in the study was lake water spiked with nitrogen and various concentration of phosphorus. The laboratory work continued for 4 weeks.

3.1. Jar-test methodology.

1. Prepare the water sample needed for the experiment. Pour lake water into the 850 mL of the beaker and add certain concentrations of phosphorus (K_2HPO_4 , 1000 mg/L) and nitrogen (NH_4Cl , 1000 mg/L) required for the experiment.



Figure 9. Jar-test biker.

2. Put the stirrer in the beaker and open the agitator to make the added nitrogen and phosphorus distribute evenly in the lake water.

3. Mix well and stop the stirrer.

4. Extract water samples from 50 mL as initial simulated lake water.

5. Put in the amount of fly ash (adsorbent) required for the experiment.

6. Open the stirrer and time it at the same time.

7. Samples of stirring beaker 5 min, 10 min, 20 min, 30 min, 60 min, 120 min, and 180 min were collected separately (the agitator does not stop).

8. Stop the stirring apparatus and allow the samples in the beakers to settle for 30 minutes.

9. Detection of phosphorus content in samples collected at different time.

3.2. Laboratory used in equipment.

The following equipment were used during experiments (Pictures from Wenqi Zhang):

- Jar-test (Kemira Flocculator 2000)



Figure 10. Jar-test apparatus.

- High Temperature Thermostat (HACH LANGE HT 200S) and Spectrophotometer (HACH LANGE DR 6000)



Figure 11. Thermostat and spectrophotometer.

- Multi TOC analyser for total nitrogen measurement



Figure 12. TOC analyser.

- HACH HQ 11D and 14d multi-meter for pH and conductivity measurement



Figure 13. Multi-meter for pH and conductivity.

- Shaker New Brunswick (INNOVA, 40R)



Figure 14. Shaker.

- Scaltec Analytical balance (SBC 31)



Figure 15. Analytical scale.

- Labware - pipettes, conical flasks, tube stands, beakers

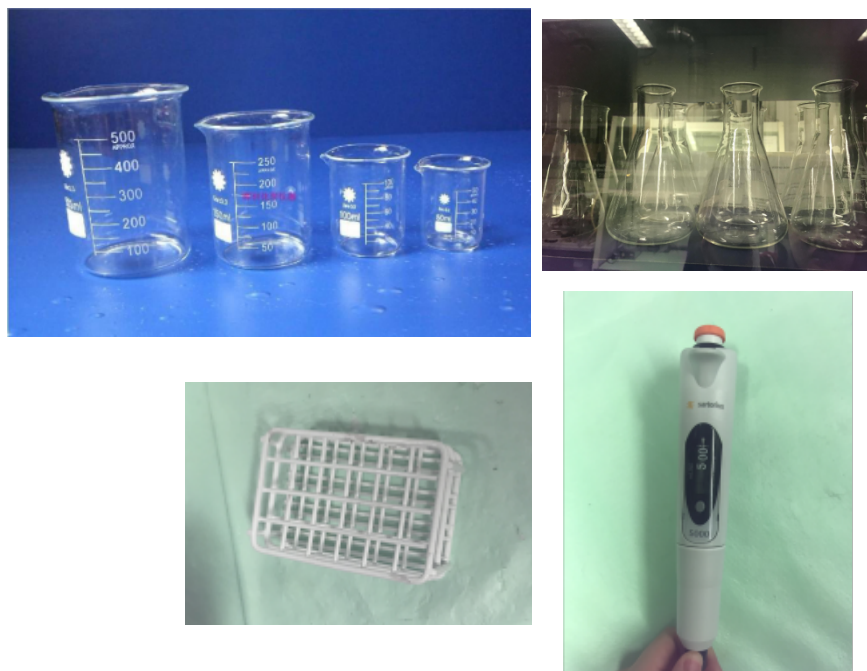


Figure 16. Labware used in the study.

3.3. Fly ash and other chemical materials

- Fly ash number 2



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- Chemical solutions 2 M HCl, 1M NaOH and HCl for adjusting pH

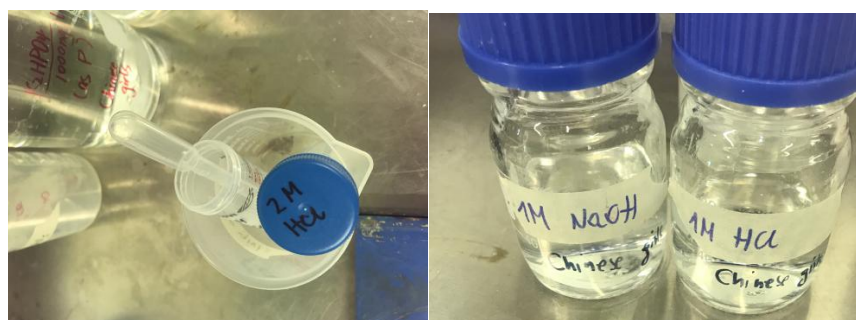


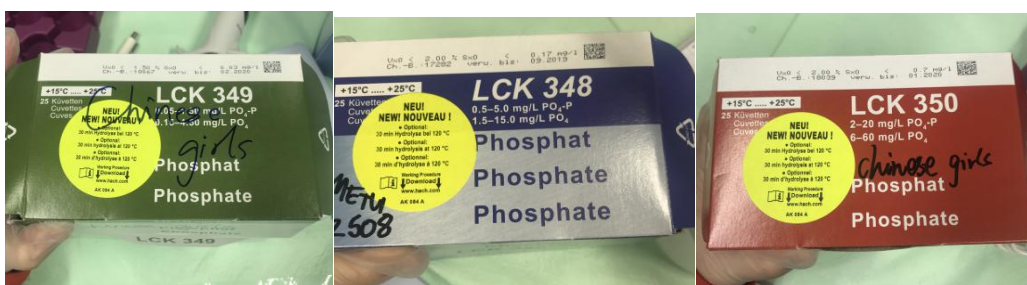
Figure 18. Chemical solutions - acids and base.

- Phosphorus solution (K_2HPO_4 , 1000 mg/L) and nitrogen solution (NH_4Cl , 1000 mg/L)



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- Cuvette tests (HACH-LANGE) for phosphorus measurement, including LCK349 test (for 0.05-0.5 mg/L PO_4-P), LCK348 test (for 0.5-5 mg/L PO_4-P), LCK349 test (for 2-20 mg/L PO_4-P)



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4. RESULTS AND DISCUSSION

4.1. Phosphorus and nitrogen removal (%) and fly ash adsorption capacity (mg/g) were calculated:

Phosphorus removal and nitrogen (%): $(C_o - C_x) / C_o * 100$

C_o : PO_4 -P or nitrogen concentration of initial water sample

C_x : PO_4 -P or nitrogen concentration of water collected at different time (5 min, 10 min, 20 min, etc.)

Fly ash adsorption capacity for phosphorus (mg/g): $(C_o - C_x) * V / m$

C_o : PO_4 -P concentration of initial water sample

C_x : PO_4 -P concentration of water collected at different time (5 min, 10 min, 20 min, etc.)

V: Volume of treated water sample

m: Mass of fly ash use in the experiment

4.2. 1A test – effect of adsorbent dose

Prepare 4 different doses of fly ash, add 1 mg/L phosphorus and 2 mg/L nitrogen into the water lake sample. Stir for 3 hours. Collect sample after 5 min, 10 min, 20 min, 30 min, 60 min, 120 min and 180 min.

Several parameters were measured:

- pH, conductivity, and concentration of PO_4 -P of initial water sample,
- pH and PO_4 -P of water samples collected at different time were measured,
- pH and conductivity of the remaining water samples in the beaker after the stirring.

The percentage of phosphorus removal is shown in Figure 21.

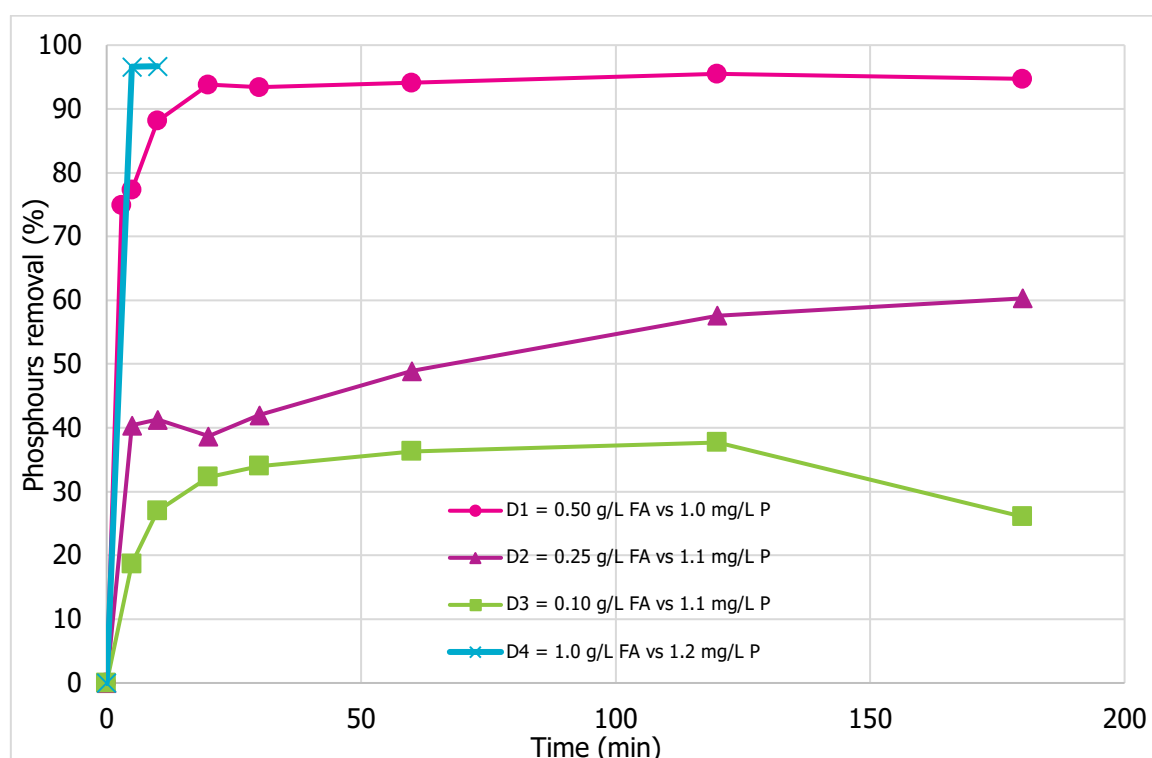


Figure 21. Efficiency of phosphorus removal (1A).

In Figure 21, there is a curve of only two data – where the highest dose of fly ash was applied (1 g/L). This dose was too high for this experiment. It removed the phosphorous within a few minutes of the process to very low concentrations which were below the range of cuvette tests used for spectrophotometric analyses. However, these data were shown only for comparison. The removal rate of the highest curve – fly ash dose of 0.5 g/L, reached 94.7% at the end of the test. The next curve represents the removal of phosphorous by fly ash dose of 0.25 g/L. The efficiency after 180 minutes was 60.3% and it is 34.4% less than the result obtained for 0.5 g/L of fly ash. The removal rate of phosphorous by the smaller dose of adsorbent was 26.1%. But after 2 hours of the test, the removal rate significantly dropped, probably because of the analytical error. Comparing the highest tested dose with the efficiency obtained for the smaller amount of fly ash, the removal difference is 68.6%. It can be seen from the chart 1 that the application of higher amount of fly ash gives better results in terms phosphorus removal (for the same initial concentration of phosphorus). Calculated adsorption capacity of fly ash for phosphorus (in mg/g) is shown in Figure 22.

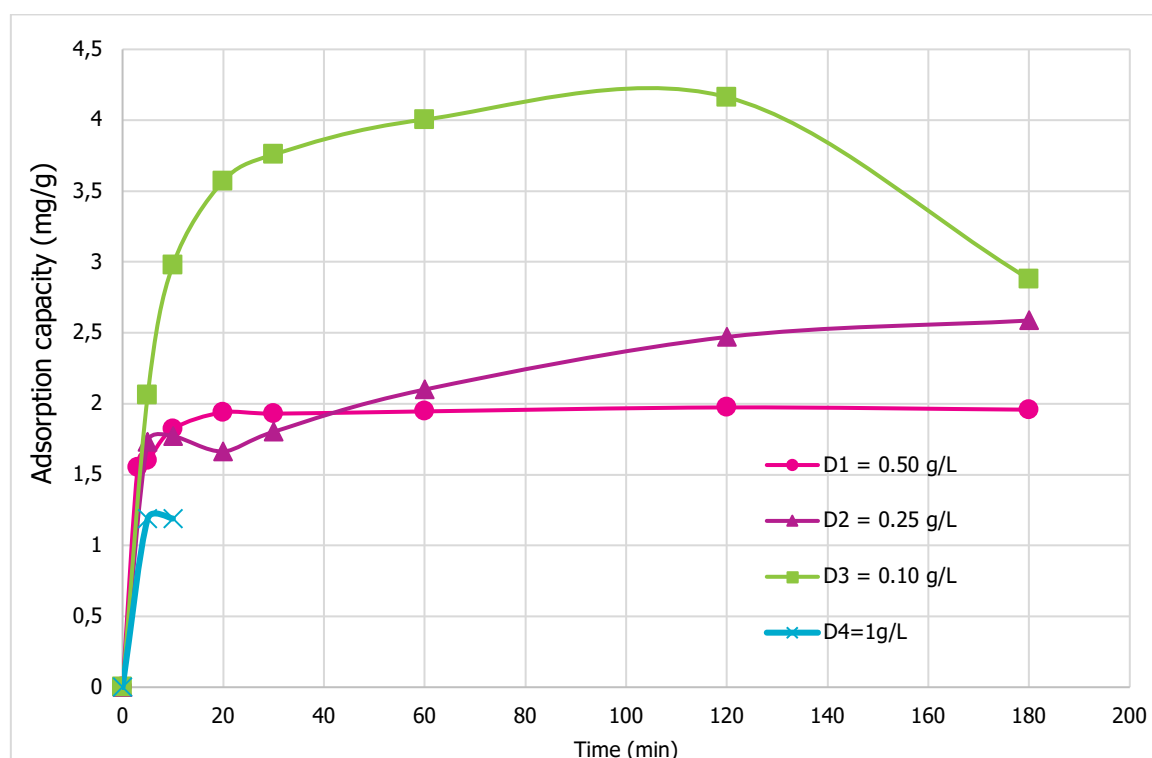


Figure 22. Adsorption capacity of fly ash for phosphorous (1A).

In Figure 22, as expected the higher calculated adsorption capacity for phosphorous was obtained when the smaller amount of fly ash was dosed into the treated water sample. In general, with the longer contact time the adsorption of phosphorous increased in case of all tested doses of fly ash. There was one noticeable exception for the 0.1 g/L of fly ash - after 120 minutes the adsorption suddenly dropped, and most probably it was an effect of analytical error. For the second dose (0.25 g/L), the value of adsorption capacity was 2.587 mg/g. Compared with the maximal tested dose, the difference in phosphorous adsorption was only 0.293 mg/g. The most stable curve in the chart is with the highest content of fly ash (0.5 g/L). It can be seen that adsorption was rapid in the first 20 minutes and then slow down. Based on obtained results it was decided that 0.5 g/L of fly ash will

be suitable dose for experiment 1B. From Figure 21 and 22, trend for the same amount of fly ash curves is the same. At different doses, the larger the removal rate, the smaller the adsorption capacity. These two charts show that the most stable set of data was obtained for 0.5 g/L of fly ash.

4.3. 1B test – effect of initial phosphorous concentration

Prepare one dose of fly ash (the same amount for three jars), add different concentration of phosphorus (1 mg/L, 5 mg/L, 10 mg/L) and 2 mg/L nitrogen into the water lake sample. Stir for 3 hours. Collect sample after 5 min, 10 min, 20 min, 30 min, 60 min, 120 min and 180 min.

Several parameters were measured:

- pH, conductivity, and concentration of $\text{PO}_4\text{-P}$ of initial water sample,
- pH and $\text{PO}_4\text{-P}$ of water samples collected at different time were measured,
- pH and conductivity of the remaining water samples in the beaker after the stirring,
- total nitrogen and DOC (in all collected samples).

The percentage of phosphorus removal is shown in Figure 23.

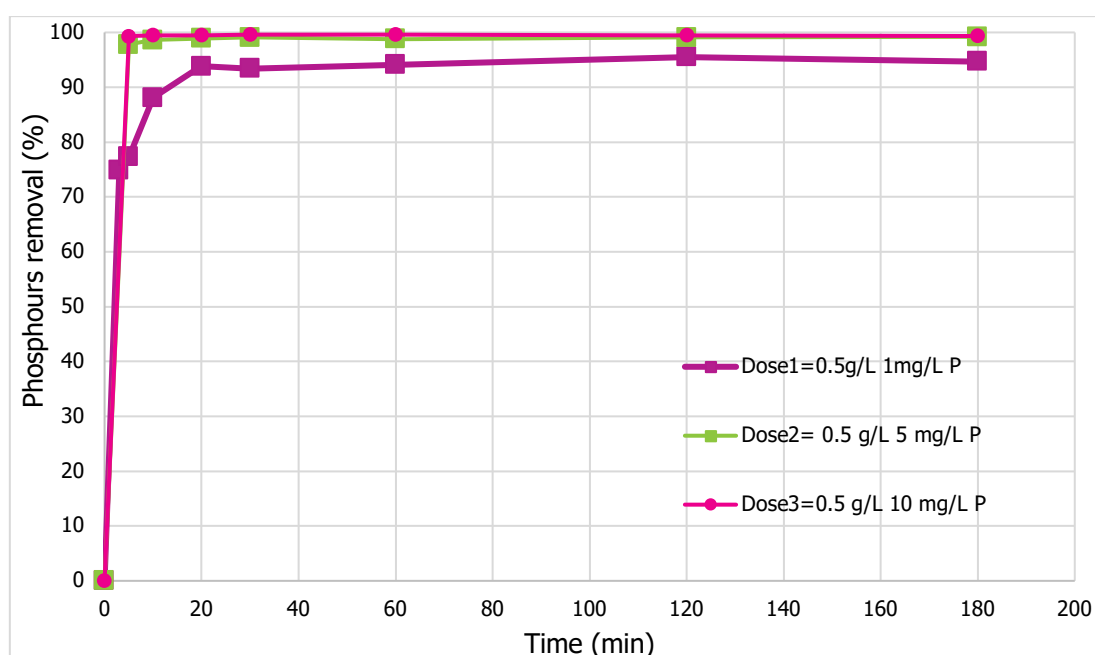


Figure 23. Efficiency of phosphorus removal (1B).

In Figure 23, it can be seen that the fly ash was very effective in removal all tested phosphorus concentrations. The removal rate of 5 mg/L and 10 mg/L of phosphorus was the same and reached 99.2% and 99.4%, respectively. Within the first 5 minutes almost all phosphorous has been removed from treated water. The continuation of the test till 180 min did not bring major changes in phosphorous removal. The lowest curve in the chart represents data obtained for the lowest initial concentration of phosphorus (1 mg/L). Here the removal was noticeable slower at the beginning of the process, however the final removal rate was only 4.7% lower comparing to higher concentrations of phosphorous.

It can be seen that for the same amount of fly ash and different phosphorus concentration, the higher phosphorus content in treated water sample, the stronger ability of adsorbent to remove phosphorus.

Calculated adsorption capacity of fly ash for phosphorus (in mg/g) is shown in Figure 24.

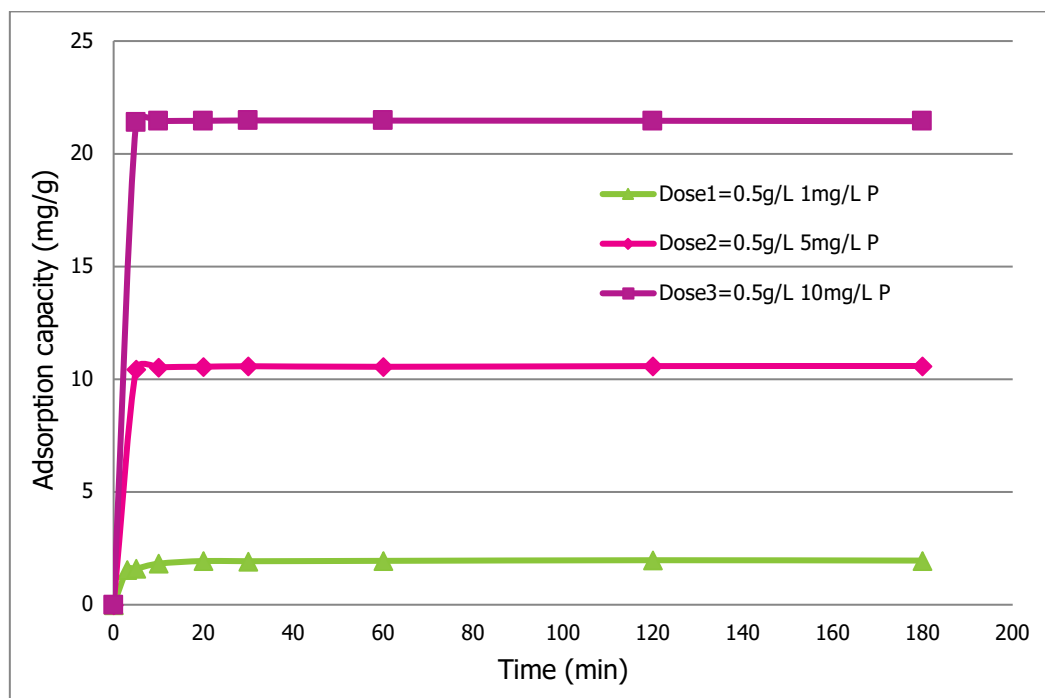


Figure 24. Adsorption capacity of fly ash for phosphorous (1B).

The adsorption capacity of fly ash depends on the initial concentration of phosphorous, as shown on Figure 24. In general, the phosphorus removal is directly proportional to the adsorption capacity. For the same amount of fly ash, the higher phosphorus concentration, the higher adsorption capacity of fly ash for this pollutant. For all tested phosphorous concentrations, very fast removal was observed within the first minutes of the process and then remained almost constant to the end of the test. The calculated maximal adsorption capacity of fly ash after 3 hours of contact time was 21.446 mg/g, 10.588 mg/g and 1.958 mg/g for initial amount of phosphorous of 1 mg/L, 5 mg/L and 10 mg/L, respectively. The removal mechanism of phosphorus from simulated water was not investigated in this study, but according to the literature, the removal mechanism of phosphate by fly ash may involve not only adsorption but also precipitation (depending on solution pH and content of calcium in fly ash) [26].

The changes in nitrogen concentration and dissolved organic carbon (DOC) with time are shown in Figure 25 and 26, respectively.

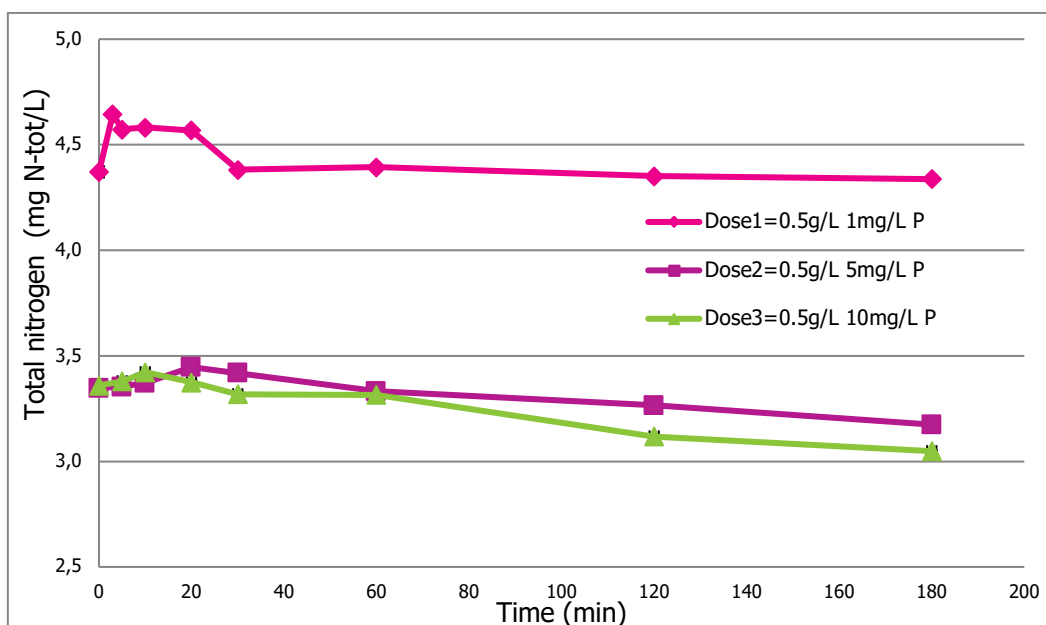


Figure 25. Efficiency of nitrogen removal (1B).

As can be seen in Figure 25, the content of total nitrogen in the simulated water sample slightly increase at the beginning of the process (first 5 minutes) and then its concentration gradually decreased with time. However, the overall removal rate of total nitrogen was not significant indicating that tested fly ash was not a good adsorbent for treatment nitrogen-rich waters.

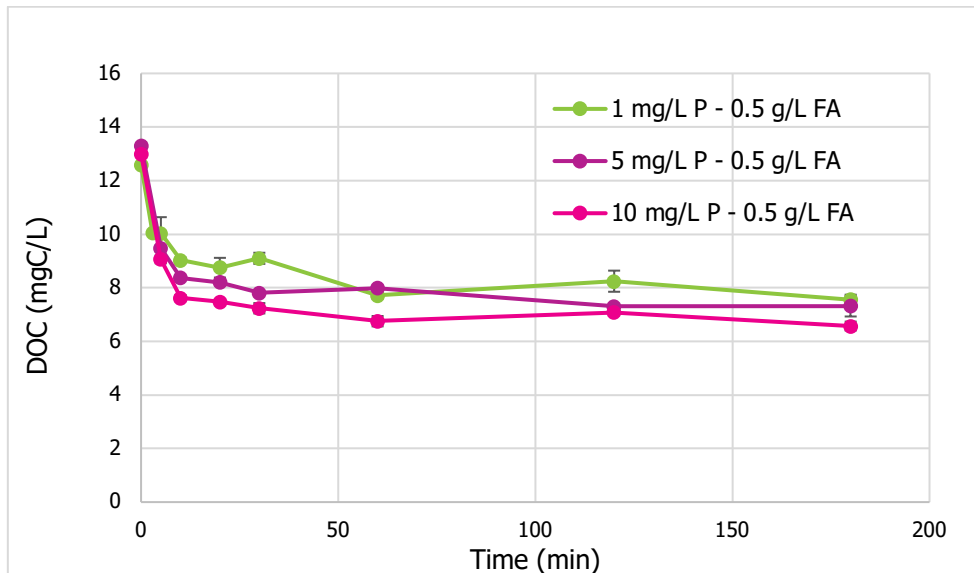


Figure 26. Efficiency of DOC removal (1B).

In case of organic matter, it can be seen from Figure 26 that all applied doses of fly ash efficiently reduced the content of DOC in treated water. The initial concentration of dissolved organic matter was about 13 mgC/L and after 180 minutes of the process DOC was between 6.5 and 7.5 mgC/L. Obtained experimental results indicate that the tested fly ash has a good removal ability of DOC and thus can be successfully used to improve water quality.

4.4. 1C test – effect of solution pH.

Prepare one dose of fly ash (the same amount for all jars), add the same concentration of phosphorus (1 mg/L) and nitrogen (2 mg/L) into the water lake sample. Adjust the pH of treated water to 5, 6 and 8 and keep it constant during the test. Additionally, run one jar without pH adjustment and controlling. Stir water with adsorbent for 3 hours. Collect sample after 5 min, 10 min, 20 min, 30 min, 60 min, 120 min and 180 min.

Several parameters were measured:

- pH, conductivity, and concentration of $\text{PO}_4\text{-P}$ of initial water sample,
- pH and $\text{PO}_4\text{-P}$ of water samples collected at different time were measured,
- pH and conductivity of the remaining water samples in the beaker after the stirring,

The percentage of phosphorus removal is shown in Figure 27A and 27B.

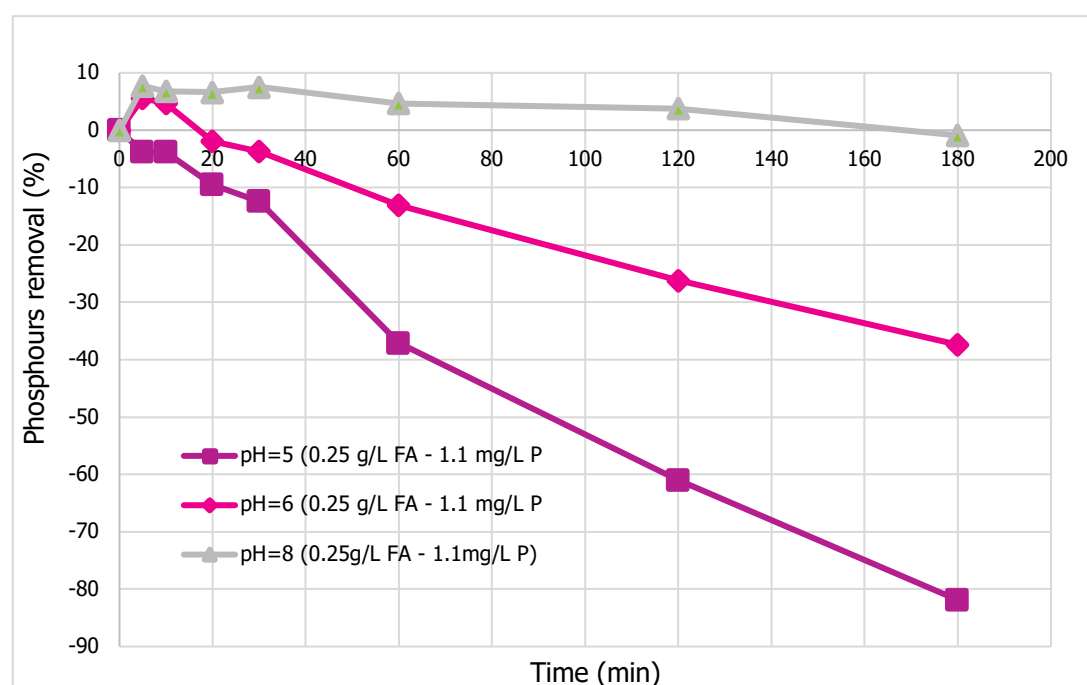


Figure 27A. Efficiency of phosphorus removal at pH=5, pH=6 and pH=8 (1C).

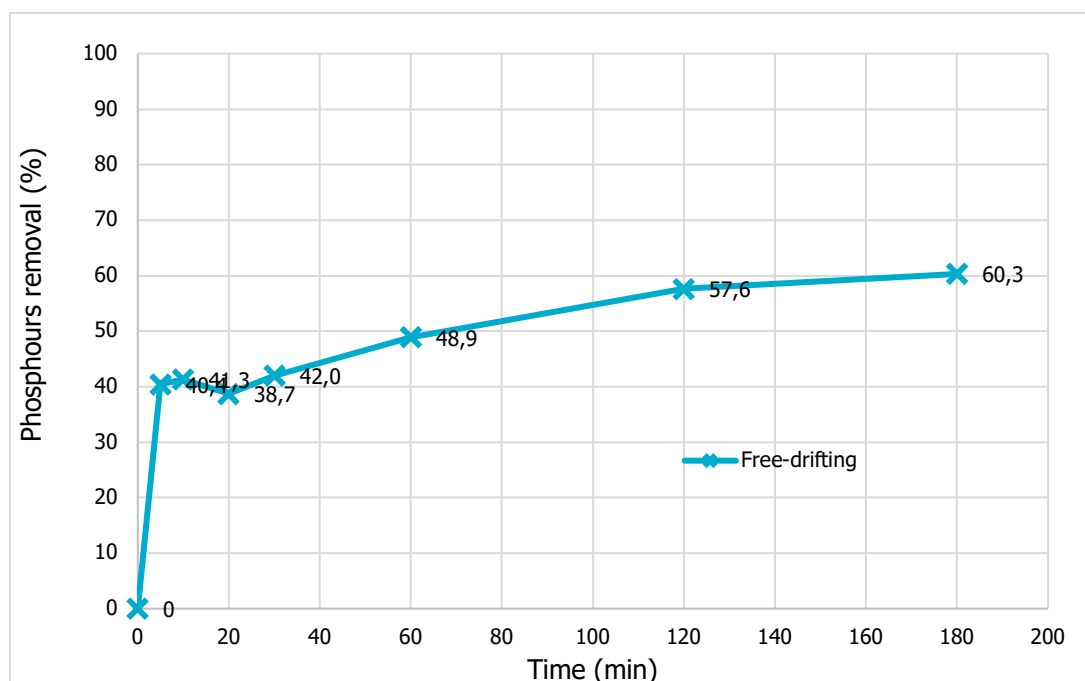


Figure 27B. Efficiency of phosphorus removal at free-drifting pH (without controlling) (1C).

In the experiment without pH adjustment and its controlling during the test (Figure 27B), the applied dose of fly ash can effectively remove phosphorus from water (up to 60%).

In the experiments where pH was adjusted and kept constant during the 3 hours of mixing (Figure 27A), the phosphorous was released into the water sample resulting in negative values of percentage removal. Most probably the phosphorous was in the composition of fly ash and it tends to be released into the solution depending on its pH. However, to explain correctly observed trend, the adsorbent composition and removal mechanism of phosphorous should be examined (but it is not an aim of this study). For the alkaline conditions (pH=8) the slight removal was observed at the first 5 minutes and then efficiency gradually decreased to zero. For pH=6, the similar pattern was observed – slight increase of phosphorous removal at the beginning (within 10 min) and then gradual decreased below zero. At the acidic conditions (pH=5), the increase of phosphorous concentration above its initial value was noticeable from the first minutes of the tests.

The adsorption capacity of fly ash for phosphorus at various pH (in mg/g) is shown in Figure 28; but these results have been shown only to illustrate the trend (the lack of physical sense). The test with free-drifting pH confirmed the ability of fly ash to remove phosphorous from water under applied conditions (adsorption capacity 2.587 mg/g).

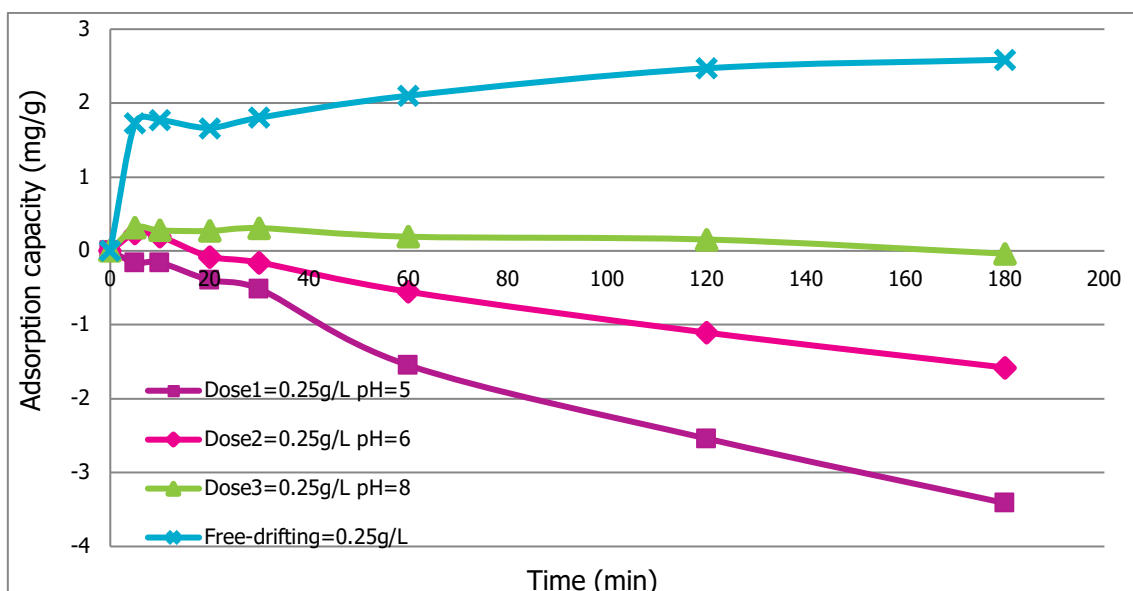


Figure 28. Adsorption capacity of fly ash for phosphorous (1C).

4.5. The changes of water pH

It is known that fly ash is a strong alkaline material, therefore is able to increase solution pH significantly. The changes of pH values recorded during the experiments (test 1A and 1B) are presented in Figure 29.

The pH of simulated water sample was about 7.0-7.5. It can be seen, that in all performed tests, pH of treated water jumped rapidly to value of 10.5-12 within the 5-10 minutes and maintained almost constant to the end of the process.

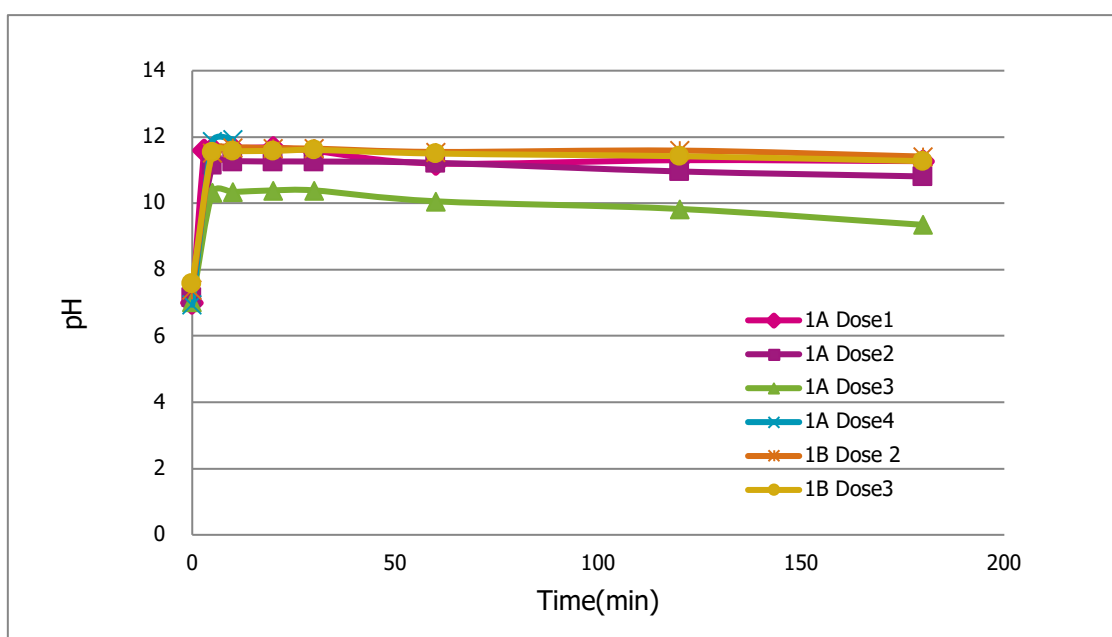


Figure 29. Comparison of pH changes in test 1A test and 1B.

4.6. DOC and phosphorus removal vs time

It was observed that fly ash can be also used as a potential adsorbent for organic matter removal from water (Figure 30). The presented data are obtained in test 1B where 0.5 g/L of fly ash was dosed into the water. It can be seen that apart from phosphorous, fly ash was able to successfully reduce the DOC concentration by about 50% (from 13 mgC/L to 6.57 mgC/L) within the 3 hours of treatment.

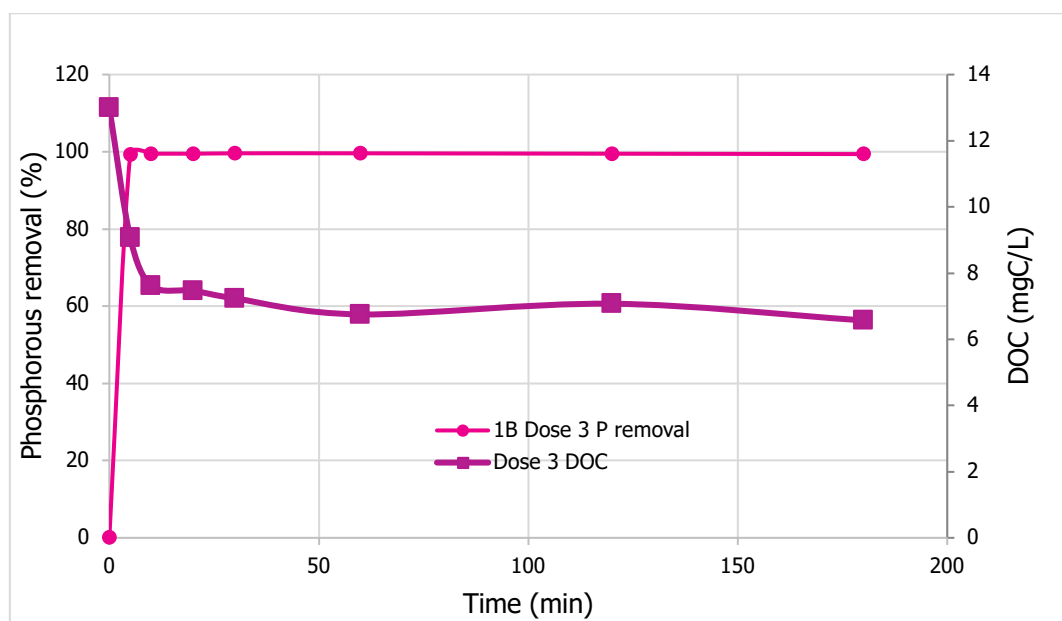


Figure 30. Efficiency of DOC and P removal vs time (data from 1B Dose 3).

5. CONCLUSIONS

In the test 1A – where the effect of adsorbent dose on process efficiency was analysed, it was found that the treatment performance depends on the amount of fly ash used in the process. Percentage removal of phosphorus from water increased from about 26% to 95% with the increase of fly ash dose from 0.1 to 0.5 g/L.

The results from experimental run 1B showed that under the similar process conditions (i.e. dosage of fly ash, pH), the higher adsorption capacity of fly ash was obtained for higher initial concentration of phosphorus in treated water. For the tested phosphorus concentrations (1, 5, 10 mg/L) the removal was very effective and reached almost 100%.

The ability of fly ash to remove phosphorus was also analysed in terms of water pH (test 1C). The pH of simulated water sample was adjusted to desired value (5, 6, 8) and maintained constant during experiment. It was observed, that under conditions with controlled pH, there was no removal of phosphorus. Moreover, the fly ash increased the amount of phosphorus in treated water. Most probably the phosphorus was in the composition of fly ash and it tends to be released into the solution in acidic and weak alkaline environment. However, to explain correctly observed trend, the adsorbent composition and removal mechanism of phosphorus should be examined.

As the tested fly ash was an alkaline material, the significant increase of solution pH was observed (in experiments without controlling pH). The increase of pH was from about 7.0-7.5, which was the initial pH of simulated water sample, to pH about 10.5-12 after 3 hours of the process.

It was confirmed, that fly ash can be also used as a potential adsorbent for organic matter and nitrogen removal from water. Fly ash was able to successfully reduce the DOC concentration by about 50%, however was less effective in total nitrogen removal (up to 10%).

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