THE REMOVAL OF RESIDUAL CONCENTRATIONS OF PHOSPHORUS FROM WASTEWATER BY MEANS OF COAGULATION AND FLOTATION

Stepan Lappo
Abstract

Phosphorus is a vital element in human’s lifecycle. It is required for humans and for other organisms to live. Life activities of some of these organisms cause big problems for humans. Eutrophication process is caused by excessive income of phosphorus and nitrogen to natural water resources. The main aim of this project was to test flotation unit together with coagulants and flocculants for removing of phosphorus from wastewater in a water basin of water reservoir Švihov.

Research consisted of laboratory analyzes with subsequent verification of the results in the field. Coagulants and flocculants were tested, using conventional jar tests. For these tests were used wastewater from target wastewater treatment plant with artificial addition of phosphate in the form of KH₂PO₄. It was done for better visibility of the coagulation results. Flotation experiments were done on a pilot scale flotation unit, provided by the KUNST company, on wastewater treatment plant of the Pacov city.

Using jar tests the best available combination of coagulant and flocculant was found (FeCl₃ and 827 BS with dosage of 1.25 mg/l for both of them). Different dosages of coagulants and flocculants were assessed, basing on subsequent analyses. Was measured pH value, as it is critical value for the environment and it cannot be less than 6. Also assessment was based on residual phosphates concentration, traces of aluminum and iron from coagulants and COD value. During subsequent flotation tests was found that at certain ratio of Fe/P, there is additional consumption of coagulant in the sampling water. We supposed, that it happened because of breakthrough point for inorganic phosphorus, which is situated between Fe/P ratios of 2.6 and 4.6.

It is important to conduct additional experiments on less equipped treatment plants in the area, where effectiveness of application of flotation unit, together with chemicals can be determined better for these territories and conditions. Together with additional studies informative conclusions could be done.
Acknowledgement

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ABBREVIATIONS AND SYMBOLS

P = phosphorus

N = nitrogen

Ca = calcium

Mg = magnesium

Fe = iron

Al = aluminum

pH = hydrogen value

$H_3PO_4$ = phosphoric acid

$H_2PO_4^-$ = dihydrogen phosphate ion

$HPO_4^{2-}$ = hydrogen phosphate

$PO_4^{3-}$ = phosphate

BOD = biological oxygen demand

$G_c$ = velocity gradient for rapid mixing

$\mu$ = dynamic water viscosity

$V$ = volume of mixing tank

$\tau_c$ = residence time in the mixing zone

$n$ = total number of particles per unit water volume

$\alpha$ = collision efficiency

$K$ = Boltzmann constant
T = absolute temperature

G_v = velocity gradient for floc formation

d = collision diameter

\( \nu_{tip} \) = mixing velocity

KH_2PO_4 = monopotassium phosphate

COD = chemical oxygen demand

RPM = rotations per minute

K_2Cr_2O_7 = potassium dichromate

HgSO_4 = mercury (II) sulfate

Ag_2SO_4 = silver sulfate

H_2SO_4 = sulfuric acid

(NH_4)_6Mo_7O_24 = ammonium heptamolybdate

Fe_2(SO_4)_3 = iron(III) sulfate

FeCl_3 = iron(III) chloride

Al_2(SO_4)_3 = aluminium sulfate

AlCl_3 = aluminium chloride
1. INTRODUCTION

Nutrients, which are flowing to water bodies from different sources can cause eutrophication. Eutrophication is a photosynthetic enrichment of water bodies by algae and cyanobacteria that progresses from oligotrophic, mesotrophic, to eutrophic states (Table 1) (Novotny, 2009).

Main outcome of eutrophication includes algae growth and aquatic weeds growth. These consequences of eutrophication have negative effects on fish life and economic use of fresh water resources for industrial activities, recreation, agriculture and drinking purposes. Algae growth in surface water bodies causes oxygen shortage, which leads to fish deaths and affects other water biota. The major problem of algae growth in freshwater resources is cyanobacteria, which may cause bad odors and unpalatability in drinking water. It also causes formation of trihalomethane during chlorination process on treatment plants (Carpenter et al., 1998). Trophic characteristics of fresh water resources are provided in Table 1.

Table 1. Trophic levels in lakes (modified after Brown and Simpson, 2001)

<table>
<thead>
<tr>
<th>Water quality variable</th>
<th>Oligotrophic</th>
<th>Mesotrophic</th>
<th>Eutrophic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mean</td>
<td>max</td>
<td>mean</td>
</tr>
<tr>
<td>Total Phosphorus (μg/l)</td>
<td>8</td>
<td>18</td>
<td>27</td>
</tr>
<tr>
<td>Total Nitrogen (μg/l)</td>
<td>660</td>
<td>11600</td>
<td>750</td>
</tr>
<tr>
<td>Chlorophyll a (μg/l)</td>
<td>1,7</td>
<td>4,5</td>
<td>4,7</td>
</tr>
<tr>
<td>Peak Chlorophyll a (μg/l)</td>
<td>4,2</td>
<td>11</td>
<td>16</td>
</tr>
<tr>
<td>Secchi Depth (m)</td>
<td>9,9</td>
<td>28</td>
<td>4,2</td>
</tr>
</tbody>
</table>

Nutrients (phosphorus and nitrogen) are transported to lakes and rivers as either a diffuse source inflow (Fig. 1) or a point source inflow. Point source pollution includes sewage discharges from municipalities and industrial wastewater loads (Yiping Wu and Ji Chen,
2013), while diffuse pollution generally comes from roads, agricultural fields and other land uses (Carpenter et al., 1998). Share of diffuse source pollution has being on the increase since the end of 20th century as a result of change in land use pattern. According to professor Novotny (Novotný, 2009), the concentration of nutrients in key tributaries of the Želivka river have already reached level of hypertrophic, which was the result of agriculture development in the region.

Figure 1. Processes of transport of P and N from agricultural lands (Carpenter et al., 1998)

Wide conversion of natural lands to agricultural fields and urban territories in Europe enhanced supply of nutrients to water resources through diffuse loading. Moreover, runoff from urban roads cannot be totally controlled by the sewage system and eventually end up in water bodies without any treatment. Controlling these diffuse sources is much more demanding than treating the point source inflow, and decades will pass until it will be possible to control them appropriately (Schindler, 2006).

After the “Green revolution” in 1960s industrial fertilizers became very popular in agriculture in Eastern Europe. This trend resulted in high amount of nutrients running into water bodies. This situation is extremely unsustainable. Farmers are paying extra for fertilizers and citizens are paying for water quality degradation (Novotný, 2009).
In agriculture there is an opportunity to decrease contribution to nutrient load by applying of appropriate dosage of fertilizers that is required by plants to reduce free P in soils. Substantial decrease in P load can be achieved by creation of riparian zones, buffer stripes, conservation tillage, cover crops and retention ponds. By vegetation barriers in riparian zones P transport to streams can be reduced by 50-85%. Key method of reducing urban P runoff is through optimization of sewer systems, reduction of different kinds of erosion, creation of retention ponds, wetlands and greenways to manage urban stormwater loads. (Carpenter et al., 1998). Huge amount of P is contained in manure. Applying of fertilizers cause accumulation of nutrients in soil and only about 5% of P and N run to water sources, while using of manure results in 20% runoff of P and N. (Carpenter et al., 1998).
2. PHOSPHORUS

Phosphorus is a critical element for any live organism on our planet. Shortage of phosphorus can limit crop production and cause health problems to animals. The main industrial application of phosphorus are in areas of fertilizers production, food additives, detergents and pharmaceutics production (Panasiuk, 2010).

Phosphorus in water does not directly cause any health hazards, however, it is a source of indirect toxicity caused by algae growth. Phosphorus and nitrogen cause eutrophication in lakes, rivers and estuaries. It happens when phosphorus input exceeds ability of ecosystem to consume it (Panasiuk, 2010).

One of the major reasons for eutrophication of water bodies is presence of P. It can affect trophic state of a water resource even in small concentrations (Table 1). It is necessary to mention that presence of P alone in surface waters does not change the trophic conditions, its effect on trophic conditions of surface waters depends on such parameters as temperature, amount of light and form of P (Shaw et al., 2003).

Phosphorus is non-renewable element, and that is why it is of great importance to recycle it. A lot of phosphorus lost every year because of recovery absence, therefore it is important to develop and apply methods for phosphorus recycling (Panasiuk, 2010).

2.1 Forms of phosphorus

Total P in natural water sources consists of dissolved part and suspended part (attached to particles). Both dissolved and suspended P can be either organic or inorganic. Dissolved inorganic bounded P consists of orthophosphates and polyphosphates. Suspended inorganic bounded P is created by different phosphates (Ca, Mg, Fe, Al, etc.), which exist in water column separately or chemically or by sorption bounded with other suspended components (Minnesota Pollution Control Agency, 2007). Phosphorus cycle is shown on the Fig. 2 and forms of phosphorus at different pH value represented at Fig. 3.
Inorganic dissolved P is converted to organic P when utilized by aquatic plants. Natural process of inorganic P generation is provided by animals which consume organic phosphorus by eating plants, other animals or by degradation of decomposing plants and animal material. After death of animals or plants they sinks to the bottom where by bacterial decomposition organic P from their tissues converts to inorganic P. The P tends to move downstream along with current of the water flow until it will be taken up by plants or will be bounded to particles when settling down to the bottom (United States Environmental Protection Agency, 2012).

Figure 2. Phosphorus cycle (Modified after United States Environmental Protection Agency, 2012)
2.2 Outcomes of water contamination by nutrients

One of the most significant nutrient is P, which determines ecological conditions of water body (limit of algae growth), therefore it is necessary to monitor and control its content. Amount of available P in water determines presence of different species of microorganisms. Water quality improvement would primarily depend on the amount of P in it, however there are other factors which also affect state of water body and it is important to monitor all of them (temperature, light, nitrogen, etc.). The following organisms can be presented in water resource and their ability for reproduction depends on P content (Martinek, 2012):

- Phytoplankton, which creates optical homogenous suspension
  These organisms have high specific growth rate and even with small increase in amount considerably affect water transparency. They create substantial obstacle for
utilizing water for drinking needs. Most frequently these algae appear in shallow eutrophic and hypertrophic basins.

- Cyanobacteria, creating algal bloom
  The term algal bloom is used to describe phenomenon where a huge amount of algae accumulated on water surface and create visible layer. This type of algae has relatively low specific growth rate because of low ratio between surface area and volume. Algae substitute deficiency of growth rate with ability to bound oxygen and absence of consumers while growing. Generally, they are reproduced in summer periods and cause different problems, such as production of toxins, deficiency of oxygen, shift of water quality, etc.

- Diatoms
  This kind of algae also cover water surface and prevent gas exchange between water and atmosphere. The difference with cyanobacteria is that diatoms does not have gas bubbles to remain on the surface. That is why they are producing oxygen bubbles by photosynthesis. The oxygen does not penetrate to water layer but return to the atmosphere. These algae are reproduced in spring periods and indicate change in trophic state of water body.

- Green algae
  These algae do not produce toxins and have positive effect on oxygen content in water body. In basins where they prevail, the first two types of algae can not be reproduced. However, when it comes to death of green algae (August, September) they become a source of deficiency of oxygen and bad odor.
- Macrophytes
  These kind of plants has positive effect on water body (reduce movement of water mass, prevent flowing of sediment and strengthen bank), however by growing, they decrease area for fish activities and because of sediment decomposition affect oxygen regime of water body.

Excessive growth of microorganisms in reservoirs results in broad variations of dissolved oxygen content, between oversaturation in hot period of day to the low oxygen concentration in cold night hours. These microorganisms settle to the bottom, where they consume oxygen, resulting in anoxic or even anaerobic conditions. Such conditions cause release of ammonium, phosphates, iron and manganese from sediment, which dramatically deteriorate water quality. These effects may be prevented before water body gained statues of eutrophic, however cost of such recovery will be high (Novotný, 2009).

Even if lake has a statues of eutrophic, it is possible to return it to a natural state. The process of water resource recovery is called remediation. It requires reduction of P and N inputs to the water body. It is possible to increase rate of remediation by applying other control techniques together with input control (Carpenter, 1998). However, it is also necessary to note that even after reducing external nutrient load to the water body it can still contain significant amount of phosphorus as a result of sediment degradation which releases phosphorus from the river bed. Time period of this effect may differ depending on the soil content in the region and on the period along which external load entered the lake (Schindler, 2006).
### 2.3 Phosphorus removal methods

Table 2 provides forms of phosphorus in water bodies and corresponding removal methods. To ensure reliable sufficiently low phosphorus concentration in the effluent from wastewater treatment plant it is necessary to combine treatment technologies and apply three-stage process. Usually these stages are physical, biological and chemical. Combination of these methods provide phosphorus concentrations around 0.5-1 mg/l and lower (Water Environment Research Foundation, 2009).

Table 2. (Modified after Water Environment Research Foundation, 2009)

<table>
<thead>
<tr>
<th>Species</th>
<th>Common conversion or removal method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic-P</td>
<td>Organic phosphorus can be converted to orthophosphate and polyphosphate, some organics degrade very slowly</td>
</tr>
<tr>
<td>Orthophosphate</td>
<td>Most abundant phosphorus species</td>
</tr>
<tr>
<td></td>
<td>Reactive species in chemical reactions and consumed in biological growth</td>
</tr>
<tr>
<td>Polyphosphates</td>
<td>Condensed orthophosphates</td>
</tr>
<tr>
<td></td>
<td>Possibly reacts with metal salts</td>
</tr>
<tr>
<td></td>
<td>Can be used for biological growth</td>
</tr>
<tr>
<td>Chemical phosphorus</td>
<td>Precipitated phosphates formed by reacting orthophosphates with metal salts, or precipitates as phosphate hydroxides</td>
</tr>
<tr>
<td>Biological phosphorus</td>
<td>Phosphorus incorporated into the biomass for growth</td>
</tr>
<tr>
<td></td>
<td>Excess phosphorus may accumulate under certain conditions</td>
</tr>
</tbody>
</table>
2.3.1 Physical methods

Phosphorus can be present in water in form of solid material and also in dissolved form. Physical methods used for phosphorus removal include:

- settling (e.g. settling basins)
- infiltration (filters)
- adsorption and absorption (wetlands)

Settling is a cheap, passive method of phosphorus separation. It requires big areas for sedimentation tanks. It is also called clarification and can be done in units of different construction, such as horizontal clarifier, vertical clarifier, flotation unit and others (Salanko, 2013). Two most common shapes of clarifiers shown on Fig. 4. Disadvantage of this method is that it does not remove dissolved phosphorus, but only suspended, bounded with solid particles. This method is usually used for pretreatment and requires additional processing. However, it also can be used as a part of chemical or biological treatment, when in the first stage to the water added coagulant and flocculant and on the second stage enlarged particles removed in clarifiers or in case of biological processing, water is treated with microorganisms, which are subsequently separated in clarifiers.

![Diagram of sedimentation basins](image)

Figure 4. Two most common shapes of clarifiers (Sarai 2006)
Filtration is a method where filtrating material is used. During the filtration process more than 80% of particulate is captured, while less than 2% of dissolved material removed (Weiss, 2011). Share of soluble phosphorus for municipal wastewater is about 90% (Tanyi, 2006). This means that conventional sand filters (Fig. 5) will not provide required water quality regarding phosphorus content and must be applied together with other treatment methods.

Disadvantages of filtration is that it removes only particulate contaminants and useful filtration depth is low (only upper layer of medium provide treatment), that is why regeneration of this layer is needed.

Figure 5. Conventional sand filter (Ernst)

Good example of adsorption method is wetlands application. Wetlands treat wastewater by natural processes. Human-made wetlands are areas, which combine fully vegetated territories, with anoxic regime, with open-water territories, and with aerobic regime. Plants in the anoxic area filter contaminants out of the water with their roots. The processes inside wetland are
somewhat similar to biological treatment (Safe drinking water foundation, 2008), however, main processes remain settling and adsorption to wetland materials.

Disadvantages and complexities, connected with wetlands application are large territories, used for their operation, unpredictability and instability of the process and lack of data for understanding of the process (Hammer, 1989).

2.3.2 Chemical methods

Chemical removal of phosphorus is widely done through the application of aluminum, iron and calcium compounds. Chemicals can be added in different stages of the treatment process. The biggest disadvantage of the chemical P removal is additional sludge, which is generated during sedimentation process (Strom, 2006). However, they are able to reduce P to a very low level. More detailed coagulation is described in Chapter 3.

Ion-exchange resins are used to adsorb phosphorus. This method did not find broad usage, but it looks promising as a final treatment stage. Advantages of this method are absence of sludge and ability to reuse resin after regeneration. Among disadvantages can be mentioned as short operation time, necessity of regeneration, and decreasing of exchange efficiency by co-existing nutrients ions (Zarrabi et al., 2014).

2.3.3 Biological methods

Biological treatment of P is usually achieved through assimilation in aerated ponds, where P is used for biomass growth (Strom, 2006). One of the biological methods is enhanced biological phosphorus removal (EBPR). EBPR method is very interesting for application on wastewater treatment plants, because it allows to reach very low P concentrations, produces less sludge than convenient biological processes and maintains operational costs on the moderate level (Panasiuk, 2010).

The basis of the process is to create such an environment to force biomass to consume more P than is needed for their life activities. It is done by special consequences of anaerobic-aerobic conditions (Fig. 6).
Consumption of P is effected by microorganisms called polyphosphate accumulating organisms (PAO). Moreover, PAOs are able to consume carbon sources during anaerobic stage and store them in form of polymers. For P consumption and storage of polyphosphates during aerobic conditions, PAOs require energy sources, such as carbon, accumulated during anaerobic phase. Some POAs also can use nitrate or nitrite instead of oxygen as acceptor for electron, therefore at the same time occurs reduction of P and N with decreased consumption of oxygen. However, it has been noticed that reliability and stability of this method can be a problem. The process is very sensitive and depends on many factors (temperature, oxygen content, ratio of BOD to P), that is why it requires strict control (Panasiuk, 2010). One more possible trouble with EBPR can be presence of glycogen accumulating organisms (GAOs) along with PAOs. The problem is that GAOs as well can exist under anaerobic conditions and consume carbon, while not consuming P under the aerobic conditions. One of the solution of this problem is to increase VFA (volatile fatty acids) amount in the anaerobic stage.

Figure 6. Process flow diagram for an EBPR process (modified after Panasiuk, 2010).
3. COAGULATION

Coagulants are chemicals which are used to neutralize surface charge of contamination particles to allow them to collide and form bigger particles. Bigger particles will settle down faster and, therefore will require less area of settling tanks.

As was mentioned above, for chemical treatment different types of coagulants are used. The process may run in accordance to two schemes (Minnesota Pollution Control Agency, 2006) (Fig. 7):

- addition of coagulant during the secondary treatment process, just before the secondary clarifier;
- addition of coagulant to the feed of primary clarifier and just before the secondary clarifier.

Figure 7. Two-point chemical addition (Minnesota Pollution Control Agency, 2006)
Second scheme is very typical because it is very effective in term of coagulant application to eliminate P from water. Dosage of chemicals is determined according to the initial concentration of P.

The dosage of coagulant required to decrease P concentration is dependent on many factors, such as target concentration of P, type of coagulant, temperature of wastewater, etc. For target concentration above 2 mg/l, it will be sufficient to add 1 mole of aluminum or iron per mole of P. For P concentrations between 0.3-1.0 mg/l dosage in range of 1.2-4 moles of aluminum or iron per mole of P should be applied (Minnesota Pollution Control Agency, 2006).

Solubility of precipitates of aluminum or other salts strongly depends on the pH value, therefore the most efficient P removal occurs in the pH range 5-7 for salts of aluminum and 6.5-7.5 for ferric salts (Minnesota Pollution Control Agency, 2006). When applying iron or aluminum salts it is also necessary to take into account other background reactions apart from the main one. These background reactions affect consumption of metal salt, therefore coagulant dosage should be determined experimentally and cannot be calculated based on the reaction with phosphorus (Panasiuk, 2010).

Chemical removal of P is inevitably linked to the flocks’ separation. It can be done either by precipitation and subsequent removal with a mechanical or hydraulic method, or by using flotation unit (physical methods). Application of flotation increase rate of flocks separation, and decrease the humidity of removed foam compared to the sediment. However, it is necessary to assume that effectiveness of the flotation depends on the physical characteristics of contaminants, particularly by wetting angle “θ”. Small θ corresponds to hydrophobic particles, which can be easily separated from water by flotation. These kind of particles include oils and petroleum products (Ponomariov, 2009).

Flocculants can be either cationic, anionic or non-ionic, depending on the charge of the polymer. This electrical charge helps to interconnect particles in wastewater. Such interactions usually occur between ions.

Coagulation and flocculation remove suspended matters from water, but they apply different methods for that (Fig. 8). Charged particles of the coagulant attach to the contaminants and
neutralize its’ charge, then Van der Waals forces provide binding of particles which enables them to settle down. Big influence on the efficiency of the process is the charge of the salt ions. Coagulation is better if charge is higher (Panasiuk, 2010).

Figure 8. Mechanisms applied in flocculation (a) and coagulation processes (b). (Panasiuk, 2010)

The quality of the coagulation process is vitally dependent on the provided mixing. Overmixing is not dangerous for coagulation, while insufficient mixing will lead to uncompleted process. Rapid mixing should be provided for 1 to 3 minutes (Prakash et al., 2014). If the coagulant is not completely mixed, local under- and overdosing occurs (Delft University of Technology, 2014).

The parameter which express mixing intensity is called velocity gradient or G-value (equation 1). It is defined as follows (Delft University of Technology, 2014):

\[ G_c = \sqrt{\frac{p}{\mu \cdot V}} \]  

(1)
where:

\( G_c \) – velocity gradient for rapid mixing (s\(^{-1}\))

\( P \) – dissipated power (W)

\( \mu \) – dynamic water viscosity (N\(\cdot\)s/m\(^2\))

\( V \) – volume of mixing tank (m\(^3\))

In practice, the recommended \( G \)-value for coagulation is 1500 s\(^{-1}\), at a minimum.

Generally, two mixing systems can be applied, mechanical mixing and static mixing. In the first system mixing is provided by mechanical mixers, which dissipate coagulant in water, while in the second system mixing caused by gravity forces (Delft University of Technology, 2014).

G-value for static mixers (equation 2) can be presented as:

\[
G_c = \sqrt{\frac{\rho g \Delta H}{\mu \tau_c}}
\]  

(2)

where

\( \tau_c \) – residence time in the mixing zone

The most common example of static mixer is the cascade, where water falls over a weir into a receiving body. Coagulant is dosed in the turbulent space that is caused by the falling water. Flocculation, on the other hand requires gentle mixing, because during this stage particle size increases and rapid mixing will disturb flocks. The growth of flock occurs, while particles collide with each other. After flocks reached their optimum size, particles are ready to be removed by sedimentation or flotation. This stage is lasts from 15 minutes to one hour and more. Formation of flocs in the flocculation process can take place under natural circumstances (perikinetic floc formation) or by dissipation of mixing energy (orthokinetic floc formation) (Delft University of Technology, 2014). Perikinetic floc formation is based on
the Brownian motion, in which particles collide. The decrease in the total number of particles was described by Von Smoluchowski as a function of time (equation 3):

\[-\frac{dn}{dt} = \frac{4kT}{3\mu} n^2\]  \hspace{1cm} (3)

where

n – total number of particles per unit water volume (m\(^{-3}\))

\(\alpha\) – collision efficiency (-)

K – Boltzmann constant (JK\(^{-1}\))

T – absolute temperature (K)

Not all collisions will result in attachment of flocs, hence the collision efficiency is incorporated into the equation. Experiments show that this type of floc formation is fast, however results in poor settling characteristics of the formed flocs (Delft University of Technology, 2014).

The collision frequency of the particles can be increased by mixing. The total number of particle decreasing with time according to the following equation (4) (Delft University of Technology, 2014):

\[-\frac{dn}{dt} = \frac{4}{3} \alpha d^3 n G_v\]  \hspace{1cm} (4)

where

\(G_v\) – velocity gradient for floc formation (s\(^{-1}\))

\(\alpha\) – collision efficiency (-)

d – collision diameter (m)

n – number of particles
Substituting $n \cdot d^3$ with volumetric concentration $c_v = \frac{1}{6} d^3 n \pi$ for spherical particles (equation 5):

$$- \frac{dn}{dt} = \frac{8 \alpha n c_v g_v}{\pi}$$

Which results in (equation 6):

$$\frac{n}{n_0} = e^{-k_a c_v g_v t}$$

Using this equation it is possible to calculate that for particles with diameter 1μm orthokinetic floc formation takes place only when velocity gradients higher than 10 s$^{-1}$ are applied. Otherwise, perikinetic floc formation is dominating (Delft University of Technology, 2014).

Floc formation is influenced by number of parameters, such as residence time, residence time distribution, velocity gradient for floc formation and floc volume concentration. Residence time is usually varies between 500 and 3600 sec. It is determined by carrying out with jar tests. Residence time distribution results in higher complexity of the real floc formation process in comparison to theoretical. To make distribution more even, impeller mixers are applied. They should be installed in line, along the flow direction (Delft University of Technology, 2014).

The mixing velocity is greatest at the tip of the mixing blade and can be calculated by equation 7 (Delft University of Technology, 2014):

$$v_{tip} = 2 \pi r N$$

If the tip velocity is higher than 1 m/s, formed flocs are broken up. Radius of mixing blades can be determined, when tip velocity is known.

To avoid floc break-up flocculation chamber is divided into several compartments, where mixing velocity gradually decrease from first to last (Delft University of Technology, 2014).

There are number of drawbacks in using of chemicals for P removal (Panasiuk, 2010), such as additional sludge production, difficultness to accurately calculate required dosage, because of
constant fluctuation of parameters, more difficult recovering of P from the sludge in comparison to the EBPR, operator on wastewater treatment plant has to contact with chemicals what causes safety concerns, additional transport costs, high prices of reagents, losses of huge amount of P in sludge.

4. FLOTATION THEORY

Flotation itself is a combination of physical and chemical processes, used for purification of water, which is controlled by properties of gas-liquid-solid system and changes of these properties by insertion of different reagents to the system (Bulatovic, 2007).

The decisive role in flotation plays interfacial interaction. The properties of three-phase system are complex, thus theoretical explanation of it is based on hypothesis and approximations. Interfaces between phases possess a surface energy, which determines the most of the details of flotation. The surface energy is an excess energy on the surface of interacting particles, which is higher than energy inside the bulk phase (Bulatovic, 2007).

4.1 Mineral particle phase

The most complex of these three phases is mineral phase, because of numerous of different minerals in one particle and also because of many changes, happening in the particle. It also may complicate content of liquid phase, by releasing ions and cations. Major role in the flotation process plays surface character of a mineral particle. Surfaces of particles of the same mineral specie may have different physiochemical properties, which means that adsorption effect of added reagent also may vary for these particles. This phenomenon is called heterogeneity of a mineral surface. In 1950, Gardner (Bulatovic, 2007) made classification of minerals, according to their flotation properties, shown in Table 3.

Table 3. Classification of minerals by Gardner (Bulatovic, 2007)

<table>
<thead>
<tr>
<th>Group</th>
<th>Minerals</th>
<th>Representatives</th>
</tr>
</thead>
</table>


In reality, the mineral phase is never the one mineral only. It is always a multi mineral system consisted of many minerals. There are always chemical interaction between different minerals. Properties of a particular mineral depend not only on the mineral itself, but also on the interactions in the multi-mineral system. This means that even though that flotation theory has an understanding of individual minerals surface interaction it does not guaranties that in real multi-mineral system minerals will interact in the same way (Bulatovic, 2007).

### 4.2 Liquid phase

The liquid is a substance where the flotation takes place. The key process is an attachment of air bubbles to solid particles. Interaction between mineral particles and the reagents applied in some way related to liquid (water) properties (Bulatovic, 2007).

When foreign ions are presented in water, hydration occurs, which looks like concentration of water molecules around the foreign ions. Hydration process means that attractive energy between water dipoles and ions is much greater than attraction between dipoles. The energy of hydration varies, depending on valiancy, temperature, polarities, etc. From the flotation point of view, with rising polarization of water dipoles, water loose its’ ability to dissolve matter.
Moreover, diffusion of foreign ions is more difficult in polarized water, hence, hydration of ions is directly connected to the solvent actions of water (Bulatovic, 2007). It is hard to determine the effect of particular impurity in water on the flotation process. In some cases pollutant cations do not affect the process, while in other it may decrease the effectiveness of reagents. It is known from plant practice, that presence of organic or biological contamination negatively affect floatability. Also, flotation process may be affected by gases which are dissolved in water. This type of impurities may be adsorbed by mineral particles, which cause their oxidation and affects solubility (Bulatovic, 2007).

4.3 The air phase

Air, injected to the flotation unit form bubbles, which are purposed to carry hydrophobic minerals to the foam phase (Bulatovic, 2007). The flotation process proceed in accordance to complex phenomenon occurring on the surface of mineral particles and air bubbles interface. Bulatovic (2007) claims that electrical characteristics is one of the most important properties of mineral surfaces. They can be described by two potentials – electrochemical and electrokinetic.

Mineral particles in water loose ions, while interacting with water and other particles. This gain charge to particles’ surface. In the process of adsorption of reagents to particles surface, electrical double layer plays very important role. This layer is characterized by concentration of ions around surface of the minerals, according to their charges (Bulatovic, 2007). The total double layer yields by the potential difference between surface of the particle and the solution. Schematically potential and double layer are presented on Figure 9. Electrokinetic interactions, combining mechanical and electrical effects proceeds in the diffuse layer. Zeta potential is an electrokinetic variable, which is used to characterize adsorption ability of different reagents.
Figure 9. Schematic representation of the double layer and potential drop across the double layer (Bulatovic, 2007)

The process of flotation contains adsorption interactions. Adsorption may be either chemical (chemisorption) or physical (physisorption). Physisorption is performed by weak Van der Waals forces and its’ strength rises with surface area, the same as for chemisorption, however chemisorption is usually stronger and does not depend on the temperature so much (Adichemistry, 2015).

One of the parameters to measure the efficiency of flotation is the rate of flotation, which can be expressed as amount of floated particles per unit of time. Unfortunately, there are no common method to determine the rate of flotation. A number of kinetic models developed for that purpose, however there are several problems related to these models, including differences in flotation variables, difficultness to express flotation process, using equation, etc. Even though, the rate of flotation is the most reliable method to describe kinetics of flotation (Bulatovic, 2007).
5. MATERIALS AND METHODS

5.1 Study site

Water reservoir Švihov (Fig. 10) was built in 1965 – 1975. The purpose of the reservoir is to provide drinking water to the capital city Prague (70% of the drinking water consumption) (Novotný, 2009) and some other surrounding regions. The reservoir is one of the biggest in Central Europe and the biggest in Czech Republic. Maximum volume of the reservoir is approximately 266.57 mil. m³. Maximum depth is 52 m and average depth is 18 m. Water for purification taken from depth 25 or 33 m (Martinek, 2012).

There is a great potential for rapid and critical deterioration of water quality in the Švihov reservoir. High concentrations of nutrient near the coastline causes cyanobacteria bloom. Nutrient inflow to the reservoir provide threat for water supply system and may cause its’ collapse. The problem of cyanobacteria is an emergency situation, which requires actions along the whole watershed. Blooms caused by nitrogen and phosphorus, originating from point sources and diffuse sources. These problems are cause by specialties of these area, where agriculture together with cattle breeding are applied widely. This provides sufficient amount of nutrients to the reservoir (Novotný, 2009).

All eighteen river systems, which form the Želivka reservoir system are classified as poor quality water according to WFD guidelines. The only thing that prevents complete cyanobacteria bloom in the Prague water supply system is the plug flow in Švihov reservoir. After the algal blooms will reach water intake, the treatment plant will be unprotected against filter clogging and toxins infiltration to drinking water system. Treatment plant will require expensive renovation to satisfy water quality requirements (Novotný, 2009). Therefore, it is important to prevent continuation of contamination of the reservoir and its’ tributaries.

Spread of algal blooms and hypertrophic conditions of reservoirs have occurred only twenty or thirty years ago, mostly as an outcome of the overuse of industrial fertilizers, phosphate detergents and often lack of treatment of point wastewater sources. If the shift to hypertrophic
condition in the Švihov reservoir will occur, the process of reversing back to an acceptable condition will be very costly (Novotný, 2009).

In this project to improve removal of P from municipal wastewater, we applied coagulation and flocculation with subsequent flotation. In flotation process contaminants are removed by injecting high pressured air into the water followed by removal of foam from the top of the floating facility. In comparison with conventional sedimentation this method is much faster and require less space to remove bonded contaminants, moreover foam contains less liquid fraction than sediment, collected from settling tanks (Ponomariov, 2009).

Figure 10. Location of the reservoir Švihov.
5.2 Jar tests

The first part of this work was determining of coagulant, which will give the best results for our particular wastewater from treatment plant in the city of Pacov. Jar tests were applied in the laboratory of Water Technology and Environmental Engineering Department of the Institute of Chemical Technology in Prague. For these purposes outflowing water from the Pacov wastewater treatment plant was taken. Totally 4 barrels of 25 liters were taken one after another. Maximum time, which barrel spent in a fridge before jar test was one week. In each batch of Pacov water we artificially added P in form of KH$_2$PO$_4$ to reach concentration of 1.2 mg/l. It was done, to provide sufficient concentration of phosphorus to increase visibility of results from application of different coagulants. Phosphorus concentration after artificial regulation was measured corresponding to the method, described in section “analyzing”.

For jar tests water from Pacov wastewater treatment plant was filtrated, using filter papers Munktell, Grade: 388, Dia 150 mm, 84 g/m$^2$ with pore size of 12-15μm. Volume of water in jars was 800 ml and stayed the same for each test. In this experiments we used 5 coagulants, to determine the best dosage and most effective coagulants. The coagulants, their market names and producers are provided in the Table 4. After the best available coagulant was chosen, 7 flocculants were applied to settle down suspended coagulated particles (Table 5).

Table 4. List of coagulants, applied in this work

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Market name</th>
<th>Producer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrum chloride</td>
<td>PIX-111</td>
<td>Kemifloc</td>
</tr>
<tr>
<td>Ferrum sulphate</td>
<td>PIX-113</td>
<td>Kemifloc</td>
</tr>
<tr>
<td>Aluminum sulphate</td>
<td>Aluminum sulphate</td>
<td>Kemira</td>
</tr>
<tr>
<td>Polyaluminium chloride</td>
<td>PAX-18</td>
<td>Kemira</td>
</tr>
<tr>
<td>Melamine-formaldehyde resin</td>
<td>FL 42</td>
<td>SNF Floerger</td>
</tr>
</tbody>
</table>
Table 5. List of the flocculants, applied in this work

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Market name</th>
<th>Producer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymeric medium anionic flocculant</td>
<td>Praestol 835 BS</td>
<td>Ashland Deutschland</td>
</tr>
<tr>
<td>Polymeric medium anionic flocculant</td>
<td>Praestol A 3040 L</td>
<td>Ashland Deutschland</td>
</tr>
<tr>
<td>Polymeric medium anionic flocculant</td>
<td>Praestol 2540 TR</td>
<td>Ashland Deutschland</td>
</tr>
<tr>
<td>Polymeric anionic flocculant</td>
<td>Praestol K 144 L</td>
<td>Ashland Deutschland</td>
</tr>
<tr>
<td>Strong cationic flocculant</td>
<td>Praestol 857 BS</td>
<td>Ashland Deutschland</td>
</tr>
<tr>
<td>Cationic flocculant</td>
<td>Sokoflok K 62</td>
<td>Sokoflok</td>
</tr>
<tr>
<td>Anionic flocculant</td>
<td>Sokoflok A 16</td>
<td>Sokoflok</td>
</tr>
</tbody>
</table>

To determine which coagulant and flocculant gave the best results after each jar test, samples were analyzed for different parameters. We analyzed our investigating wastewater to determine COD, left orthophosphates, pH, and left traces of metal from coagulants (Al or Fe).

5.3 Coagulation

All of the coagulation tests were run under the same conditions: after addition of coagulant, the sample was mixed for 1 minute on 180 RPM, 10 minute on 25 RPM, these values were recommended by the producer of flotation unit. After mixing, the mixing device was removed from mixture and flocks were allowed to settle down for 20 minutes. After that, 50 ml sample from each jar was collected, filtered and was stored for subsequent testing and pH was measured.
5.4 Analyzing

The procedure for determination of COD in Czech Republic is described in the document, called TNV 75 7520. It starts with collection of 2.5 ml of sample to a testing tube. Then fastly adding 1.5 ml of oxidation solution and 3.5 ml of catalytical solution.

Oxidation solution is made of 750 ml of water, where 1.022 g of $K_2Cr_2O_7$ is suspended, then 167 ml of sulfuric acid and 33.3 g of HgSO$_4$ are added and final mixture is diluted with water to rich volume of 1000 ml. Catalytical liquid is prepared from 1 l of sulfuric acid, where 10 g ±0.1 g of Ag$_2$SO$_4$ is saturated.

After two solutions were added, test tubes were closed and mixed well. Then they were placed to thermoreactor at 148 °C for two hours. After thermoreactor tubes were chilled, COD was measured in WTW spectrophotometer.

COD shows how much of oxygen will be required to oxidize organic matter, contained by solution. Organic matter, outflowing from wastewater treatment plant will then settle down in the water reservoir, therefore it should be as low as possible.

The determination of orthophosphates in water was done according to the document ČSN EN ISO 6878. Before the analyzes, reagent, made of 5 ml of H$_2$SO$_4$, 2 ml of (NH$_4$)$_6$Mo$_7$O$_{24}$, 1 ml of antimony potassium tartrate and 2 ml of ascorbic acid was prepared. To the test tubes were added 5 ml of sample and then 0.5 ml of prepared reagent, mixed and after 15 minutes, orthophosphates measured in WTW spectrophotometer at 690 nm.

Measuring of pH was done only after 50 ml samples were collected to eliminate possible measuring mistakes. For the measuring, digital pH meter produced by WTW company was used.

5.5 Flotation unit

The pilot scale flotation unit for the experiments was provided by the Kunst company (Fig. 11, 12). Suspension comes to flotation unit after the flocculation stage (Fig. 13). At first the suspension is mixed with pressurized water (recycle stream from the flotation tank).
Pressurized water is saturated with air under pressure of 3 to 5 bars. Aeration of the recycle stream done in a saturation vessel 2.1 m high and 0.2 m in diameter (Fig. 11, on the left). The mixture of recycle stream and suspension flows into flotation tank, which has volume of 4.5 m³, where with pressure reduction fine bubbles are produced. Microbubbles attach to flocs and rise them to the surface. The floating foam layer is removed by a skimmer, which can be operated continuously or discontinuously (Fig. 11, 12) (Houdková et al., 2014, 1).

Figure 11. Flotation unit (Pečenka, 2015)
Figure 12. Scheme of the flotation unit. (Modified after Houdková et al., 2014, 2)

Figure 13. Flocculation unit (Pečenka, 2015) (from left – flocculant tank with pump, fast mixing tank, slow mixing tank)
6. RESULTS

6.1 Coagulation experiments

Results, which can be found in appendix A and B, contain values of pH after coagulation, residual phosphate concentration, values of COD, and traces of residual iron and aluminum (traces of coagulants). These values were measured, because their amount in the outflow from wastewater treatment plant is limited, by a Czech norm NV. 23/2011 Sb (Czech government, 2010). This norm, when applied to Pacov wastewater treatment plant, requires pH value to be 6-9, total phosphorus concentration less than 8 mg/l and COD value less than 170 mg/l.

It is seen from the results in appendix A, that dosages of coagulants higher than 1.25 mg/l provide significant drop of pH. This means that alkalinity of wastewater from Pacov is able to balance acidity, provided by 1,25 ml/l of all used inorganic coagulants. Visually coagulation tests are presented on Figures 14-17 and in appendix C.

Phosphates concentration decreased by addition of coagulant, therefore the closer it to zero, the better. However, reasonable dosage should be applied. Balance between cost of coagulant, and residual phosphates should be found. For example, Fe₂(SO₄)₃ with dosage of 3.75 ml/l provided the best result of phosphates removal (0.019 mg/l), but the dosage is 3 times higher, than FeCl₃ with almost the same result (dosage of 1.25 ml/l and 0.027 mg/l of residual phosphates).

Flocculants addition should provide better precipitation of the coagulated particles by the increase of their size. However, it is possible that over dosage will increase settling time. As seen from the results in appendix B, flocculants do not affect pH values, therefore, comparison was done among another values.

From the results of flocculation tests in appendix B it is possible to see certain trends of phosphates concentration, COD value and concentration of metals (traces of coagulant). Couple FeCl₃ and 835 BS show even drop on every of above mentioned parameters and then, irrespectively of dosage from 1 ml to 2.5 ml/0.8 l, these parameters were on the same level.
Dosage of 3 ml/0.8 l increased residual phosphates and amount of residual metals from coagulant, while COD value raised to 20 mg/l at dosage of 1 ml/0.8 l, otherwise was around 15 mg/l for every dosage.

For FeCl₃ and 3040 L residual phosphates concentration and residual iron concentration constantly increased with one fluctuation at dosage of 2 ml/0.8 l, were iron concentration dropped to 1.437 mg/l and phosphate concentration raised to 0.079 mg/l.

For couple FeCl₃ and 827 BS lowest concentration of phosphates and residual iron was at dosage of 1 ml/0.8 l, while COD concentration at this dosage was the highest. Subsequent increasing of dosage showed the same trends for all three parameters. At dosage of 1.5 ml/0.8 l they increased, and then decreased (except residual iron) and remained almost constant.

For couple FeCl₃ and 133 L residual phosphates and iron show similar trends with three minimums at dosages of 0.5, 2 and 3 ml/ 0.8 l, while COD has maximum at dosage of 1.5 ml/0.8 l (the same for iron and phosphates) and in overall decreasing. For couple FeCl₃ and 2540 TR trends for residual phosphates and iron are also the same with maximum at dosage of 1.5 ml/0.8 l, however, maximum for phosphates is sharper than for iron. COD also has maximum at the same dosage and in overall increasing.

We interpreted this fact such, that if coagulant reacted and settled well, contaminations are removed, whereas, when coagulant by any reason did not react well or excess amount of flocculant prevented sedimentation, contaminations remain suspended in water. According to the results of the experiment as the suitable flocculant was chosen 827 BS with dosage of 1.25 ml/l, because it shows the best combination of residual phosphates (0.017 mg/l) and residual iron content (0.79 mg/l) at such low dosage.

Results of jar tests represented in form of photos of jars after coagulation was done and settling of the flocks were observed. All photos of jar tests provided by Ing. M. Pečenka, Tables with results can be found in Appendix.
Other photos can be found in Appendix.

### 6.2 Flotation experiments

Flotation experiments were done in two batches. First three experiments were done on 23rd – 24th of September and the last one was done on 11th – 12th of October. The results of these experiments presented in tables 6 and 7.
Table 6. Results of the flotation experiments

<table>
<thead>
<tr>
<th>Sample</th>
<th>Molar ratio Fe/P</th>
<th>P-PO43 [mg/l]</th>
<th>Δ</th>
<th>%</th>
<th>P_total [mg/l]</th>
<th>Δ</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inflow</td>
<td>2.6</td>
<td>0.520</td>
<td>0.380</td>
<td>73.1</td>
<td>0.606</td>
<td>0.232</td>
<td>61.7</td>
</tr>
<tr>
<td>outflow</td>
<td></td>
<td>0.140</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inflow</td>
<td>2.8</td>
<td>0.456</td>
<td>0.347</td>
<td>76.1</td>
<td>0.616</td>
<td>0.219</td>
<td>64.4</td>
</tr>
<tr>
<td>outflow</td>
<td></td>
<td>0.109</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inflow</td>
<td>4.6</td>
<td>0.342</td>
<td>0.268</td>
<td>78.4</td>
<td>0.361</td>
<td>0.286</td>
<td>79.2</td>
</tr>
<tr>
<td>outflow</td>
<td></td>
<td>0.074</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 7. Iron balance

<table>
<thead>
<tr>
<th>Molar ratio Fe/P</th>
<th>Amount of added Fe [mg/l]</th>
<th>Inflow Fe to flotation [mg/l]</th>
<th>Total amount of Fe inflow [mg/l]</th>
<th>Outflow Fe from flotation [mg/l]</th>
<th>Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.6</td>
<td>2.15</td>
<td>0.374</td>
<td>2.524</td>
<td>0.972</td>
<td>1.552</td>
</tr>
<tr>
<td>4.6</td>
<td>3.79</td>
<td>0.402</td>
<td>4.192</td>
<td>0.981</td>
<td>3.211</td>
</tr>
</tbody>
</table>

Wastewater treatment plant in Pacov already had satisfactory outflow water quality when we came there, however, flocculation together with flotation removed more than 60% of residual total phosphorus in every experiment (Table 6). Existing treatment process includes addition of coagulant (Fe₂(SO₄)₃) to the outflow of activation tank, before secondary clarifiers and some traces of iron can still be found in the outflow from treatment plant. Table 7 shows overall amount of iron inflowing to the flotation unit and outflowing from it. From Table 6 it is seen, that at ratio Fe/P equal to 4,6 total phosphorus removal is increased significantly, while phosphates removal increased less.
7. DISCUSSION

Analyzing results of jar tests it is important to find reasonable tradeoffs. All parameters should be balanced as much as possible. Certain dosage of coagulant should provide sufficient phosphates and COD removal, should not leave too much of heavy metals (aluminum and iron) and be cost efficient. Excessive amount of metals (aluminum and iron), accumulating in live matter (animals, humans, plants) will cause hard diseases. Therefore, over dosage of coagulant is very dangerous and should be avoided. According to these requirements the best available coagulant was determined. We chose FeCl$_3$ with dosage of 1.25 mg/l, as it provides reasonable values for all measured parameters. Already at this dosage it is provided outflow phosphates concentration of 0.022 mg/l, COD concentration of 13.9 mg/l and residual iron concentration of 0.841 mg/l. Fe$_2$(SO$_4$)$_3$ has phosphates concentration of 0.023 mg/l, but dosage of coagulant is 1.875 mg/l and pH is lower. Al$_2$(SO$_4$)$_3$ at dosage of 0.5 ml/0.8 l provided outflow aluminum concentration of 0.223 mg/l, however residual phosphates has concentration of 0.118 mg/l. Sample with 0.5 ml/0.8 l dosage of Fe$_2$(SO$_4$)$_3$ had outflow residual iron concentration of 0.789 mg/l, but phosphates concentration was 0.114 mg/l. Many coagulants showed better decreasing of COD, however dosage of coagulants was higher, therefore pH drop was bigger.

The final stage of the project was to apply laboratory determined dosages on the testing scale flotation unit on a real wastewater treatment plant. Results of these experiments were analyzed with the same methods. Combination of coagulation and flotation allowed to decrease total phosphorus content by 60% and more, depending on the Fe/P ratio. These results are similar to Water Environment Research Foundation (2009) results, which claim that solids, produced under a higher Fe/P ratio will have lower phosphorus concentration, than solids, produced under lower Fe/P ratio. A lower phosphorus concentration in solids is better to achieve low effluent phosphorus concentration, because certain amount of TSS with lower phosphorus content will have less phosphorus than the same amount of TSS with higher phosphorus content.
Comparing results of iron balance in the results of the flotation experiments (Table 7) it is seen, that amount of outflowing iron at different initial molar ratios are very close to each other. This may mean that extra iron in the case of ratio of 4.6 reacted with bigger amount of phosphates and with some organic contaminations. This resulted in a bigger amount of sludge, additional costs of chemicals, but at the same time in a better purification effect, however, sufficient treatment effect can be reached at the lower dosage of coagulant. This dosage should be determined on a treatment plant, which does not have chemical treatment and do not provide sufficient reduction of phosphates.

Any of ratios, represented in Table 6 (results of flotation tests) provide sufficient treatment according to norm for outflow from wastewater treatment plants. Even water, inflowing to the testing unit is treated sufficiently. This is because this particular treatment plant applies coagulant to enhance treatment process efficiency. Future experiments are planned to be done on a less equipped treatment plants for better understanding of coagulation efficiency on phosphates removal. Less equipped treatment plants may not always have sufficient phosphates removal, hence, experiments on these sites will be more efficient and applicable in practice.

Results of the flotation and flocculation experiments depends on the temperature. The lower the temperature, the longer and weaker chemical reactions in water. This is important to notice, when comparing obtained results with another similar experiments. Unfortunately, in the middle of October outside temperature became too low to continue experiments, therefore this work is limited with flotation experimental data. However, it is possible to find certain trends even with this amount of tests.

Experiments showed, that considerable increasing of Fe/P ratio does not provide the same considerable improvement in treatment process, however, inflowing water phosphorus content at ratio of 4.6 was about twice lower than phosphorus content at another concentrations and this could affect the results. Ratio of 2.3 provided total phosphorus treatment of 67% and final concentration of 0.294 mg/l which is quite similar results as has Tanyi (2006).
8. CONCLUSION

This work was focused on finding the best combination and dosages out of available coagulants and flocculants and subsequent testing of flotation unit, provided by KUNST Company to remove phosphorus from wastewater. Laboratory tests were done in the laboratory of Department of Water Technology and Environmental Engineering of University of Chemistry and Technology, Prague, under supervision of Professor Jiří Wanner, Dr. Martin Pečenka and PhD. student František Martínek. Field tests were done on the site of Pacov wastewater treatment plant, where flotation unit were installed.

Laboratory tests included set of jar tests where different coagulants were tested and then samples from each experiment undergone analyses to find COD content, residual phosphates amount, pH values, and coagulant traces in water. After that, the coagulant with the best results were chosen and tested together with different flocculants, to find the best couple coagulant-flocculant. For evaluation of the results, the same analyzing methods were applied.

Subsequent flotation experiments on site demonstrated high efficiency for removing of phosphorus in combination with coagulant. Application of coagulation together with flotation significantly improved phosphorus removal. Dosage of FeCl₃, when molar ratio Fe/P was 2.3 removed 67% of total phosphorus and when ratio was 4.6 – 79% of total phosphorus.

Even though Fe/P ratio of 4.6 twice lower than 2.3, P removal efficiency is only 12% better. Residual iron for both cases is almost the same, and we proposed that it is because of increased removal rate of organic substance (which is not supported by analyzes).
REFERENCES


Table 8. Results of the jar tests with corresponding coagulant dosage

<table>
<thead>
<tr>
<th>Dosage [ml]</th>
<th>Fe₂(SO₄)₃</th>
<th>FeCl₃</th>
<th>Al₂(SO₄)₃</th>
<th>AlCl₃</th>
<th>FL 42</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH</td>
<td>PO₄</td>
<td>COD₁</td>
<td>Traces of coag [mg/l]</td>
<td>pH</td>
</tr>
<tr>
<td>0.5</td>
<td>6.9</td>
<td>0.114</td>
<td>12.76</td>
<td>0.789</td>
<td>6.7</td>
</tr>
<tr>
<td>1</td>
<td>6.3</td>
<td>0.079</td>
<td>11.06</td>
<td>0.926</td>
<td>6.0</td>
</tr>
<tr>
<td>2</td>
<td>3.9</td>
<td>0.056</td>
<td>10.13</td>
<td>2.02</td>
<td>4.6</td>
</tr>
<tr>
<td>3</td>
<td>3.3</td>
<td>0.019</td>
<td>4.77</td>
<td>9.65</td>
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</tr>
<tr>
<td>4</td>
<td>3.0</td>
<td>0.024</td>
<td>4.91</td>
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<tr>
<td>5</td>
<td>2.9</td>
<td>0.021</td>
<td>1.64</td>
<td>28.7</td>
<td>2.7</td>
</tr>
</tbody>
</table>
Table 9. Results of the jar tests with dosage of FeCl₃ of 1.25 ml/l and corresponding flocculant dosage

<table>
<thead>
<tr>
<th>Dosage [ml]</th>
<th>835 BS</th>
<th>3040 L</th>
<th>827 BS</th>
<th>K 133 L</th>
<th>2540 TR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH</td>
<td>PO₄</td>
<td>COD₇</td>
<td>pH</td>
<td>PO₄</td>
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<td>6.51</td>
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<td>20</td>
<td>0.614</td>
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<td>6.48</td>
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<td>0.081</td>
<td>14.3</td>
<td>0.891</td>
<td>6.46</td>
</tr>
</tbody>
</table>

Appendix B
Appendix C

Figure 18. Tests 1-3 with Al$_2$(SO$_4$)$_3$

Figure 19. Tests 4-6 with Al$_2$(SO$_4$)$_3$

Figure 20. Tests 1-3 with AlCl$_3$

Figure 21. Tests 4-6 with AlCl$_3$
Figure 22. Tests 1-3 with FL 42

Figure 23. Tests 4-6 with FL 42

Figure 24. Tests 1-3 with Fe$_2$(SO$_4$)$_3$

Figure 25. Tests 4-6 with Fe$_2$(SO$_4$)$_3$
Figure 26. Tests 1-3 with FeCl₃

Figure 27. Tests 4-6 with FeCl₃

Figure 28. Tests 1-3 with FeCl₃ and 835 BS

Figure 29. Tests 4-6 with FeCl₃ and 835 BS
Figure 30. Tests 1-3 with FeCl$_3$ and 3040 L

Figure 31. Tests 4-6 with FeCl$_3$ and 3040 L

Figure 32. Tests 1-3 with FeCl$_3$ and 827 BS

Figure 33. Tests 4-6 with FeCl$_3$ and 827 BS
Figure 34. Tests 1-3 with FeCl$_3$ and K 133 L

Figure 35. Tests 4-6 with FeCl$_3$ and K 133 L