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# Purification of wastewater from chlorophosphate flame retardants production process

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ABSTRACT

The aim of the research was the removal of phosphorous excess in the wastewater from the chlorophosphate flame retardants production process, before transfer the wastewater stream to WWTP. The tested wastewater, contains 7 $g/dm^3$ of phosphorus (P) and COD level is 72–78 g $O_2/dm^3$. Removing phosphorus from wastewater was performed by precipitating insoluble iron(III) phosphate(V) with the use of iron(III) chloride. At pH < 2 and molar ratio Fe/P = 1.1 up to 65% phosphorus recovery was achieved; at pH > 3.0 the recovery rate increased up to 70%. The best results were obtained for pH~4.5 and Fe/P ratio about 2.0. The phosphorus removal process is connected with decrease of COD value in wastewater. The best results were obtained for Fe/P in the range 1.5–2.0 and pH ~4. The best results of purification process were obtained with the final COD value 13–23 g $O_2/dm^3$ and the total P concentration below 0.001 $g/dm^3$. The flow sheet of the purification wastewater process was proposed.

*Keywords:* Wastewater; Phosphorus removal; Precipitation; Recovery; Iron; Organophosphorus flame retardant

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## 1. Introduction

Phosphorus is a vital element for every life form and it is also an essential ingredient of fertilizers, which assure a large yield of crops. This is why it is essential for the food safety of society [1]. An opened phosphorus cycle has a serious and negative effect on the environment. An excess of phosphorus and nitrogen disturbs the biocenotic balance, causing negative environmental effects. The phosphorus compounds introduced through sewage into reservoirs are mostly in the form of orthophosphates (V), which are immediately drawn and used by the fauna and flora, leading to eutrophication. For this reason, the dumping of phosphorus into surface waters is limited and controlled, which was the impetus for the development of techniques for the removal of phosphorus from wastewater and sewage. Currently, phosphoric raw materials, next to fuels and certain metals are on a highlighted list of twenty so-called "critical" raw materials for Europe, e.g. raw materials important for the economic development of EU member countries, while at risk of supply [2]. The policy of sustainable phosphorus management currently being implemented in the EU consists of: (1) lower consumption of phosphoric feedstock with higher efficiency of utilisation, (2) minimisation of direct phosphorus loss and reduction of waste which cannot be reused and (3) an aspiration to a economically, socially and environmentally acceptable reduction of phosphorus consumption [3]. Thus, a significant increase of interest in the technologies of phosphorus recovery from sewage and industrial waste waters can be observed nowadays.

In 2011, Sartorious identified 22 commercially valuable technologies for phosphorus recovery. The technologies can be divided into "wet" and "thermochemical". The latter entails the recovery of phosphorus from an ash remain-

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ing after an incineration of solid residues [4]. The typical wet methods of phosphorus recovery are based on the transformation of water dissolved phosphorus into insoluble precipitates. In terms of simplicity, they are the most practical: the chemical precipitation of phosphorus, iron, aluminum or calcium salts and calcium hydroxide are used most frequently.

Organic esters of phosphorus acid have numerous applications and the production scale in Europe reaches thousands of tonnes per year. The basic applications are flame retardant agents, plasticisers and lubricants. Organophosphorus flame retardants, including chlorophosphates, comprise the biggest share of that tonnage [5].

The second half of the twentieth century up to today is a period of revolution in the technology of products resulting from the application of polymeric materials. Organic synthetic polymers are now the basis for many vital materials, even high-tech ones, that are replacing traditional materials. Their importance is growing, as they are lightweight, easy to process and cheap.

The combustion of organic materials based on carbon chains cannot be totally eliminated, only reduced to an acceptable level. Where it is necessary for the safety of people, polymeric materials are chemically or physically modified with retardant additives. If a fire occurs, these additives prevent damage from it. The easiest way to prevent fire or limit its range is to use these flame resistant materials, obtained by introducing flame retardant additives (FR) into a polymer. Their role is to change the process of natural pyrolysis combustion; these are chemical compounds or their mixtures which delay the ignition of material or decrease the rate of the pyrolysis reaction or the oxidation of polymers or plastics during contact with a flame [6]. Organophosphorous compounds used as monomers or as additives form an important group of flame retardants. Their importance is permanently growing, as they perform an adequate effect also in low percentage and so they do not significantly influence the properties of the polymer matrix. These compounds mostly perform their flame retardant functions in a condensed phase, by increasing the amount of carbonaceous residue or char. There are two char forming mechanisms: (a) redirection of the chemical reactions involved in decomposition in favour of reactions yielding carbon rather than CO or $CO_2$ and (b) formation of a surface layer of protective char [7–9].

The use of organophosphorus flame retardant in products made of polymeric materials is essential, but it leads to surface waters pollution. These compounds are detected in the environment, including surface waters. The primary sources of the discharge of these substances into the environment are production processes, including industrial wastewater [5, 10–12].

Phosphorus removal from waste waters rich in organophosphorus compounds is most frequently done using iron or aluminum compounds [10–14]. Water soluble phosphoric acid esters are weakly dissociated in water so their precipitation must be preceded by hydrolysis to obtain orthophosphate (V) ions. Removing phosphorus is based on ionic reactions which lead to water insoluble orthophosphates. Precipitation using iron(III) salts can be described by the equation:

$$Fe^{3+} + PO_4^{3-} + 2H_2O \rightarrow FePO_4{\cdot}2H_2O\downarrow$$

Precipitation of iron(III) phosphate(V) occurs while obtaining hydroxides as a by-product:

$$Fe^{3+} + nH_2O \rightarrow Fe(OH)_n^{(3-n)+} + nH^+ \text{ where } n = 1\text{–}4$$

Indeed, the processes of iron phosphate (V) precipitation from industrial waste waters and sewages are even more complicated, and for the present there is no unambiguous solution referring to the composition and structure of the precipitated compounds. The composition of the precipitation products strongly depends on other impurities in sewage. According to particular authors, metal-hydroxy-phosphate complex compounds also are produced. To simplify, it can be assumed that in strongly acidic conditions mainly $FePO_4{\cdot}2H_2O$ precipitates. However when pH > 3, except pure iron(III) phosphate(V) other insoluble hydroxide forms are obtained. According to publications [15–18], the optimal pH for iron removal by precipitation is 4–6, but the authors claim that the effective maximum can be closer to 4 or closer to 6 depending on the sewage composition.

The aim of the research was the removal of phosphorus from the water stream in a chloro-organic and organophosphorus flame retardant production process before wastewater treatment. It was assumed that at least 70% mass of total phosphorus could be removed.

## 2. Materials and methods

Removing phosphorus from wastewater from chloro-organophosphorus flame retardant production was performed by precipitating insoluble iron(III) phosphate(V) with the use of iron(III) chloride. The wastewater contained 7 kg/m$^3$ of total phosphorus in the form of organophosphorus compounds, soluble organic compounds and other impurities ($Na^+$, $Cl^-$). Precipitation was performed in a 2 dm$^3$ reactor equipped with a stirrer, thermometer and pH electrode connected to a WTW stationary pH meter.

1 dm$^3$ of wastewater (starting pH approx. 12.2) and 40% mass. $FeCl_3$ with the Fe/P molar ratio 1.0 – 2.0 were introduced to the reactor with a stirrer. The pH of the solution was adjusted to between 1.0-5.0 with 10% mass. NaOH and HCl 1:1. The reaction was carried out for 1 h at room temperature. After the precipitation, sedimentation and flocculation was aided with polyelectrolyte medium molecular anionic polyacrylamide flocculant (Magnafloc 10, BASF). The precipitate was separated using a Büchner funnel. The filtrate was tested for P and Fe content and COD. Total phosphorus, and iron were determined using Inductively Coupled Plasma–Optical Emission Spectroscopy (Thermo Scientific™ iCAP™ 7400 ICP-OES Duo) analysis for both liquid and solid phases. The determination of total iron, and phosphorus in the solid phase was achieved by acidic digestion of the dry solids obtained after drying the samples overnight at 105°C. COD analysed by photometric determination according ISO 6060 using nanocolor tube test (Nanocolor 500D). The percentage recovery was calculated on the basis of phosphorus mass balance.

The specific area of precipitates was determined with a Gemini VII (Micromeritics) analyser which is designed to determine the single and multi-point area by BET method between 0.001 and 4000 $m^2/g$. The samples were degassed in 130°C for 1 h and subsequently the measurement was performed (A). An attempt of phosphorus and iron recovery for reusing was made. For this reason, the precipitate was dissolved in HCl and $H_2SO_4$ (20% mass.). Total phosphorus content, available phosphorus and iron in the obtained solution and the remaining precipitate was determined.

## 3. Results and discussion

### *3.1. Phosphorus removal*

The tested wastewater was real industrial wastewater. It was created as a side-stream in phosphoorganic esters production. It is so rich in phosphorus, that the phosphorus removal process should be performed before sending it to an industrial water treatment plant (WTP). The typical phosphorus removal processes are widely presented in literature frequently involving urban waste and industrial leachate where phosphorus content is 10–100 fold lower. High concentrations of phosphorus and organic impurities in the tested waste required a chemical method. Concerning literature information [15–20] a relatively effective and not expensive iron(III) chloride was chosen.

Cation $Fe^{3+}$ precipitates highly insoluble iron(III) phosphate(V) from a solution containing orthophosphoric anions (solubility product: $FePO_4$ $1.30 \cdot 10^{-22}$). Theoretically, stoichiometric ratio Fe:P = 1.0 and acidic pH should be the most favorable in iron phosphate precipitation but in the case of waste with high organic compound content, an excess of Fe and pH > 2 (3–6) should be applied. The present work confirmed this argument. The results of our own studies regarding phosphorus removal are presented in the Fig. 1.

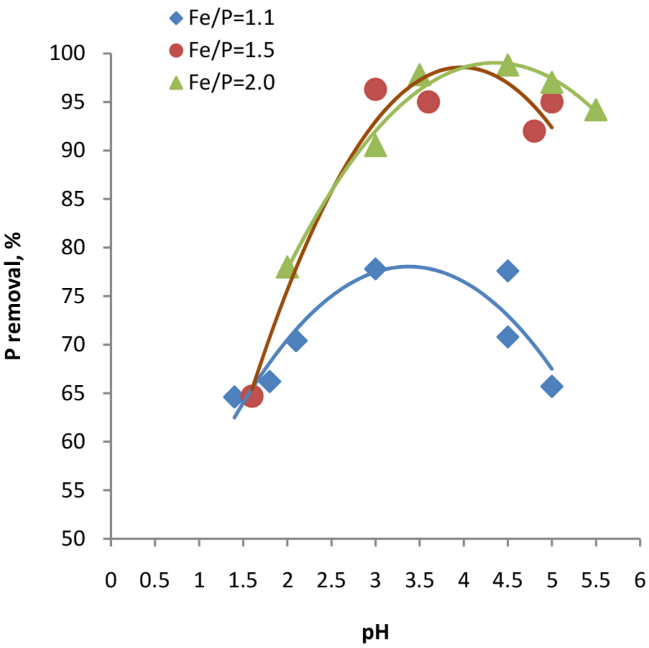

Fig. 1. Effect pH and molar ratio $Fe^{3+}/P$ on phosphorus removal in batch system using ferric chloride.

An over 90% mass recovery of P from the tested waste was obtained at 50–100% excess of iron (Fe:P = 1.5–2.0). Maximum of phosphorus recovery curve in dependence on pH for Fe/P 1.1 occurs at pH ~ 3.0; for the curves of the larger excess of the ferric reagent, the maximum moves towards less acidic solutions (~4.0 for Fe:P = 1.5 and ~4.5 for Fe:P = 2).

In the precipitation reaction of iron(III) phosphate(V), the dissolved orthophosphates take part, essentially $H_2PO_4^-$, $HPO_4^{2-}$ and $PO_4^{3-}$ ions. Non-dissociated forms do not participate in precipitation reactions. The processes which accompany the chemical phosphorus bonding in weakly soluble compounds are coagulation, flocculation and solid particle separation. Very small particles of suspension formed in the precipitation reaction have the same electric charge. Organic precipitates usually have a negative charge. An addition of a metal salt neutralizes the surface charge and, as an effect of van der Waals forces, the particles approach each other and bind, which is accompanied by an increase of the sedimentation rate [21]. The excess of iron ions also hydrolyzes with precipitation of sparingly soluble hydroxide (solubility product: $Fe(OH)_3 = 3.2 \cdot 10^{-38}$). A mechanism of the surface area neutralization, coagulation is the next stage of phosphorus removal after precipitation. Coagulated particles join together into larger agglomerates (flocculation) and fall to form a relatively stable precipitate [17]. Iron(III) chloride has at least two functions: as a precipitating agent and coagulant. Polyelectrolyte aids the flocculation. For coagulation using iron salts, the most favorable pH is 4–8 [21]. Better results of phosphorus recovery at higher pH values can be explained by the great importance of the coagulation and flocculation effects simultaneously with chemical the precipitation of orthophosphates.

Mass distribution of P and Fe between the purified waste and precipitated solid is presented in Figs. 2 and 3. Iron moves to precipitate to a greater extent than it could be assumed from stoichiometry. It is favored by higher pH, which is better for forming sparingly soluble hydroxides.

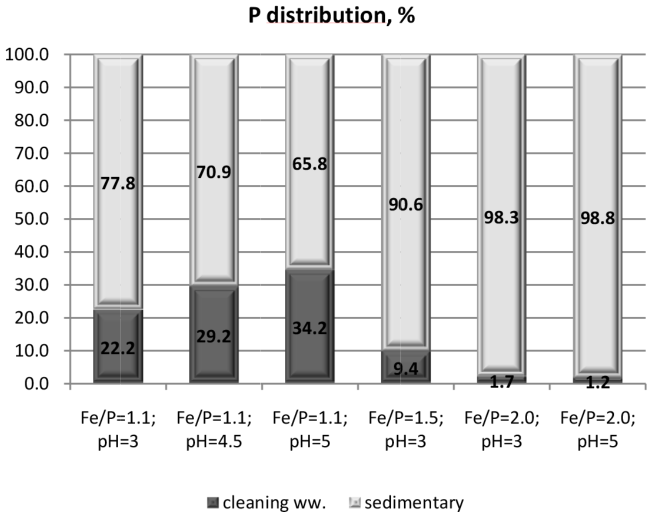

Fig. 2. Phosphorus (P) distribution between cleaning wastewater and precipitate, depending on the process parameters.

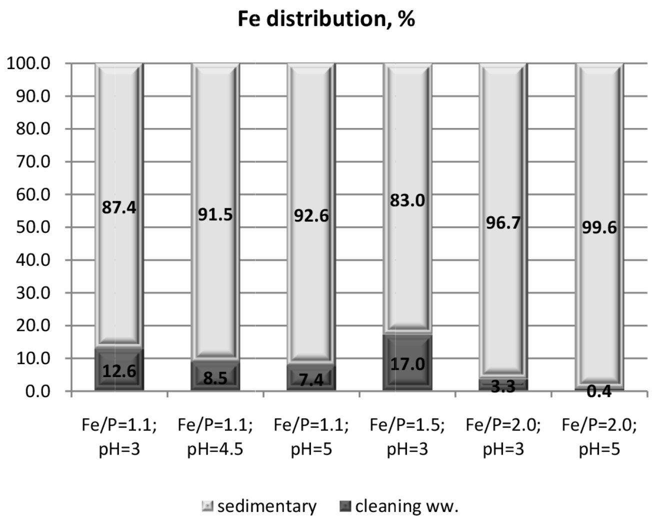

Fig. 3. Quantitative distribution of introduced iron between cleaning wastewater and precipitate, depending on the process parameters.

For the chosen samples, the specific surface area of waste precipitates was determined after drying. Specific surface area values are relatively high (Table 1). Developed surface of the precipitate aids adsorption of compounds and ions present in the solution, which also favors the wastewater purification effect. This pertains also to organic compounds. Adsorption is also a method used for phosphorus removal from wastewater, especially at low phosphorus concentrations [22,23].

The presented results confirm that the real mechanism of phosphorus removal from wastewater with iron (III) chloride is very complicated and is not limited to chemical reactions. The efficacy of phosphorus removal from wastewater is aided by coagulation, flocculation and adsorption on the surface of precipitate particles. In the precipitation products, on iron (III) phosphate (V) and iron (III) hydroxide particles, organic compounds are also present.

### 3.2. Organic material removal

It was observed that chemical dephosphatation of wastewater is accompanied by a significant decrease of organic compound content in purified leachate (Table 2), which was determined by a COD analysis. It could be also stated that without dependence on process conditions, the COD value decreases by about 50–65% mass. Content of organic compounds only slightly decreases with an increase of pH and a precipitation agent quantity (increase of Fe/P ratio). It can be assumed that organic compound removal is an effect of adsorption on the surface of inorganic precipitate particles. The higher the pH, the higher the specific surface area of the precipitate. It results also from a greater share of hydroxides in the precipitate. These factors seem to favor the organic compounds removal from the wastewater.

Table 1
Specific surface area of the precipitated solids depending on process parameters

| Process parameter | | BET specific surface areas, m$^2$/g |
|---|---|---|
| Molar ratio Fe/P | pH | |
| 1.1 | 4.5 | 91.8 |
| 1.1 | 5 | 102.2 |
| 1.5 | 4.5 | 92.0 |
| 2.0 | 3 | 83.1 |

Table 2
Characteristics of the selected experiments of the simultaneous phosphorus and organic impurities removal

| Lp. | Process parameter | | P removal, % mass | COD reducing, % mass |
|---|---|---|---|---|
| | Molar ratio Fe/P | pH | | |
| 1. | 1.0 | 1.7 | 63.1 | 52.56 |
| 2. | 1.1 | 1.8 | 66.2 | 58.30 |
| 3. | 1.1 | 2.1 | 70.4 | 56.66 |
| 4. | 1.1 | 3 | 77.8 | 55.77 |
| 5. | 1.1 | 4.5 | 77.6 | 68.10 |
| 6. | 1.1 | 5 | 65.7 | 47.82 |
| 7. | 1.5 | 3 | 96.3 | 61.20 |
| 8. | 1.5 | 3.6 | 95 | 58.30 |
| 9. | 1.5 | 5 | 95 | 62.30 |
| 10. | 1.5 | 4.8 | 92 | 63.41 |
| 11. | 2.0 | 3 | 90.5 | 56.41 |
| 12. | 2.0 | 4.5 | 98.8 | 63.20 |
| 13. | 2 | 5 | 97 | 64.20 |
| 14. | 2.0 | 2 | 78 | 59.10 |
| 15. | 2 | 3.5 | 97.8 | 58.20 |
| 16. | 2.0 | 5.5 | 94.2 | 66.30 |
| 17.* | 1.1 | 2.0 | 70.4 | 81.90 |

*Experiment with $H_2O_2$ addition; Fe:$H_2O_2$ 1:3

The addition of hydrogen peroxide decreased the COD by 80% in relation to the initial value, but it did not affect the degree of phosphorus removal. This solution is significantly more expensive, however it may be necessary in phosphorus removal processes accompanying phosphorus and iron recovery. The initial experiments of phosphorus and iron recovery from post-process waste precipitates made by extraction testify that the prior organic compounds removal is essential. Recovery of 45% Fe (by sulfuric acid) and 34% Fe (by hydrochloric acid) was possible by extraction with 20% $H_2SO_4$ and HCl 1:1. By the same method, 20% (sulfuric acid) and 17% (hydrochloric acid) of phosphorus was recovered. The obtained level of COD is sufficient for the wastewater stream purification. A further decrease of COD will take place in a normal process in WTP.

### *3.3. Proposed process for removing phosphorus from organophosphorus flame retardant agent production*

Based on the presented results, this method of purification of the wastewater stream from a phophoorganic flame retardant agent production process is proposed. The scheme of the process is shown in Fig. 4. The post-process water is introduced directly to the precipitation reactor, where it is mixed with $FeCl_3$ solution according to the proper stoichiometric Fe/P value, preferably 1.5–2.0. The pH is fixed with an NaOH solution at the level of 4.5 ± 0.5. Then the product is thicened by sedimentation. Decanted liquid can be directly forwarded to a WTP plant similar to the filtrate in the next step.

Alternatively, pre-cleaning wastewater from excesses of iron before reaching wastewater treatment plant can be proposed. After sedimentation and filtration by precipitation of iron with calcium hydroxide solution. Precipitated waste solid is safe to store. An intention was to recycle a part of the ferric coagulant to the process and use the recovered phosphorus, for example in fertilizers. However it turned out that the high level of organic impurities and their characteristics make this solution very difficult. Various techniques should be considered, taking into account oxidation of organic impurities in wastewater or incineration of waste precipitate and recovery of phosphorus from the obtained ash in the known way [3,4].

## 4. Conclusions

The aim of the presented work was to create a concept of phosphorus removal from very special industrial waste, generated during the ester type, organophosphorus flame retardant agent production process. The purified stream is contaminated with organic compounds that are very soluble in water but not dissociated. Despite a relatively high level of phosphorus in wastewater, typical chemical dephosphatation methods are not very effective, because phosphorus in the solution was not in orthophosphate form. Methods which are possible to apply in typical industrial conditions, not requiring special devices, big investments and special chemicals were taken into consideration.

The studies confirm that is possible to obtain a high degree of phosphorus removal by application of iron(III) chloride in stoichiometric excess. A higher than 90% level of phosphorus removal from wastewater was achieved using a 50–100% stoichiometric excess of iron(III) chloride. The precipitation of phosphorus and iron compounds is accompanied by a 50% decrease in COD, which is an additional positive effect of the applied method. Based on the obtained results, a simple flow sheet of the process of phosphorus and partially organic compounds removal from the wastewater is proposed.

The waste precipitate mainly consists of iron phosphate and many organic compounds, which makes it useless for

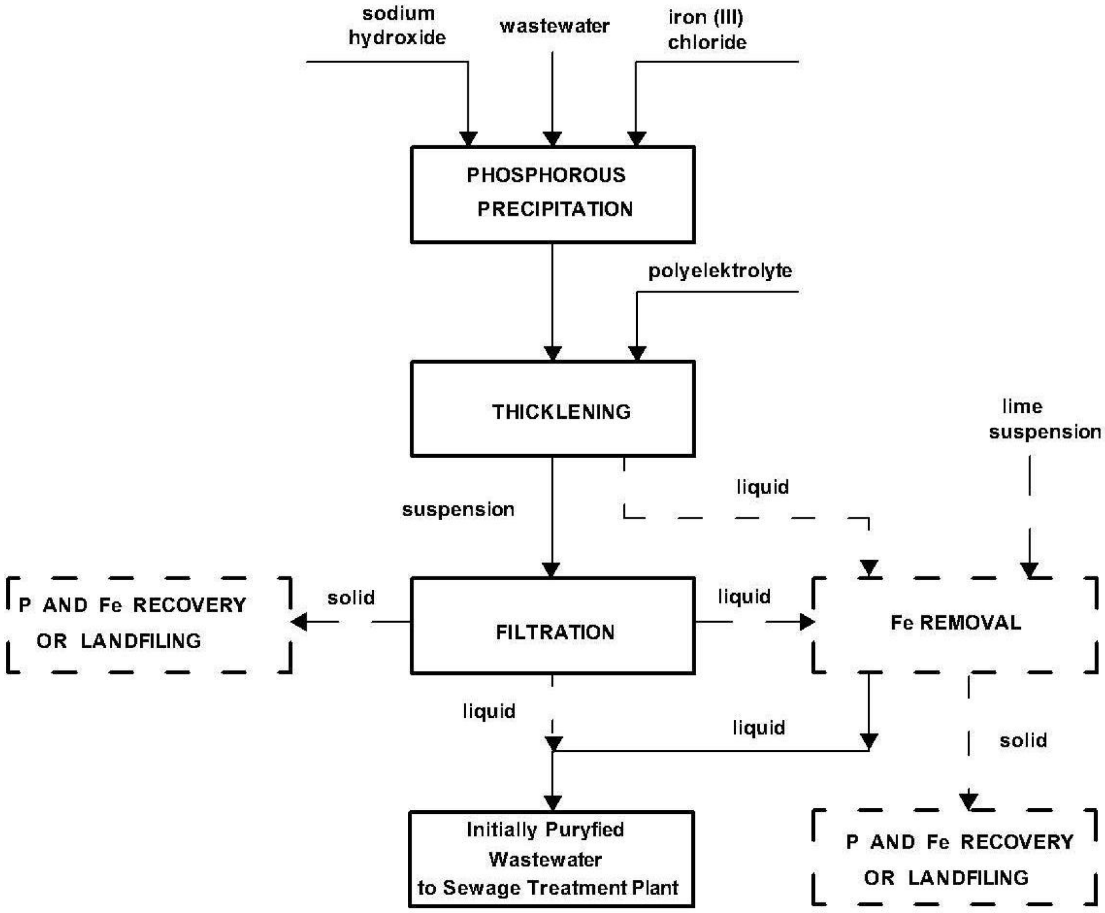

Fig. 4. Flow sheet of the proposal industrial water cleaning process

fertilizer applications. The removal degree is very good, but reusing iron and phosphorus is difficult and recovery is not effective. The process should be maintained in order to reuse iron and phosphorus one more time. Phosphorus as a fertilizer and iron in the form of flocculant. Due to the characteristics of the coprecipitated impurities, reuse of recovered phosphorus (i.e. fertilizers) is not possible without previous organic compound removal by deep oxidation or precipitate incineration and processing the obtained ashes in the known way.

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