NEW TECHNOLOGIES OF PHOSPHORUS REMOVAL FROM WASTEWATER

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ABSTRACT

Development of phosphorus removal technologies from municipal wastewater has been presented in this paper . This led to application of present methods such as : enhanced biological phosphorus removal and chemical precipitation. Trends and directions of scientific activities conducted by numerous research centres were presented . Selected proposal of non-conventional phosphorus removal technologies has been briefly described and their advantages together with disadvantages were listed . The paper presents the evolution of the attitude towards phosphorus removal and its influence on wastewater treatment.

KEYWORDS

Phosphorus removal; wastewter treatment; water resources protection

INTRODUCTION

Increasing input of nitrogen and phosphorus compounds to receiving surface waters, especially to lakes and artificial reservoirs lead to increase of primary production of water born organisms and finally its consequence is disappearance of oxygen in waters. The phosphorus is present in water environment in smaller quantities than nitrogen and it is necessary for all kind of living phytoplankton organisms so its concentration is of crucial importance in water quality protection.

Beginning from 1970s phosphorus removal from wastewater has been recognised as one of basic processes necessary to be done in all wastewater treatment plants. Continuous development of knowledge concerning phosphorus occurrence, mechanism of its removal and evolution of process technologies led to modern technical solutions which allow to efficient removal of this wastewater constituent.

In this paper trends and directions of development of phosphorus removal from municipal wastewater has been presented , described was scientific works and new treatment technologies. Less emphasis had been put on technologies of enhanced biological removal and chemical precipitation despite these technologies are still being developed , these technologies were described are checked in operation and presented in numerous papers in the past (*Barnard 1975, 1982,1983; Sedlak 1991;WEF MoP 1992, Aspegren 1995; Bernacka, Kurbiel Pawłowska 1995, Aspegren1995, Kurbiel i Rybicki 1995*)

DEVELOPMENT OF PHOPHORUS REMOVAL FROM MUNICIPAL WASTEWATER

History of the phosphorus removal technologies

Due to the difficulties with biological treatment plants (designed for organic matter removal only at that time) in the end of 19th century great effort was made on test then implementation of treatment technologies based on physical and chemical methods. Chemical precipitation with the lime (*Wardle 1893*) then with the use of alum and iron salts *(Wakeford 1911, Kershaw 1911*) were introduced. These chemicals precipitated phosphorus unintentionally, besides presumed organic matter removal (expressed as the BOD).

However till 1950s phosphorus removal was recognised as the not important process and had not been investigated. During the World War II in the United States some tests were completed on chemical precipitation of phosphorus from wastewater but the main aim of these tests was to obtain a fertilizer for the agriculture in the period of dramatic shortage of mineral phosphorus fertilizer constituents (apathites) usually imported from the North Africa (*Sawyer 1944*).

Investigation on the nature of the eutrophication process initiated in late *1940s (Rudolfs 1947, Lea et al. 1954*) led to advanced (high effective) phosphorus removal technologies . Beginning from 1960s in Switzerland chemical precipitation had been implemented in operation, it was performed by adding chemicals before primary clarifiers in conventional biological treatment plants (*Stumm 1962, Boller 1987, 1993*). Similar methods were applied in Scandinavian countries where chemicals were added before primary clarifiers or directly to the activated sludge chamber (*Balmer and Hultman 1988*).

Simultaneously with chemical methods in 1960s investigations had started on application of biological mechanism to phosphorus removal. It started from Levin and Shapiro (1965) who reported on phosphorus uptake by an activated sludge exposed to sequence of continuous aerobic and anaerobic conditions . They observed that phosphorus uptake exceeded needs for the photosynthesis. They proved that approx. 80% of phosphorus uptake from wastewater under aerobic conditions - they named the observed high phosphorus removal a „luxury uptake”. They also observed in further investigations that uptake and release of phosphorus are reversible processes. These authors however did not explain entire mechanism of the process. Shapiro later proposed to expose return sludge to such conditions prior to return to the aeration basin to strip out phosphorus. That was a predecessing of the Phostrip process.

The basis for modern multiphase biological rectors for integrated phosphorus and carbon compounds removal were observations made by Barnard (*Barnard 1973, 1982,1983*) who modified Wuhrmann,s reactor (*MoP 1992*) constructed in 1950s. Barnard equipped this reactor (known later as the „Bardenpho” reactor) with the inner recirculation system . It meant that mixed liquor is directed from final zone of aerobic chamber to anaerobic chamber at the same time the reactor was equipped with another chamber - anaerobic to perform phosphorus release under anaerobic conditions . All further improvements are based on principles described by Barnard.

Non-technological attitudes towards reduction of the phosphorus sources

Parallelly with works on decrease of the risk of eutrophication intensive investigations were performed on minimalization of these compound content in wastewater incoming to the plant. There are three main sources of phosphorus in municipal wastewater , their input in total phosphorus load is as follows:

- human excreta 30 - 50%
- detergents 50 - 70%
- industry 2 - 20%

Due to the fact, that the load from human excreta is difficult to control and the industrial input is relatively low, in 1970s some programs were established to minimize even eliminate phosphorus-containing detergents from washing powders. It led to positive changes in concentration and structure of phosphorus compounds in wastewaters incoming to the wastewater treatment plants. In late 1970s sludge load per capita in raw municipal wastewater varied between 4.0-5.0 gP/cap*day (*Cywiński et al. 1972, 1983, WEF MoP, 1992*) after a phosphate ban was introduced this quantity dropped to 2.5-3.0 gP/cap**day (Boller 1987, Balmer&Hultman 1988*)
Comparison between year 1971 and year 1991 is shown in Fig. 1 below. *(Jenkins Ferguson Menar 1971,Sedlak 1991*). It is visible how concentration decreases and the structure changes in time.

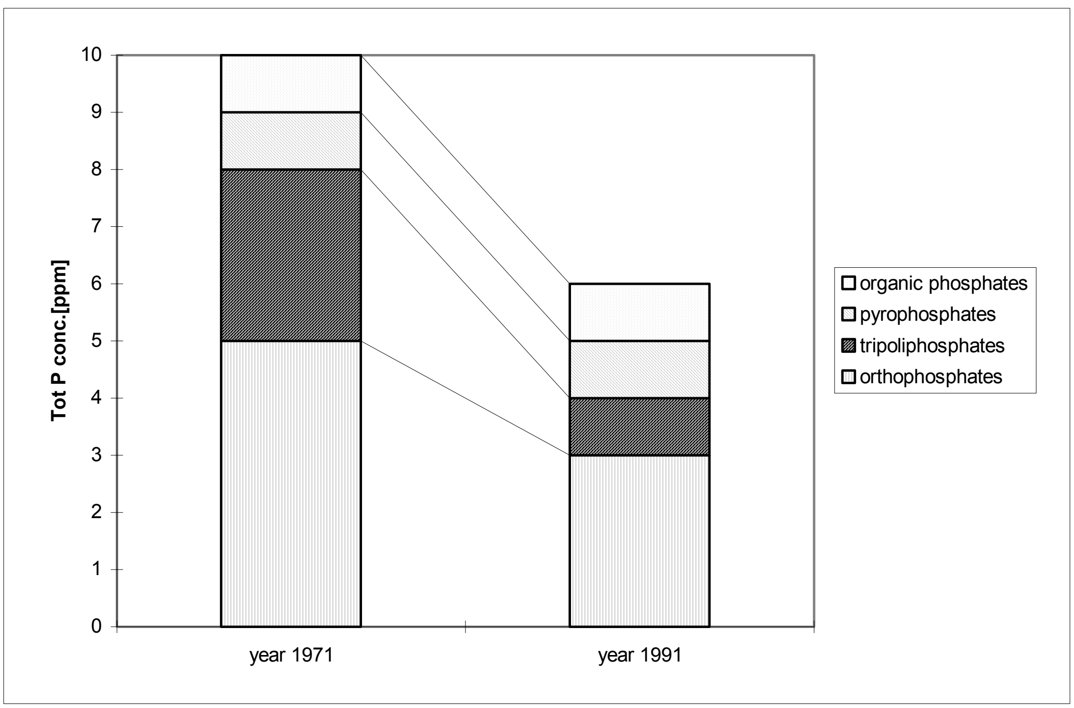

Fig.1. Changes in structure of phosphorus compounds in municipal wastewater between year 1971 and year 1991

ADVANCED PHOSPHORUS REMOVAL TECHNOLOGIES AND TRENDS OF THEIR DEVELOPMENT

The phosphorus is present in wastewater in soluble form , only approx. 15% of total phosphorus load can be removed with the use of sedimentation process. That is the reason why all applied methods are based on one general principle on convertion of soluble phosphorus compound into non-soluble compound: either as precipitated chemical compound or as phosphorus built-in into microorganism cell, final step is separation of bound (precipitated or built-in) phosphorus from treated wastewater. Due to the main effect applied removal technologies are divided into groups:

- physical-chemical (precipitation: primary, simultaneous or final)
- biological (enhanced biological removal)
- combined (Phoredox)_

Physical - chemical phosphorus removal - application and directions of development

Conventional physical-chemical methods
Adding trivalent metal salts performs chemical processes of phosphorus removal as usually applied: aluminium and iron. Depending on dosage point this process may be used in various technological schemes as:

- primary precipitation in mechanical wastewater treatment plants (older constructions)
- primary precipitation before further biological treatment
- simultaneous precipitation (adding chemicals to final zones of activated sludge reactor)
- final precipitation

Despite relatively large experience in operation these processes are still investigated, and efforts are focused on optimization of dosing point. Due to the observation that primary precipitation causes decrease of biodegradable organic compound concentration, this method must be applied very carefully and is rather rare in newly constructed plants. Simultaneous precipitation is used very often especially as an optional operation scheme during periods of reduced efficiency of biological phosphorus removal.

Contact filtration is applied at plants designed to ensure stable, low concentration of phosphorus in the outflow (e.g. discharge of treated wastewater to protected waters), where efficient suspended solid removal is required. Investigations on other physical-chemical technologies of phosphorus removal contain numerous processes, most detailed were described following processes:

- electrolytical method
- crystallization
- magnetic separation
- adsorption

Treatment with the use of electricity

First use of electricity for wastewater treatment was patented in England in year 1856, but no success in routine operation was reported *(Creighton&Franklin 1919)*. Development of direct use of electricity for treatment proceeded in 19th Century. In 1889 Webster (also in England) applied electrical related treatment. It was in fact chemical precipitation by iron compounds (oxides) formed on one of electrodes. Plant operations showed satisfactory results. Later on the 'Landreth Direct Oxidation Process which was electrolytic precipitation combined with lime precipitation *(Creighton&Franklin 1919)*. This process was presented as economically feasible. Sixteen years later Report of Committee on Sewage Disposal *(1935*) summarized full-scale application the Landreth Process as not so successful. most of operators reported that no visible advantage was observed over lime-only use. So idea was suspended for some time.

In 1950's Föyn initiated works on electrolytic treatment of municipal sewage which were mixed with seawater. His tests were one of first investigations addressed towards nutrient removal. During long-term operation he obtained reliable phosphorus removal, reducing its content in treated wastewater down to 1,0 mgP/L (*Föyn 1964).*

Further development was reported by Groterud i Smoczynski (1991) who tested two layouts of application:

1. Al. electrode for phosphorus electroprecipitation
2. carbon electrode for electrochlorination

As a results of their tests they stated that keeping stable level of chlorides concentration is of great importance for economical feasibility of the process. Their observations confirmed advantage of seawater addition however there is no full-scale experience of this process. Increase of salinity of treated wastewater makes this method unsuitable for water reuse for industrial circuits. Fig. 2 shows the system of electrocoagulation together with chlorination while table 1 shows technical parameters of tests

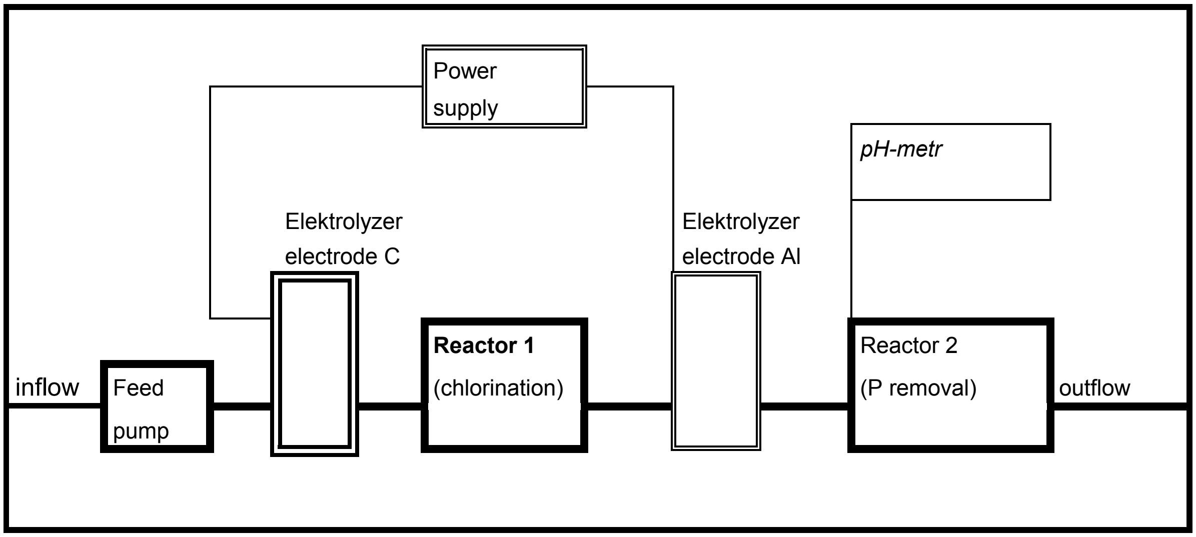

Fig.2. The process scheme of electrolytical method
[Grϕterud i Smoczyński (1991)]

Tab 1. Operation parameters of electrolytical method vs. Cl' ions concentration
[Grϕterud i Smoczyński (1991)]

Initial concentration of Cl' ions	[mg/dm^3]	0	10	25	50	75
Voltage	[V]	16	9.2	6.5	4.8	3.8
Energy consumption for 90 % P removal	[W*s*m^{-3}*10^6]	3.3	1.9	1.3	1.0	0.8
Conductivity	[µs*cm^{-1}]	36	66	100	160	252

Crystallization process

This method was presented by Joko (1984) , who showed long-term operation of installation for phosphorus removal from biologically treated wastewater by crystallization of hydroxyapathyte $Ca_5(OH)(PO_4)_3$.

Principle of operation is to direct biologically treated wastewater (with no EBPR) through the reactor's bed where proper concentration of Ca ions is kept. The stoichiometry of this reaction is:

$$3HPO_4^{2-} + 5Ca^{2+} + 4OH^- \rightarrow Ca_5(OH)(PO_4)_3 + 3H_20$$

Joko completed tests on Yamato (Japan) WWTP, which confirmed reduction of P level from 1-4 mgP/dm3 in biologically treated wastewater down to 0.3 – 1.0 mg P/dm^3 after crystallization. Another observation was that filling the reactor with crystallization seeds could do increase of the process efficiency. The most effective were synthetic seeds made of phosphate oxide (P_2O_5) , calcium oxide (CaO) and fluorite (F).

The main advantage of the crystallization method is that final product can be applied as a fertilizer without further processing. The disadvantages are: complexed process and increase of salinity

The crystallization scheme applied in Yamato is presented on fig 3.

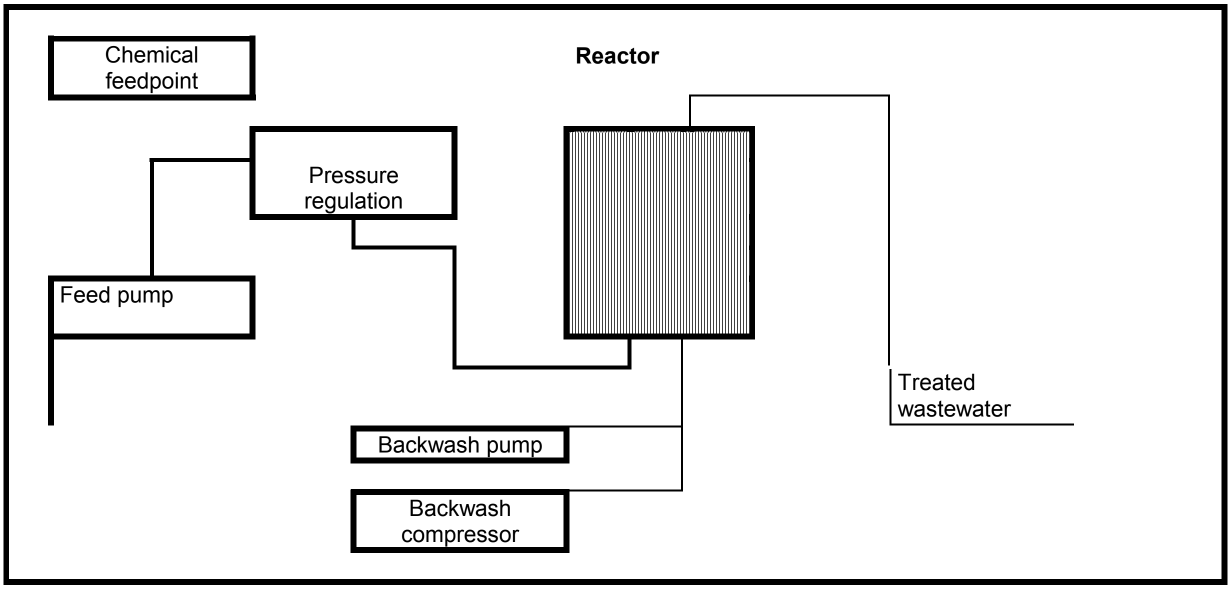

Fig.3. Crystallization applied in Yamato
[Joko 1984]

Magnetic separation

This technology was examined by *De Latour (1975)* who found it an effective method if applied after alum or iron salts addition. Further investigations proved that this method is reliable auxiliary for chemical coagulation of phosphorus (*De Latour 1975).* The concept of magnetic separation system for the phosphorus removal was proposed as 'new' by *(van Velsen et al. 1991)* as to be very promising as the effluent values 0.1 - 0.5 gP/m^3 can be achieved at costs comparable with other processes.

The main principle of magnetic method is separation of particles being removed with the use of magnetic field. So this method can be applied for particulate impurities. To remove phosphorus one must convert it into insoluble form for example in the way of primary sedimentation. Besides these particles must posses magnetic properties while such properties are not common among wastewater constituents. To strengthen magnetic properties so called magnetic carriers are added, usually magnetite (Fe_3O_4) Great advantages of this process are : high elimination performance, compact process and low power input.

Figure 4 shows process scheme for magnetic separation (by van Velsen) and in table 2 selected operational parameters were shown.

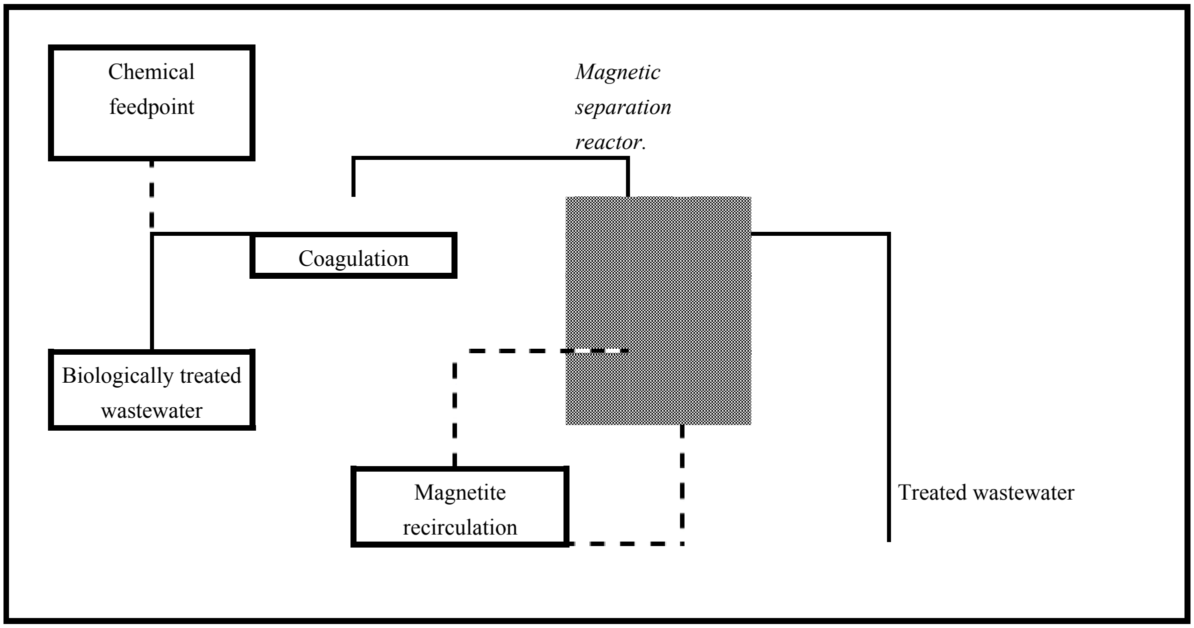

Fig .4. Magnetic phosphorus removal process
[Van Velsen 1991]

Table 2. Selected operational parameters of magnetic phosphorus **[Van Velsen** (1991)]

WWTPlant		Groesbek	Geldermalsen	
Capacity	[m^3/day]	50	20	20
Tot P inflowing the separator	[mgP/dm^3]	5	4.3	5.3
Lime dose	[mg/dm^3]	200	300	0
pH		10.6	10.7	7.0
Dose of $FeCl_3$	[mol Fe/mol P]	-	-	2.5
Dose of polyelectrolyte	[mg/dm^3]	2	2	1
Dose of magnetite	[mg/dm^3]	1	1	1
Total P conc. in separator outflow	[mgP/dm^3]	0.5	0.2	0.37
Efficiency of P removal.	[%]	90	95	93

Adsorption

Gangoli&Thodos (1973) tested adsorption of phosphorus with the use of fly ash, F1 alumina and an AHB alumina. They concluded that the adsorptive capacity for phosphates were greatest where adsorbents were used without any treatment. Another concept was a phosphorus removal by orthophosphate nucleation and use of phosphate rock in a packed column system seemed to be an applicable technology as a 'polishing' process after a lime treatment. Over 80% efficiency was reached with the use of aluminium oxide (Wiess 1992).

Trends in development of biological phosphorus removal methods

Biological methods are being developed in two directions :

- upgrading of equipment and process optimization at wastewater treatment plants
- phosphorus removal in natural systems

Phosphorus removal in multiphase biological reactors

Evolution of technical solutions based on multi-phase reactors has been described widely in literature (*Sedlak 1991, Kurbiel, Żeglin 1994, Bernacka, Kurbiel, Pawłowska 1995*). Trends in upgrading are usually directed towards conditions proper for optimization of enhanced biological phosphorus removal (*Barnard 1975, 1983*) with a special emphasis on:

- ensure fully anaerobic conditions in anaerobic zone/chambers (pre-denitrification in case of nitrate occurence in raw wastewter)
- presence of easybiodegradable carbon sources , especially SCFA (fermenters to generate SCFA from raw sludge) ;
- increase of secondary clarifiers (it is crucial to obtain effective suspended solid removal)
- use of automated process control systems based on on-line measurements;

Phosphorus removal in sequencing batch reactors (SBR)

The Sequencing Batch Reactor (SBR) technique was adopted for biological phosphorus removal in early 80´s when the United States Environmental Protection Agency (EPA) funded the full scale demonstration plant (1330 m^3/d capacity) at Culver. Works focused on the comparison of different periodic process performance characteristics and as a final result a new step- "react" (aeration without addition of wastewater) was added to conventional SBR process. The phosphorus removal was performed on the "classical" anaerobic-aerobic way. Further investigations by *Manning & Irvine (1985)* and *Irvine et al.(1987)* performed on a synthetic wastewater led to the conclusion that the best results were obtained where dissolved oxygen and nitrate nitrogen were absent during the first step of operation, which fact implies complete denitrification during "fill" period. About 50% of total phosphorus and 90% of nitrogen removal was achieved during those studies. Phosphorus removal by the metal salt addition was also proved as it is presented in another papers oh this seminar.

Fig 5. Show sequences of operation of a SBR reactor.
In table 3 mode of operation proposed by various authors nave been presented.

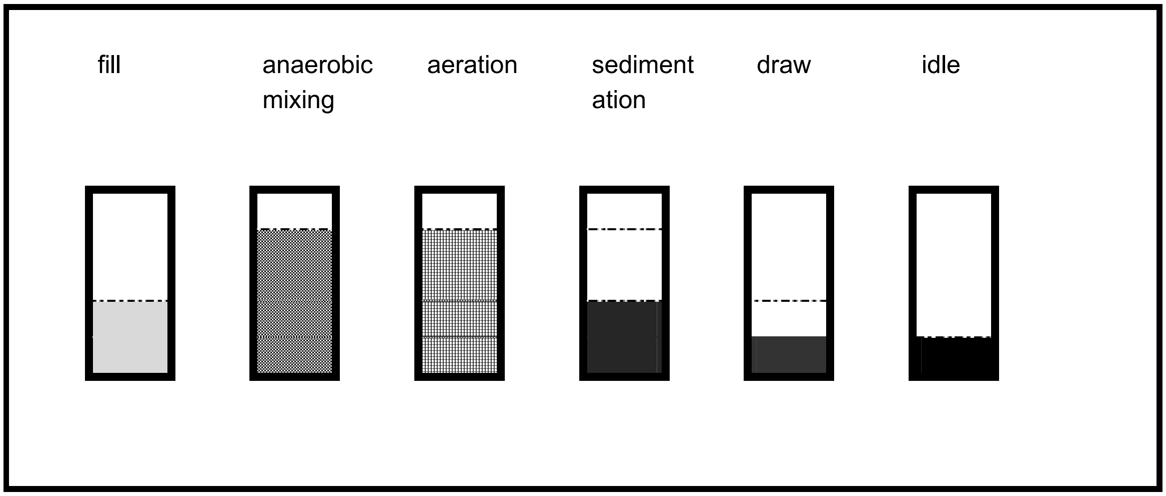

Fig.5. SBR reactor – mode of operation

Table 3. Mode of operation for SBR reactor with biological P removal

Phase / Author	Irvine (1983) low-load.	Irvine (1983) high load	Ketchum (1987)	Marklund(1993)
	time [hours]			
Anaerobic fill + mixing	1,8	3,0	4,3	1,2 - 7,5
Aeration	1,0	0,4	2,0	1,8 - 4,0
Sedimentation	1,0	0,7	0,75	1,0 - 2,0
Draw	0,4	0,7	0,75	1,0 - 2,0
Idle	0,6	0,0	0,8	0,0 - 1,3

Investigation of alternative reactors

Investigation of upgrading trickling filters for biological phosphorus removal were presented by Dichtl in 1980s, however author stated that such retrofitting is economically unfeasible. (*Dichtl et al.. 1994*)

Phosphorus removal in natural systems

Phosphorus removal in natural systems means use of phosphorus contained in wastewater back in the natural cycle in an environment. These systems are especially recommended for small communities and local systems. The most known natural systems are

- use of activated algae : exposing open cultures of algae to wastewater (*Phormidium bohneri*), 95% P removal efficiency was obtained; application of *Chloral vulgarize* resulted in lower efficiency (approx. 70%)
- wastewater treatment in ponds
- artificial and natural wetlands can be successfully applied (usually as a tertiary treatment following biological phosphorus removal). Artificial wetlands are capable to finally treat ("polish") the wastewater without the addition of chemicals.

In the Netherlands wetlands have been applied for polishing the effluent from trickling filters. Its disadvantage is that P is stored in wetland organisms mostly in roots and in dead matter and only 7% of it appear to be removable by harvesting. So suggested specialised treatment before of after wetlands for reliable and efficient phosphorus removal;

- root treatment – recommended for very small plants

TRENDS IN RESEARCH AND APPLICATION ACTIVITIES RELATED TO PHOSPHORUS REMOVAL.

Phosphorus removal technology is still being developed, most common trends in investigations on technical applicable works are as follows:

- upgrading of technical solutions
- optimization of process parameters
- new chemicals
- retrofitting of existing plants for biological enhanced phosphorus removal
- trials on recovery of phosphorus from wastewater in such a form that it will be applicable in agriculture

Another groups of investigations focus on intracellular mechanism in activated sludge microorganisms in particular

- investigations on energy storage and transfer mechanisms
- genetic tests on increase of intracellular phosphate accumulation
- biochemical changes taking place in microorganisms exposed on anaerobic/aerobic conditions
- investigations on interactions between chemical and biological processes

The recent problems are related to mathematical modelling of the process including:

- mathematical models of activated sludge processes with an emphasis on bio-P processes , based on IAWPR/IAWQ [Model Nr2] ; results were models SIPHOR, GPS-X, SIM-WORKS;
- evaluation of programs based on mathematical models to simulate then optimize various scenarios of plant operation

CONCLUSIONS

- Phosphorus removal from wastewater is of great importance for water pollution control especially in case of lakes and artificial reservoirs ; excess load of this compound in water ecosystems may lead to eutrophication;

- Despite limitation of phosphorus load discharged to municipal sewerage phosphorus must be removed from wastewater in advanced high effective plants;

- Phosphorus removal from wastewater is possible both by biological and chemical processes, process selection depends on various reasons;

- Phosphorus removal mechanisms both chemical and biological have not been fully recognized that is why in coming future this will be extensively investigated

- Future technologies of phosphorus removal will be those , which allow to recycle phosphorus as a fertilizer and direct it to the nature back..

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