BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
Publicat de
Universitatea Tehnică „Gheorghe Asachi” din Iaşi
Volumul 62 (66), Numărul 3-4, 2016
Secţia
CHIMIE şi INGINERIE CHIMICĂ

OPTIMIZATION THE PHYSICAL-CHEMICAL PROCESSES IN THE TREATMENT OF DOMESTIC AND INDUSTRIAL WASTEWATERS

BY

MARIANA MINCU*, CRISTINA MIHAELA BĂLACEANU and ANDREEA IOANA DĂESCU

National Institute for Research and Development in Environment Protection, Bucharest, Romania

Received: December 2, 2016
Accepted for publication: December 16, 2016

Abstract. Sometimes the domestic wastewaters and certain types of industrial waters, inadequately treated, as well as runoff water from fertilized agricultural lands reach in the surface waters. These are important sources of nutrients which are responsible for the appearance of eutrophication. The eutrophication is a major environmental problem that affects surface waters across the world. Decreasing of the amount of nutrients in surface waters is an increasing and topical problem for both the European Union and Romania.

Efficiency in wastewater treatment is very important for reduction of the nutrient loading in surface water, which is one of the European Union policies objectives (Water Framework Directive). In order to prevent the nutrients to reach the quantity amounts that produce eutrophication in surface waters, technologies for removal of nitrogen and phosphorus were experienced during some research conducted by INCDPM- Bucharest.

Keywords: wastewater treatment; removal of nitrogen and phosphorus; eutrophication.

*Corresponding author; *e-mail*: mincu_mariana@yahoo.com

1. Introduction

1.1. General Data Regarding Removing Nutrients from Urban Wastewater

Evolution contemporary society imposes gradually increasing level of wastewater treatment with the trend toward total treatment (Ceică *et al*., 2010; Safferman *et at.*, 2015; Nedjah *et al*., 2015).

Increased flow of pollutants in certain populated and industrialized areas and the complexity of chemicals discharged, not affected by treatment conventional led to situations where the degree of purification achieved by treatment of primary (mechanical) and secondary (biological) not be enough, imposing the application and other treatment methods in parallel with measures to prevent pollution at source (interventions in technological processes) (Ceică *et al*., 2010; Safferman *et at.*, 2015; Sawsan and Shanshool, 2009).

The remaining compounds from the treatment step have two-stage: biological and mechanical and are represented by starting with simple mineral salts, up to synthetic organic substances, sometimes with very complex structures (Domopoulou *et at.*, 2016).

Many of these remaining compounds have been known only lately due to improved analysis techniques.

Among the remaining compounds include: nitrogen and phosphorus. Their removal can be achieved through advanced treatment processes (Tociu and Diacu, 2015).

Advanced cleansing purpose consists either in reducing the flow of pollutants discharged into an emissary or to producing quality water suitable for reuse By applying advanced treatment methods, high efficiency and substances capable of removing refractory to conventional processes, is to acquire high quality water (Kulkarn, 2016).

In some areas of the world where water shortage is felt more and more and where the water quality of natural resources are close to the limit of affordability is practice advanced treatment for reuse wastewater.

1.2. The Need to Remove Nitrogen and Phosphorus from Wastewater Discharged

It has been shown that the remaining of the elements of the mechanical-biological treatment include nitrogen and phosphorus, elements responsible for the eutrophication of the emissary (lakes, rivers) (Nir *et at.*, 2009; Sawsan *et al*., 2009; Nedjah and Laskri, 2015).

After the biological treatment, urban wastewater containing significant amounts of nitrogen and phosphorus (Sawsan *et al*., 2009; Kulkarn, 2016).

These substances reached the emissary are true fertilizers that lead to eutrophication. Eutrophication is a natural phenomenon that is slow under rules but because additional nutrient intake can be harmful.

Eutrophication phenomenon dress looks different (physical chemical and biological) from case to case depending on local conditions and factors combining modifiers.

The consequences of eutrophication are (Sawsan *et al*., 2009):

– increase biological productivity measured by increase in biomass;

– occurrence of algal bloom with less transparency, colour changing water and organoleptic;

– decrease in dissolved oxygen during the night causing suffocation of fish and other aquatic organisms;

– increasing difficulties in the use of water as a source of drinking water and industrial;

– degradation of aesthetics and hygiene conditions of water with repercussions on human health.

Environment issues and those related to the road of wastewater to the outfall discharge, however, are multiple and depend on the various forms in which nitrogen and phosphorus.

Reaching the drinking water may harm infant nitrate (reduced to nitrite in the intestinal tract passes into the blood stream causing infant methemoglobin or 'blue disease') (Ceică *et al*., 2010).

It is considered that the disorder may occur in a content more than 45 $mgNO^3/dm^3$; although by other author's concentrations exceeding 10 $mgNO^3/dm^3$ is already dangerous. Such concentrations can often encounter in surface water or groundwater, polluted by infiltration of domestic wastewater.

Environmental pollution aquatic eutrophication covered several European Directives such as the Water Framework Directive (2000/60 / EC) Directive Nitrates (91/676 / EEC), the Directive on urban wastewater treatment (91/271 / EEC), Directive surface water intended for drinking water (75/440 / EEC) and the Directive on the quality of freshwaters needing protection or improvement in order to support fish life (78/659 / EEC).

In Romania, the establishment of ecological status of surface waters is carried out combined system (based on quality standards physicochemical, biological and chemical) in accordance with O.M. no. 161/2006.

Thus, rivers and natural lakes there are five quality classes which are associated with the following five environmental statuses:

Quality class	Environmental status
I	Very good
II	Good
III	Moderate
IV	Low
V	Bad

Ministry Order 161/2006 establishes the following limit values for nitrogen and phosphorus compounds.

Table 1
Limit Values for Nitrogen and Phosphorus Compounds Provided by M.O. no 161/2006 for the Approval of the Norm Concerning the Reference Objectives for the Surface Water Quality Classification

Quality indicators	UM	Quality class, maximum values				
		I	II	III	IV	V
Ammonium $N\text{-}NH_4^+$	mg N/L	0.4	0.8	1.2	3.2	>3.2
Nitrites $N\text{-}NO_2^-$	mg N/L	0.01	0.03	0.06	0.3	> 0.3
Nitrates $N\text{-}NO_3^-$	mg N/L	1.0	3.0	5.6	11.2	>11.2
Total nitrogen - N	mg N/L	1.5	4.0	8.0	20.0	> 20
Orthophosphate $P\text{-}PO_4^{3-}$	mg P/L	0.1	0.2	0.4	0.9	> 0.9
Total phosphorus - P	mg P/L	0.15	0.4	0.75	1.2	>1.2

Ensuring these values can be made by appropriate wastewater treatment preventing the negative effects that they may produce on the receptors.

To avoid eutrophication it is necessary that effluent discharged from sewage treatment plants to provide quality conditions regulated NTPA 011/2002 “Technical Norms concerning the collection, treatment and discharge of urban wastewater”.

Providing the conditions imposed can be achieved through proper urban wastewater treatment.

2. Experimental

2.1. Methods for Removing Nitrogen and Phosphorus

They have undertaken numerous researches to find solutions more efficient for removing nitrogen and phosphorus from wastewater (Nir *et al*., 2009).

The procedure used to remove nitrogen and phosphorus can be classified into two categories:

– physico-chemical;

– biological.

The choice of process or a combination of methods depends on many factors, among which we can mention:

– nitrogen and phosphorus removed;

– end use of the treated water (*e.g*., recirculation);

– economic conditions.

Table 2 presents some physico-chemical processes that can be applied for the removal of nitrogen and phosphorus.

Table 2
Physico-Chemical Processes Can be Applied for the Removal of Nitrogen and Phosphorus

Chemical element	Process for the removal
Nitrogen	Stripping
	Ion exchange
	Electro dialysis
	Electrochemical treatment
	Chemical precipitation
Phosphorus	Ion exchange
	Electro dialysis
	Electrochemical treatment
	Chemical precipitation
	Absorption

2.2. The Removal of Phosphorus by Precipitation

The method most economical and the easiest reported in the literature for the removal of phosphorus from the wastewater with reagents based on the precipitation of phosphorus-containing ionic forms of aluminum, iron and calcium (Parsons and Smith, 2008).

The choice of precipitating reagent and the location of the treatment depends on a number of factors among which there are:

– initial concentration of phosphorus and chemical form at the point of treatment;

– the degree necessary to remove phosphorus;

– the resulting sludge settling speed and its use;

– the cost of chemical reagents.

The precipitation may be followed by a rapid sedimentation or filtration.

Chemical species used as sources of metal ions for the precipitation of phosphorus can be:

– For Al: $Al_2(SO_4)$. 14 H_2O or $Al_2(SO_4)$. 18 H_2O

– For Fe: $FeSO_4$. 7 H_2O

– For Ca: CaO sau $Ca(OH)_2$

Recent data from the literature recommended precipitation of phosphorus from wastewater, the calcium phosphate through the use of the crystallization seed (limestone or calcite).

2.3. Pilot Plant for the Removal of Phosphorus Chemical Route

Taking into account both the recommendations of the literature and the experimental laboratory was installed a pilot for phosphorus removal by chemical.

The pilot plant is a compact comprising:

– Reaction basin;

– Lamellar settling modules provided with.

When designing the installation it was taken in consideration the following conditions:

– wastewater flow -1 L/s;

– reaction time 20 min;

– settling time 30 min.

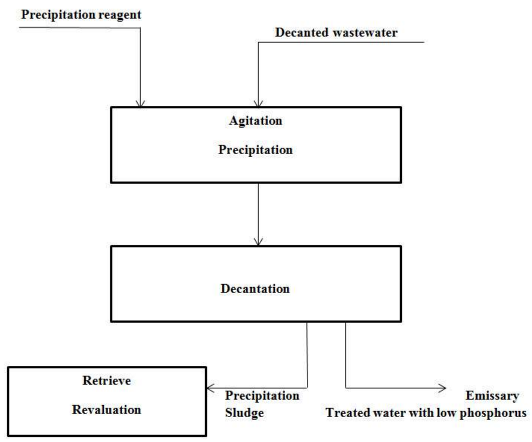

Fig. 1 − Flow chart of phosphorus removal installation of biologically treated by precipitation with chemical regents.

Flowchart of the installation is shown in Fig. 1.

The plant was operated in continuous flux and followed cyclic on interval of about 4 h/day.

2.4. Experimental Conditions

For the experiments it was use wastewater settled and was carried out phosphorus precipitation in three variants:

I. precipitation with $FeCl_3$ and $Ca(OH)_2$;

II. precipitation with $Ca(OH)_2$;

III. precipitation with $Ca(OH)_2$ and addition of crystallization germs.

Phosphorus removal efficiency was determined taking into account the concentrations of phosphorus from wastewater before and after precipitation. For this samples were taken from the influent and effluent plant precipitation semi pilot a frequency range from 3-4 h to 30 in 30 min. From the momentary samples were obtained and the average sample. From these samples, the total phosphorus concentration (of average samples) and orthophosphates (the momentary samples) was determined.

The dosages of the reagents were set out above.

3. Results and Discussions

<u>Variant I - Phosphorous precipitation with solution 10% $FeCl_3$</u>

The dose of $FeCl_3$, used in experiments carried out in this solution was 200 mg /dm^3 (sol.10%).

It was added $Ca(OH)_2$ solution 10% for pH correction, respectively:

– test 1 - pH - 7-7.5

– test 2 - pH - 8- 8.5

The precipitation reagents were introduced into the reaction chamber in a discontinuous, because it could not ensure the addition thereof to continuously at a constant rate.

The results obtained in these experimental variants are presented in Tables 3 and 4.

- Experimental results on the removal of phosphorus from municipal wastewater obtained in semi pilot precipitation plant:

  - Variant I: - precipitation with $FeCl_3$ – sol 10%
    - dose 200 mg/dm^3
  - Test 1: - correction pH - with $Ca(OH)_2$ sol 10%
    - pH - 7.0 -7.5

Table 3
Experimental Results on Phosphorus Removal from Urban Wastewater Variant I, Test 1

No.	Type of probe	Orthophosphate mg P/dm^3 Average value	Total phosphorus mg/dm^3 Average probe	pH
1	Entry plant	1.162	2.02	6.5
2	Output plant	0.576	1.1	7.5

After precipitation-decantation in the pH range 7.0-7.5 phosphorus concentration has been reduced by approx. 50%, installation effluent showing following characteristics (Table 3):

– Phosphorus - 1.1 mg P/dm^3
– Orthophosphate - 0.576 mg P/dm^3

- Variant I: - precipitation with $FeCl_3$ – sol. 10%
  - dose 200 mg/dm^3
- Test 2: - correction pH - with $Ca(OH)_2$ sol. 10%
  - pH - 8.0-8.5

Table 4
Experimental Results on Phosphorus Removal from Urban Wastewater Variant I, Test 2

No.	Type of probe	Orthophosphate mg P/dm^3 Average value	Total phosphorus mg P/dm^3 Average probe	pH
1	Entry plant	1.99	2.272	7.0
2	Output plant	0.413	0.568	8.0-8.5

In the pH range of 8.0-8.5, efficient on the removal of phosphorus increased to cca. 75%, and the effluent of the installation shows following characteristic (Table 4).

– Phosphorus - 0.568 mg P/dm^3
– Orthophosphate - 0.413 mg P/dm^3

Variant II - phosphorus precipitation with $Ca(OH)_2$ sol 10%

In this embodiment, two tests were carried out in the different pH areas, namely:

– Test 1 - precipitation at pH 8.0-9.0
– Test 2 - precipitation at pH > 11

The results obtained are shown in the pH (8.5-9.0) phosphorus precipitation efficiency was reduced at around 16%.

With increasing pH around 12.0-12.5, phosphorus precipitation efficiency increased to 80%, with a plant effluent total phosphorus content of 0.46 mg P/ dm^3.

- Experimental results on removing phosphorus from urban wastewater plant decanted obtained from semi pilot precipitation plant
  - Variant II : - Precipitation with $Ca(OH)_2$ – sol. 10%
    - dose 200 mg/dm^3
  - Test 1: - pH - 7.0-7.5

Table 5

Experimental Results on Phosphorus Removal from Urban Wastewater Decanted Obtained in Variant II, Test 1

No.	Type of probe	Orthophosphate mg P/dm^3 Average value	Total phosphorus mg P/dm^3 Average probe	pH
1	Entry plant	1.51	2.41	6.5
2	Output plant	0.576	1.3	7.5

Effective removal:

- Total phosphorus – 45%
- Orthophosphate – 50%

  - Variant I: - Precipitation with $FeCl_3$ – sol 10%
    - dose 200 mg/dm^3
  - Test 2: - Correction pH- with $Ca(OH)_2$ sol 10%
    - pH - 8.0-8.5

Table 6

Experimental Results on Phosphorus Removal from Urban Wastewater Decanted Obtained in Variant II, Test 2

No	Type of probe	Orthophosphate mg P/dm^3 Average value	Total phosphorus mg P/dm^3 Average probe	pH
1	Entry plant	1.99	2.272	7.0
2	Output plant	0.413	0.568	8.0-8.5

Effective removal:

- Total phosphorus – 75.0%
- Orthophosphate – 79.2%

Variant III - phosphorus precipitation with the addition of crystallization seeds

In the reaction chamber the limestone was added to precipitate phosphorus (germs of crystallization) 100 g/L, pH was adjusted with lime (sol. 10%). The pH range in which the experiments were carried out was 8.5-9.0.

The results are shown in Table 7.

Table 7

Experimental Results on the Removal of Phosphorus from Urban Wastewater Decanted Obtained in Variant III

No.	Type of probe	Orthophosphate mg P/dm^3 Average value	Total phosphorus mg P/dm^3 Average probe	pH
1	Entry plant	1.35	2.3	6.5
2	Output plant	0.548	1.30	8.5-9.0

Effective removal:

- Total phosphorus – 44.5%
- Orthophosphate – 59.4%

They have obtained the removal efficiency of phosphorus 44%, with a concentration in the effluent total phosphorus 1.3 mg P/dm^3. As shown in this pH range efficiencies are superior to those of the second embodiment, but lower than those presented in the literature and those obtained previously in the laboratory scale.

Based on experiments conducted can make the following recommendation:

– In order to achieve greater efficiency of precipitation it is necessary to ensure a constant flow of chemical precipitant;

– To prevent the deposition of precipitate in the reaction chamber shall be fitted with a stirring system installation properly;

– To achieve a good solid-liquid phase separation in the decanter, it is necessary that the length of the modules must be at least 1 m.

4. Conclusions

The objective of the research it has been the achievement of a pilot plant for the removal of phosphorus by precipitation.

The data presented highlight the following conclusions:

1. Technological scheme was established to remove phosphorus in the pilot plant, based on laboratory experiments;

2. Sizing parameters were established on the basis of pilot plant experiments performed on laboratory scale and semi pilot;

3. A conceptual design was developed to pilot plant precipitation of phosphorus at a rate of 1 L/s and this plant was made.

Installation performed is a steel building that can be experienced for different types of industrial and domestic wastewater.

The experiments carried out in precipitation semi pilot plant fueled in steady stream of domestic wastewater, have led to reductions in total phosphorus concentrations from 2-2.4 mg P/dm^3 to 0.46 mg P/dm^3 by treatment with lime and up to 0.57 mg P/dm^3 by treatment with FeCl^3 and lime.

REFERENCES

Ceică A., Bulgariu L., Lazăr L., Crețescu I, Balasanian I., *Removal of Nitrates from Water in the Presence of Competitors Anions Using Purolite Resins*, Bul. Inst. Polit., Iași, s. Chim. si Ing. Chim., **LVI**, *4*, 119-131 (2010).

Domopoulou A., Moustakas K., Kremezis P., Stavridou S., Karayannis V., *Valorization of Industrial by-Products as Coagulants in Wastewater Treatment*, Proceedings of 113th IWA Specialized Conference on Small Water and Wastewater Systems & 5th IWA Specialized Conference on Resources-Oriented Sanitation, Atens, Greece (2016).

Kulkarn S.J., *An Insight into Research and Studies on Phosphorous Removal*, International Journal of Science and Healthcare Research (2016).

Nedjah N., Hamdaoui O., Laskri N., *Phosphorus Removal of Urban Wastewater by Physico-Chemical Treatment: Waterways Uthrophication Prevention*, International Journal of Environmental Science and Development, **6**, *6*, 435-438 (2015).

Nedjah N., Laskri N., *Phosphorus Removal from Urban Wastewater via Chemical and Combined Treatment Against Eutrophication of Receiving Environments*, International Journal of u- and e- Service, Science and Technology, **8,** *7*, 303-312 (2015).

Nir T., Arkhangelsky E., Levitsky I., Gitis V., *Removal of Phosphorus from Secondary Effluents by Coagulation and Ultrafiltratio*n, Desalination and Water Treatment, **8**, 24-30 (2009).

Parsons S.A., Smith J.A., *Phosphorus Removal and Recovery from Municipal Wastewaters*, DOI: 10.2113/GSELEMENTS., **4**, *2*, 109-112 (2008).

Safferman S.I., Dong Y., Thelen J., Costantini L., Saber L., Richard Schorr R.J., Sengupta S., Revur R., *Phosphorus Removal from Domestic Wastewater Using Engineered Nano-Media*, http://www.nowra.org/Files/Resource_Library/NOWRA_Published_Research/Proceedings/Proceedings,/Safferman.pdf (2015).

Sawsan A.M., Shanshool H.A., *Phosphorus Removal from Water and Waste Water by Chemical Precipitation Using Alum and Calcium Chloride*, Iraqi Journal of Chemical and Petroleum Engineering, **10**, *2*, 35-42 (2009).

Tociu C., Diacu E., *Quality Assessment of the Aluminium Sulphate Coagulant Recovered from Metallurgical Slag Based on a Correlation of the Removed Phosphorous from Municipal*, U.P.B. Sci. Bull., **77**, *2*, 29-40 (2015).

*** Ministerial Order No 161/2006 *for the Approval of the Norm Concerning the Reference Objectives for the Surface Water Quality Classification*.
*** Directive 2000/60/EC *of the European Parliament and of the Council Establishing a Framework for the Community Action in the Field of Water Policy*.
*** Directive 91/271/EEC *Concerning Urban Wastewater Treatment*.

OPTIMIZAREA PROCESELOR FIZICO-CHIMICE
ÎN EPURAREA APELOR
UZATE MENAJERE ȘI INDUSTRIALE

(Rezumat)

În apele de suprafaţă ajung uneori ape uzate menajere şi anumite tipuri de ape industriale epurate necorespunzător, ca şi scurgerile de ape de pe terenurile agricole fertilizate, sunt surse importante de elemente nutritive responsabile de apariţia fenomenului de eutrofizare. Eutrofizarea este o problemă majoră de mediu care afectează apele de suprafaţă din întreaga lume. Scăderea cantităţilor de elemente nutritive din apele de suprafaţă este din ce în ce o problema stringentă şi de actualitate atât pentru UE cât şi pentru România. Epurarea eficientă a apelor uzate este foarte importantă pentru a reduce încărcătura de nutrienţi a apelor de suprafaţă, care este unul dintre obiectivele în politicile UE (Directiva-cadru privind apa).

Pentru ca elementele nutritive să nu mai ajungă în cantităţi care să producă eutrofizarea în apele de suprafaţă au fost experimentate tehnologii de îndepărtare a azotului şi fosforului, obiect al unor cercetări efectuate de INCDPM- Bucureşti.