Environment Protection Engineering

Vol. 31 2005 No. 2

ANNA M. ANIELAK*, KRZYSZTOF PIASKOWSKI*

INFLUENCE OF ZEOLITES ON KINETICS AND EFFECTIVENESS OF THE PROCESS OF SEWAGE BIOLOGICAL PURIFICATION IN SEQUENCING BATCH REACTORS

Despite applying various modern technologies in treatment plants it is still difficult to maintain the quality coefficient of purified sludge. Allowable concentrations of phosphorus and nitrogen compounds are often exceeded, activated sludge expands and emerges and a foam appears in aeration tank. Such factors as production of small bubbles of gas, high content of surface-active substances and water-repellents as well as the presence of thread and non-thread bacteria are responsible for emerging of activated sludge and foam formation. Different methods, mainly physical and chemical, are applied to prevent sludge expansion and foam formation. Their effectiveness, however, changes considerably. They can also cause other problems, eg. precipitation of struvite.

This paper deals with the application of natural zeolites to the treatment of surface and ground water as well as municipal sewage. The results obtained prove the zeolite improves the treatment efficiency and prevents the activated sludge from expanding. It is also an appropriate substratum for microorganism growth, increases a specific gravity of activated sludge floccules, increases the rate of its sedimentation and improves the value of its volumetric index.

1. INTRODUCTION

Despite applying modern technologies, it is still difficult to maintain the quality coefficients of purified sewage at municipal sewage treatment plants. Allowable concentrations of phosphorus and nitrogen compounds are often exceeded, activated sludge expands and emerges, and the foam appears in the aeration tank. Production of small bubbles of gas in the sewage, high content of surface-active substances and water-repellents (fats, aliphatic hydrocarbons) are considered to be responsible for emerging of activated sludge and foam formation. The factors which markedly influence the sludge expansion and its emerging are thread bacteria and non-thread bacteria with strongly hydrophobic cell walls. Bacteria often produce enzymes of surfactant properties.

* Technical University of Koszalin, Department of Water and Wastewater Technology, ul. Śniadeckich 2, 75-452 Koszalin, anielak@tu.koszalin.pl

30 different kinds of thread bacteria are found in sewage, and 10 of them are responsible for more than 90% of operating problems [1]. Different methods, mainly chemical and physical, are applied to prevent sludge expansion and foam formation. However, these methods could cause other problems, e.g. precipitation of struvite which makes mechanical cleaning of sewage more difficult. In Poland, industrial coagulants PIX and PAX are widely applied, but their considerable part passes with purified sewage to surface water. Addition of aluminium salts to the sewage decreases the content of phosphorus compounds and prevents growing of thread bacteria. There are also other mineral substances like powdered talc, silicates, bentonite and zeolite modified with iron cations applied to sewage purification in the dose of 150 g/dm^3 [2]–[4]. Also polyelectrolytes or lime are used for sewage purification. By lenghtening the time of sewage aeration its oxygenation increases. Effectiveness of all these methods is different, sometimes it surprisingly differs, depending on plant.

The tests carried out under the supervision of ANIELAK [5], [6] in order to assess the suitability of natural zeolites for purification of surface and ground waters as well as municipal sewage showed that on such porous substrate microorganisms can be successfully grown. Application of zeolites needs, however, a proper process control and optimization of technological units. This publication is one of many our papers proving that zeolites should be applied to purification of municipal sewage and evaluating conditions of effective biological and physicochemical purification of sludge.

2. INVESTIGATION METHOD

Investigation was carried out on synthetic wastewater as well as on a mixture of synthetic and real sewage (in proportion of 1:1) allowing easy adjustment of carbon, nitrogen and phosphorus compounds proportion (table 1). Wastewater was prepared once a day and sent to two laboratory SBRs (Sequencing Batch Reactors), one of them was a control reactor (figure 1). Reactors operated in 8-hour cycle, which consisted of the following phases (figure 2): filling and mixing in anoxic–anaerobic conditions; aeration, sedimentation and decantation of a purified wastewater. Decantation coefficient f was equal to 0.5 (50% of the volume of purified wastewater). At the end of aeration phase an excess sludge was removed to keep a total sludge age of 10 days constant. Aerobic sludge age (referred to oxygen conditions) was 7.2 days.

After the period necessary for growing and adaptation of activated sludge to the work in SBR system [7] qualitative analysis of purified wastewater as well as the study of the process kinetics began. The samples of the activated sludge were taken from the aeration tank of municipal sewage treatment plant in Koszalin. During the first stage laboratory tests were carried out on synthetic wastewater. The results obtained were considered to be a reference level for the second stage research carried out on actual wastewater. A natural Mexican zeolite, with clinoptylolite as its main component, was introduced into one of the reactors. The ion composition of zeolite is presented in figure 3. Once a day dusted mineral, whose graining was less than 250 μm, was dosed reaching a fixed concentration on the level of 1 g/dm^3. The test was carried out for 35 days. After purification unit had been converted in such a way as to allow mixing of real and synthetic wastewater, the sludge was adapted and the influence of organic substance load on individual biological processes as well as final process efficiency were analysed. All wastewater analyses were carried out according to Polish standards [8].

Table 1

Physicochemical characteristics of wastewater applied to the tests

Parameter	Unit	Value		
		Synthetic wastewater	Mixture of real and synthetic wastewater	
			Stage I	Stage II
pH	–	7.10	7.45	7.31
Alkalinity	mval/dm^3	4.2	3.6	4.3
COD	mg/dm^3	330	289	577
BOD_5	mg/dm^3	286	211	438
TKN	mg/dm^3	52.2	63.0	69.9
$N–NH_4$	mg/dm^3	27.45	33.46	51.37
Total phosphorus	mg/dm^3	10.80	11.40	13.00
$P–PO_4$	mgP/dm^3	10.45	9.13	9.68
COD/ BOD_5		1.1	1.4	1.3
BOD_5 / N		5.5	3.3	6.3
BOD_5 / P		26.5	18.5	33.7

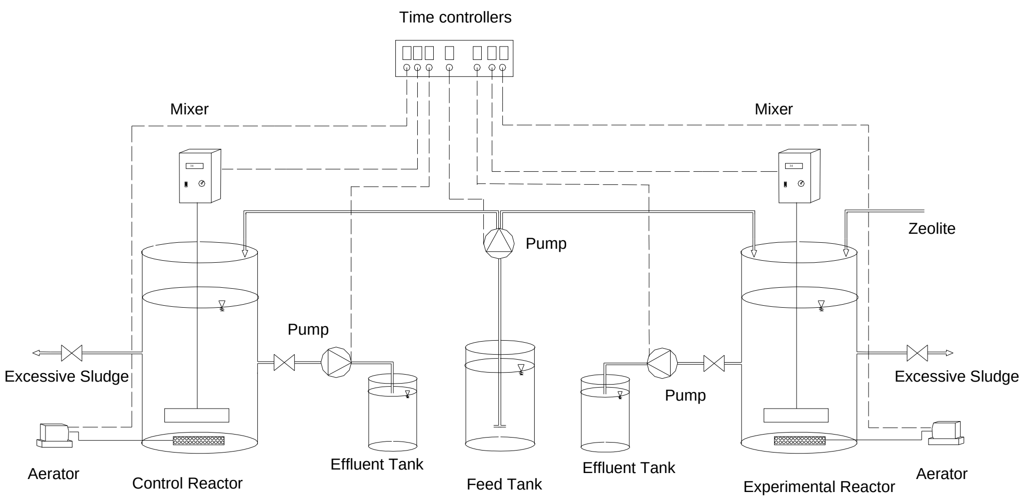

Fig. 1. Scheme of experimental laboratory-scale SBR system

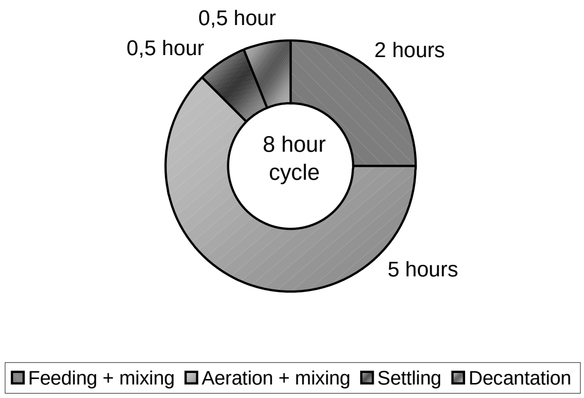

Fig. 2. Operation time of the 8-hour SBR cycle

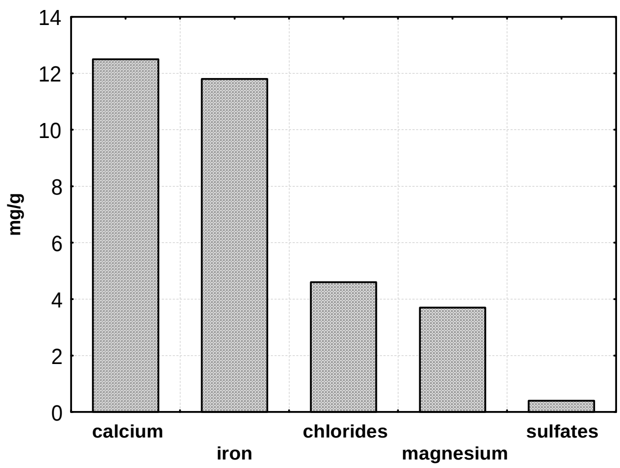

Fig. 3. Qualitative and quantitative analyses of Mexican zeolite (own results)

3. RESULTS AND DISCUSSION

3.1. PURIFICATION OF SYNTHETIC WASTEWATER WITH APPLICATION OF ZEOLITE

A Mexican zeolite in wastewater purified in a laboratory reactor of SBR type had a considerable influence on general improvement in its purification. Since the activated sludge easily sediment, the zeolites added decrease its volume index (SVI) to a slight degree only. The value of this index in the reactor with zeolite did not exceed

53 cm^3/g, while in the control reactor the SVI index approached 66 cm^3/g. The difference appeared due to building mineral grains in the floccules of activated sludge which increased its specific gravity and made a load in sedimentation process. Participation of zeolites in formation of floccule structure was confirmed by systematic microscopic examination as well as by the analysis of a residue after ignition. The average concentration of the sludge in the control reactor was 1.53 g SS/dm^3, while in the reactor with zeolite it reached 2.07 g SS/dm^3.

An increase in SBR efficiency was measured, since in the reactor, a constant concentration of zeolite was achieved. The values of qualitative factors characterizing the purified wastewater (figures 4–6) refelct not only physicochemical processes but also intensive biological processes. The concentration of organic substances denoted as BOD_5 in SBR ranged between 4 and 6 mg/dm^3 (figure 4A), while their level in wastewater in the control reactor was unstable, higher and ranged from 5 to 11 mg/dm^3. Zeolite decreased the concentration of orthophosphates (figure 4B), although ANIELAK and PIASKOWSKI [9] reported that natural zeolites did not remove these ions in physicochemical processes because of their skeleton structure with negative load, which shows affinity to cations only – especially to ammonium cations. Therefore the relations obtained proove that phosphorus was removed as a result of biological reaction intensified in the presence of zeolites.

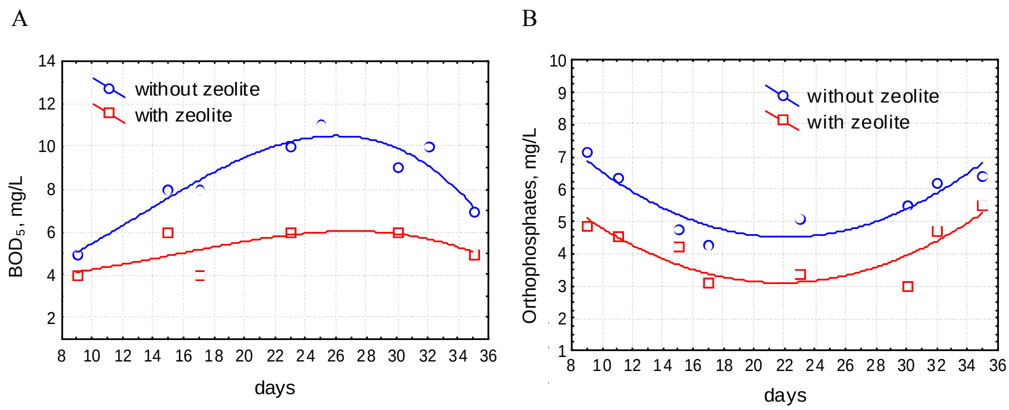

Fig. 4. Concentration of BOD_5 and orthophosphates in wastewater purified in control reactor as well as in reactor with the batch of Mexican zeolite. Zeolite concentration, 1 g/dm^3

Removal of ammonia nitrogen, despite the zeolite batch, is also a result of biochemical processes. On the 35th day of research the concentration of NH_4^+ ions in the control reactor and in the reactor with zeolite reached 22.03 mg/dm^3 and 1.73 mg/dm^3, respectively (figure 5A). A decrease in the ammonia nitrogen concentration in wastewater purified in the reactor with zeolite was observed in the whole period of research. At the same time the concentration of nitrate nitrogen in the wastewater increased from 1.71 up to

5.29 mg/dm^3 (figure 5B), and its final value was few times higher than that in the control reactor (in the range from 1.16 to 2.0 mg/dm^3). This proves that zeolite as an active carrier of the biomass, due to absorption of ammonium ions and its open skeleton structure, creates very favourable conditions for development of bacteria – especially nitrifying bacteria.

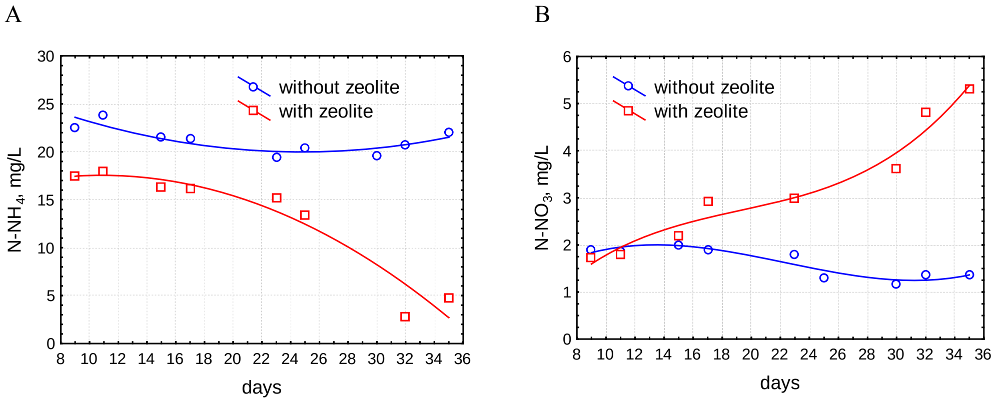

Fig. 5. Concentration of ammonia (A) and nitrate nitrogen (B) in wastewater purified in control reactor as well as in reactor with the batch of Mexican zeolite. Zeolite concentration, 1 g/dm^3

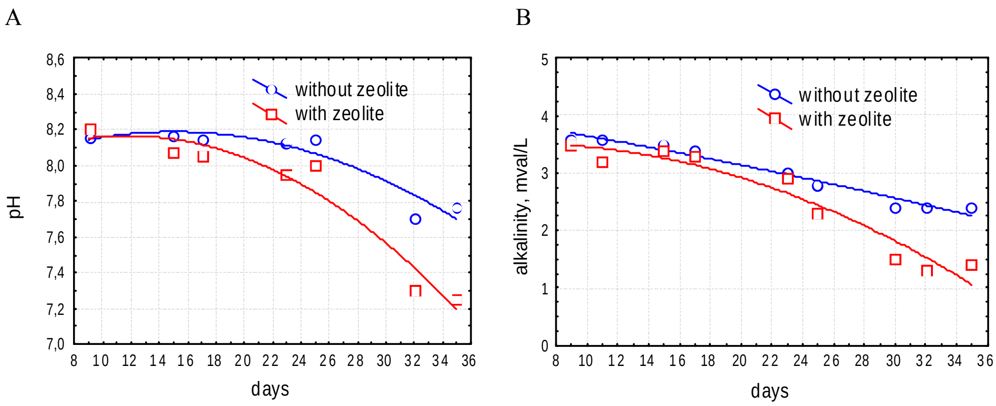

Fig. 6. pH (A) and alkalinity (B) of wastes purified in control reactor as well as in reactor with the batch of Mexican zeolite. Zeolite concentration, 1 g/dm^3

The transformations of nitrogen compounds influenced directly alkalinity and pH of purified wastewater (figure 6A, B). A considerable decrease in the values of these factors was noted in wastewater from the reactor with the batch of zeolite. In this reactor, nitrification was faster and more efficient, and after 23 days of experiment we dealt with a rapid increase in the nitrate concentration associated with a decrease in wastewater pH from 8.0 down to 7.2. The process of ammonia nitrogen oxidation was accompanied by a decrease in alkalinity, which dropped from the initial value within the range of 4.2 to 4.4 mval/dm^3 down to 1.5 mval/dm^3 in the reactor with zeolite and to 2.5 mval/dm^3 in the control reactor.

3.2. INFLUENCE OF THE LOAD OF REACTOR WITH ORGANIC WASTES ON EFFECTIVENESS OF ZEOLITE IN THE PROCESS OF PURIFICATION OF REAL SEWAGE

In order to verify the results obtained and to evaluate the influence of zeolite on the process of wastewater purification at variable load of the reactor with organic substances, the research was carried out on the sewage mixed with synthetic wastewater. Operation conditions of the reactor were not changed. In the first stage, the load of the reactor was lower by 26% (R_1 = 0.36 g BOD$_5$/dm^3·d) compared to that in synthetic wastes (R_0 = 0.49 g BOD$_5$/dm^3·d), while in the second stage the load (R_2) was increased to 0.75 g BOD$_5$/dm^3·d.

In both cases, a batched zeolite lowered an average value of the volumetric index of the sludge by 22–24% (figure 7) compared to the index value of the control sludge, which corroborated the relation obtained for synthetic wastewater.

Table 2

Parameters of activated sludge and the load of organic substances obtained in the research

Research stage	Mass of the activated sludge (g SS/dm^3)		Reactor load R (g BOD$_5$/dm^3·d)	Load of the sludge X (g BOD$_5$/g·d)	
	Control reactor	Reactor with zeolite		Control reactor	Reactor with zeolite
I	1.35	1.84	0.36	0.27	0.20
II	2.11	2.54	0.75	0.36	0.30

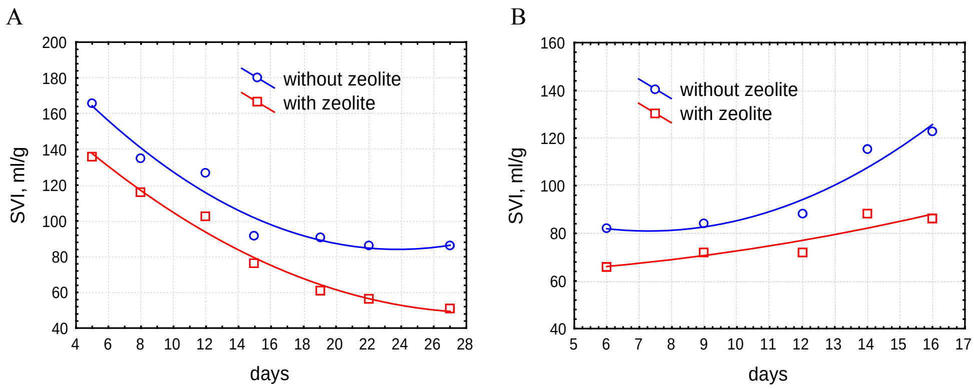

Fig. 7. Influence of zeolite on the changes in the volumetric index of the sludge at the reactor load R_1 = 0.36 g BOD$_5$/dm^3·d (A) and R_2 = 0.75 g BOD$_5$/dm^3·d (B) in control reactor as well as in reactor with the batch of Mexican zeolite. Zeolite concentration, 1 g/dm^3

Analysis of the nitrification process as well as biological phosphorus removal carried out in individual phases of the reactor operation with zeolite (figure 8A–D) showed the dependence of the process kinetics on the load of the reactor with organic substances. At the load R_1 = 0.36 g $BOD_5/dm^3 \cdot d$ intensive nitrification was carried out, while after an increase in the amount of organic substances the concentration of nitrate nitrogen decreased and the rate of phosphorus removal increased. Despite high concentration of ammonia nitrogen at the end of filling phase at the load R_2 the rate of nitrification estimated for the aeration phase of the analysed cycle was higher and reached 1.75 mgN/g SS·h . At lower load this value approached 1.20 mg N/g SS·h.

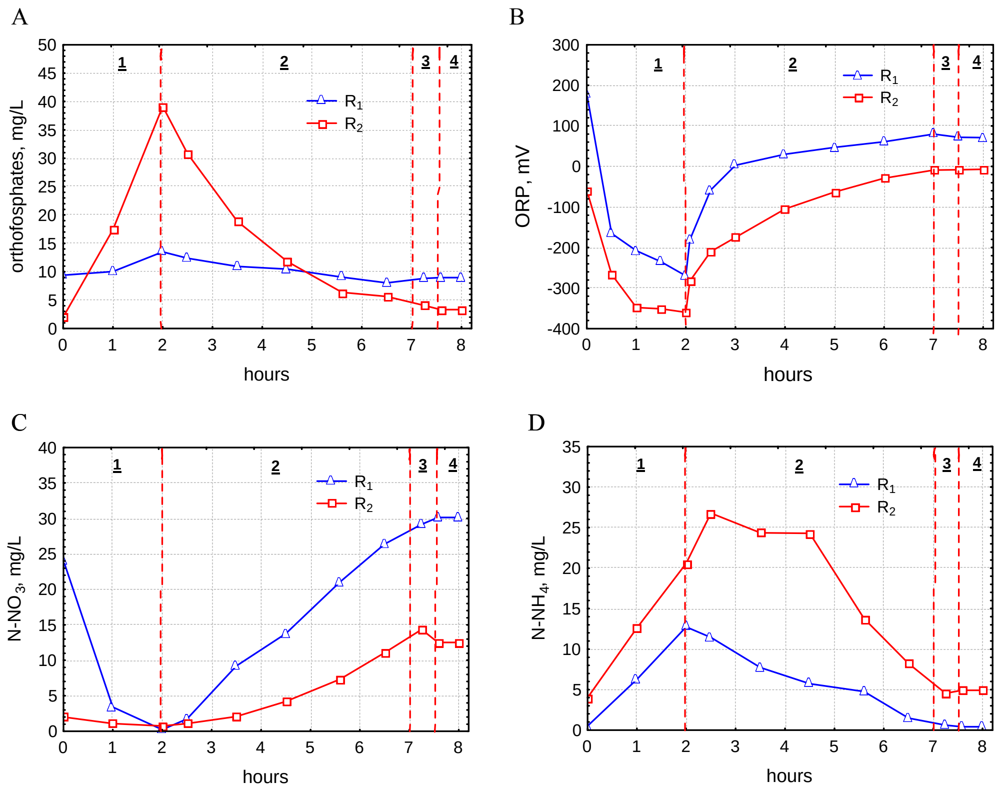

Fig. 8. Influence of the reactor load with organic substances on the dynamics of variation of selected parameters during full 8-hour working cycle of the reactor with zeolite.
Load: R_1 = 0.36 g $BOD_5/dm^3 \cdot d$, R_2 = 0.75 g $BOD/dm^3 \cdot d$.
Denotations: 1 – feeding + mixing, 2 – aerating + mixing, 3 – sedimentation, 4 – decantation

Effectiveness of the zeolite in the removal of organic substance in variable concentration is presented in figure 9 as a difference in the values of selected parameters for wastes purified in the reactor with zeolite and in the control reactor (without zeolite). At the load of 0.36 g $BOD_5/dm^3 \cdot d$ the mineral batching allowed us to decrease BOD_5 value by 56%, and COD value by 13%, while at the double load of organic impurities the reduction of both factors reached 30% and 6.1%, respectively. In the case of remaining parameters, this relation was reversed. An increase in the reactor load and the presence of the zeolite made removal of respective compounds more effective. Compared to the control reactor the nitrification process in the reactor with zeolite was more intensive, concentration of ammonia nitrogen decreased by almost 100%, while the increase in nitrate concentration reached 11.5%. This, however, did not affect adversely the process of biological phosphorus removal, which resulted in a higher rate (by 65.6%) of removing total phosphorus from the wastewater in the presence of zeolite compared with the higher rate (by 28%) of orthophosphate removal in the control reactor. In the reactor operating at the load R_1, nitrification was the main process and because of disadvantageous ratio of BOD_5/TP equal to 18.5 (good result may be obtained at the ratio higher than 20) the process of biological phosphorus removal did not occur and batched zeolite improved the quality of purified wastes in a negligible degree only. If organic load of the reactor was increased, the value of BOD_5/TP = 33.7 resulted in a higher efficiency of biological phosphorus removal being enhanced by batched zeolite; moreover, the zeolite in the reactor made nitrification highly effective. The above is not an evidence of physicochemical reaction of zeolite, but it proves that reaction of zeolite is based on increasing activity of microorganisms in the activated sludge; especially nitrification bacteria in the skeleton of zeolite that absorbs ammonium ions and is a convenient substrate for bacteria to grow on. This way zeolite becoming an active material in the sludge could also reduce the influence of an early age of sludge on nitrification by preventing from excessive removal of bacteria that carry out oxidation processes.

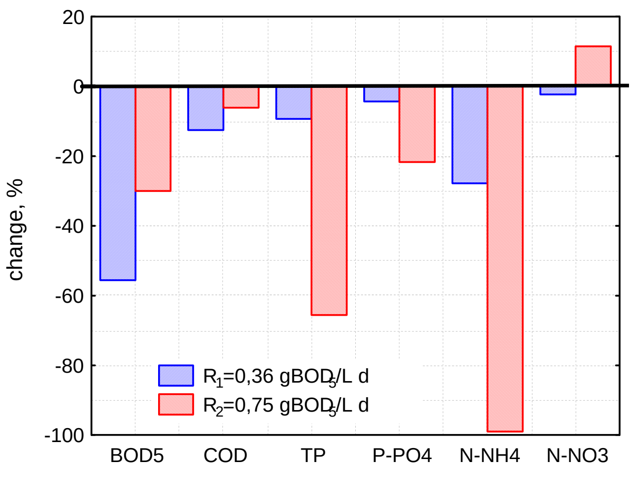

Fig. 9. Percentage variation in basic parameters of the wastewater purified in the reactor with zeolite compared to the control reactor at variable organic load

4. CONCLUSIONS

• Zeolite makes an appropriate substratum for microorganisms, increases a specific gravity of activated sludge floccules, increases the rate of its sedimentation and improves the value of volumetric index (SVI).

• The zeolite batch in a sequencing reactor supports the removal of organic compounds, nitrogen and phosphorus from the wastewater.

• In the presence of zeolite, phosphorus compounds are removed from the wastewater due to higher biological stimulation of microorganisms, while nitrogen compounds are removed as a result of both physicochemical and biological processes.

• Zeolite adsorbs ammonia nitrogen, which makes the growth of nitrification bacteria easier both on the surface and inside the porous material.

• The change in the rate of BOD_5/TP from 18.5 on 33.7 increases the efficiency of phosphorus removal from wastewater being purified with zeolite and at the same time maintains high nitrification rate.

ACKNOWLEDGEMENT

The work was supported by the State Committee for Scientific Research No. 0735/T09/2002/23.

REFERENCES

[1] LEMMER H., POPP W., *Fadenformige Mikroorganismen aus belebten Schlamm Vorkommen – Biologie Bekampfung*, Gesellschaft zur Forderung dert Abwassertechnik e.V., St. Augustin, 1992.

[2] LALLO D., *Wastewater purification in Hungary using natural zeolites*, Natural Zeolites '93, New York, 1995.

[3] ANIELAK A.M., PIASKOWSKI K., *Wspomaganie oczyszczania ścieków zeolitami w reaktorach SBR*, 2003, ZN nr 16, wyd. Politechniki Białostockiej (publikacje XII Konferencji Naukowo-Technicznej *Problemy gospodarki wodno-ściekowej w regionach rolniczo-przemysłowych*).

[4] CHMIELEWSKA-HORVÁTHOVA E., *Adhanced wastewater treatment using clinoptylolite*, Environment Protection Engineering, 1996, Vol. 22, No. 1–2.

[5] ANIELAK A.M., NOWAK R., *Influence of filtration bed building on micro-organisms development in the process of manganese and iron removal from water*, Environment Protection Engineering, 2002, Vol. 28, No. 3–4.

[6] ANIELAK A.M., *Examples of the Application of Electrokinetic Potential in Environment Engineering*, Environmental Engineering Studies (Polish Research on the Weg to the EU), Kluwer Academic/Plenum Publishers, 2003.

[7] PIASKOWSKI K., *Wpływ parametrów procesowych na usuwanie związków biogennych w laboratoryjnym reaktorze typu SBR*, Rocznik Ochrona Środowiska, 2003, Tom 5, wyd. Środkowo-Pomorskie Towarzystwo Naukowe Ochrony Środowiska.

[8] HERMANOWICZ W., DOJLIDO J., *Fizycznochemiczne badanie wody i ścieków*, Arkady, 1999.

[9] ANIELAK A.M., PIASKOWSKI K, *Skuteczność naturalnych zeolitów w usuwaniu związków fosforu z roztworów wodnych*, Gaz, Woda i Technika Sanitarna, 2001, nr 5.

WPŁYW ZEOLITÓW NA KINETYKĘ I EFEKTYWNOŚĆ PROCESU BIOLOGICZNEGO OCZYSZCZANIA ŚCIEKÓW W REAKTORACH SEKWENCYJNYCH

Oczyszczalnie ścieków komunalnych pomimo stosowania nowoczesnych technologii wciąż mają problemy z utrzymaniem parametrów jakościowych ścieków oczyszczonych. Często przekraczane jest dopuszczalne stężenie związków fosforu i azotu, zachodzi puchnięcie i wypływanie osadu czynnego, w komorze napowietrzania powstaje piana. Wypływanie osadu czynnego i powstawanie piany są związane z wytwarzaniem w ściekach drobnych pęcherzyków gazu, znaczną zawartością substancji powierzchniowo czynnych oraz substancji hydrofobowych (tłuszczów, węglowodorów alifatycznych). Istotnym czynnikiem przyczyniającym się do pęcznienia i wypływania osadu są bakterie nitkowate, a także nienitkowate, ale z silnie hydrofobową powierzchnią komórkową. Często bakterie wytwarzają enzymy, wykazujące właściwości substancji powierzchniowo czynnych. Obecnie ocenia się, że istnieje około 30 różnych bakterii nitkowatych, z których około 10 jest odpowiedzialnych za ponad 90% problemów eksploatacyjnych. Zwalczając zjawisko pęcznienia osadu i powstawania piany, stosuje się różne metody, głównie chemiczne i fizykochemiczne. Wszystkie te metody mają bardzo zmienną skuteczność, często zaskakująco różną w wielu oczyszczalniach, a nawet mogą stwarzać nowe problemy, jak np. wytrącanie się struwitu.

Przedstawiono innowacyjne rozwiązanie problemu polegające na zastosowaniu do oczyszczania ścieków w systemie SBR naturalnego zeolitu. Wyniki badań wykazują, że przy odpowiednio prowadzonym procesie oczyszczania ścieków z zastosowaniem zeolitu można zwiększyć efektywność ich oczyszczania, nie zachodzi zjawisko ich pienienia się i wypływania osadu czynnego. Zeolit stanowi dobre podłoże dla rozwoju mikroorganizmów, zwiększa ciężar właściwy kłaczków osadu czynnego, przyspiesza jego sedymentację i korzystnie wpływa na wartość indeksu objętościowego.