# APPLICATION OF pH MEASUREMENTS FOR THE FOLLOWING THE COURSE OF BIOLOGICAL TREATMENT OF WASTEWATER AND ITS CONTROL

K. Mędrzycka[*], S. Cytawa[**] and R. Tomczak-Wandzel[*]

[*]Gdańsk University of Technology
80-952 Gdańsk, Narutowicza 11/12, Poland
Email: krystyna@chem.pg.gda.pl
[**] Wastewater Treatment Plant in Swarzewo
84-120 Władysławowo, Władysławowska 84, Poland
Email: scytawa@wp.pl

**ABSTRACT**
This paper presents the results obtained from laboratory-scale pilot plant experiments, carried out in a batch mode, similarly as in SBR system. Synthetic wastewater with the elevated content of glucose were treated. The results of continuous measurements of pH were correlated with other parameters: $NH_4$ -N, $NO_3$–N, $PO_4$ –P concentrations, redox potential and conductivity. It has been stated that pH variations reveal a strong correlations with phosphorus concentration, while there is a lack of such correlations with nitrogenous compounds concentration changes.

**KEYWORDS**
Biological system control, SBR, nitrogen and phosphorus removal, pH measurements

## INTRODUCTION

Recently, a great effort is directed to find a correlations between chemical parameters which represent the effect of the treatment process and such parameters which are easy to measure (Mędrzycka et al.). These parameters are conductivity, redox potential, oxygen content and pH. They can be easily measured with using probes and immediately registered. Finding a correlation between these parameters and chemical parameters of wastewater during its treatment is a task of many researches. This may improve control of biological treatment process.

It is well recognized that there is a strong correlation between redox potential and some of chemical parameters, which change during biological process (Podedworna, 1999). The correlations have been found with nitrogenous compounds  concentration changes, especially in the anoxic phase. This also can be applied in the control of the process and the steering of process parameters (Czerwionka, 2002).

pH is a parameter which is usually observed only in the context of the maintenance of the proper conditions in the reactor. Its measurement is performed in order to know what is a deviation from the required value and if it should be corrected. However, the observations of the pH changes during the biological process show that probably it could be possible to apply the pH measurements for the control of the process. This paper presents results which prove this.

## MATERIALS AND METHODS

The experiments were carried out in a laboratory-scale pilot plant, which was operated in a batch mode, by analogy to the SBR system. The reactor was equipped with a device for continuous measurements of pH, redox potential, oxygen concentration and conductivity. The activated sludge was taken from the SBR unit in Swarzewo Treatment Plant. In all experiments synthetic wastewater was used. Components concentration (in mg/dm$^3$) was as follow: soy broth -150, soy peptone –50, starch – 50, potassium soap – 50, urea – 30, $MgSO_4$ –7, NaCl –30, KCl –7, $CaCl_2$ –7, glucose –500, 750, 1000, 1500, 2000, 3000.

The main substrate was glucose and its concentration was varied from 500 up to 3000 mg/l. Each process consisted of two phases: first, the mixture of sludge and wastewater was only stirred mechanically without aeration (for three hours). Afterwards the aeration was switched on and the process lasted next 6 or 7 hours. During the whole process the pH, conductivity and redox potential were measured continuously (every 5 min.) and were registered by computer system. Moreover, the BOD, COD, $PO_4$-P, $NH_4$-N, $NO_3$-N were determined in the samples taken every 15 minutes.

## RESULTS

All results are presented in form of the process time-dependences. In Fig.1 the pH curves for processes with glucose concentration 1000 mg/dm$^3$ are shown

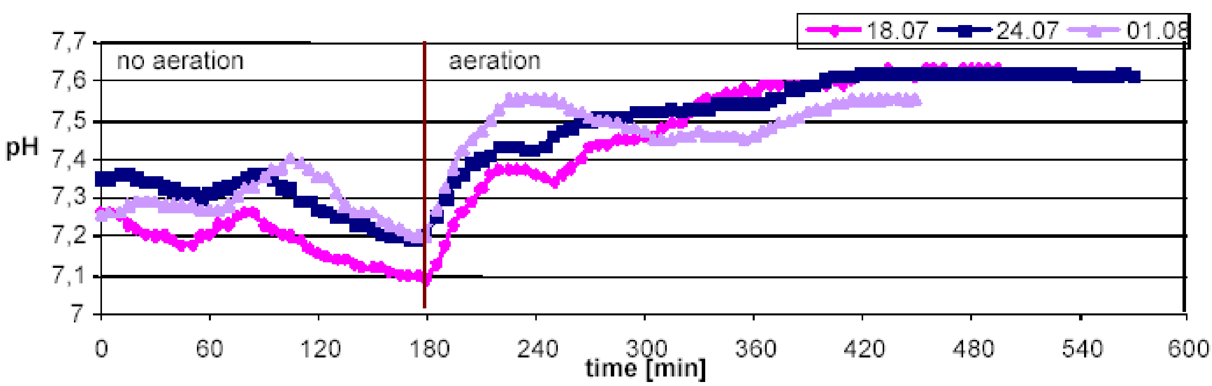



**Fig. 1.** pH changes with time

As it can be seen from Fig.1 the pH curves show characteristic minima and maxima. They are repeatable on each curve, especially those in anoxic/anaerobic phase. First, the very small maximum is observed and after about 1 hour a minimum of pH value is registered. The drop of pH from first maximal value to the minimum is about 0.05-0.1. Then, the increase of pH is visible and it rises by about 0.1-0.15. Next, the biggest drop of pH value (0.18-0.2) takes place and it ends when the aeration began. Then, the sharp increase of pH is observed up to plateau after about 4 hours of aeration.

One can ask, is it worthy while to analyse such small changes? Of course if pH measurements are carried out occasionally, these changes will not be detected. However, when continuous measurement is applied we can observe any, even very small fluctuations of this parameter. A very precise measurements of pH are necessary. The argument for detailed analysis of these relations is their repeatability, which gives a chance to exploit it for process control.

When we consider the biochemical processes which take place in bioreactor, the maximum on the pH curve in the anoxic/anaerobic phase could result from the ammonification and denitrification processes, which increase pH. However, as it is presented in Fig.2, in our experiments nitrates were not present in the anoxic phase, thus decomposition of proteins generating alkalinity could be responsible for this maximum, but not denitrification process. So, we should observe an increase of ammonia nitrogen, simultaneously with increase of pH.

However, this is not the case. Ammonia nitrogen fluctuates and on the contrary, its decrease is observed at the maximum point of pH (Fig. 2 B,C,D). However, this happens not always (Fig. 2A). Probably the carbon substrate concentration effect should be considered

Ammonia nitrogen drop can not be attributed to nitrification (nitrates not detected), but to the uptake by microbial growth. If so, one should expect the decrease of alkalinity when ammonia nitrogen is uptaken, while in the experiments the pH increase is observed, which means that proteins decomposition (ammonification) increases pH more, than nitrogen uptake decreases it. Thus, the shape of pH curve in non aerated phase can not be explained basing on ammonium nitrogen concentration changes.

In the aeration phase the drop of ammonia is parallel to the increase of pH value. If a decrease of ammonia results from nitrification, acids are released and they can be neutralized by wastewater alkalinity or a decrease of the pH should be observed (while the pH increase is registered). Thus, one can state that the pH changes during bioprocess are not reflecting the nitrogenous compounds transformations and are probably more dependent on the phosphorus removal.

In Figure 3 the curves for phosphates and pH changes are compared.

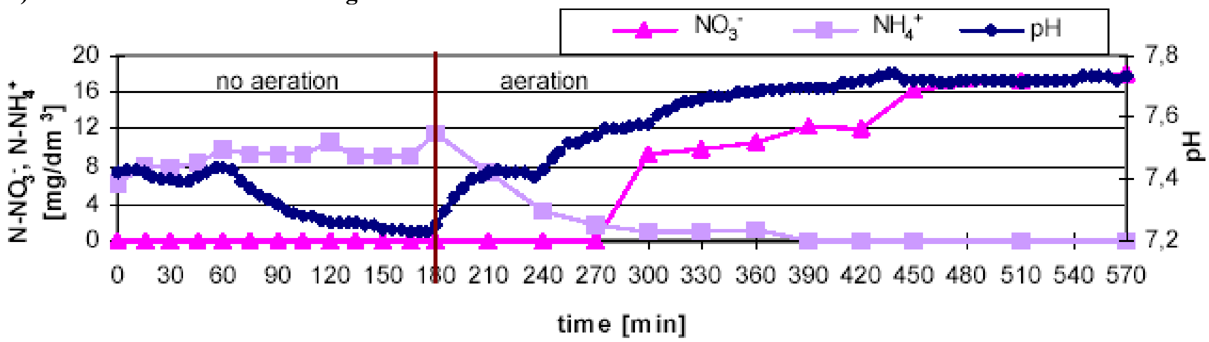
As it can be seen there is a very strong correlation between both parameters. In the non aerated phase the very slow phosphorus release is observed up to the moment, when maximum on pH curve appears. From this point the intensive increase of P concentration and a sharp drop of pH are observed simultaneously. In the aeration phase, during intensive phosphorus uptake the pH increases. This is visible in all experiments performed.

The explanation of this correlation can be based on analysis of volatile fatty acids (VFA) concentration. Its appearing decreases pH, while during phosphorus release they are consumed and pH should increase. In the presented results pH decreases till the end of anaerobic phase, which means that VFA are still generated and their content increases in spite of their accumulation in phosphorus bacteria.

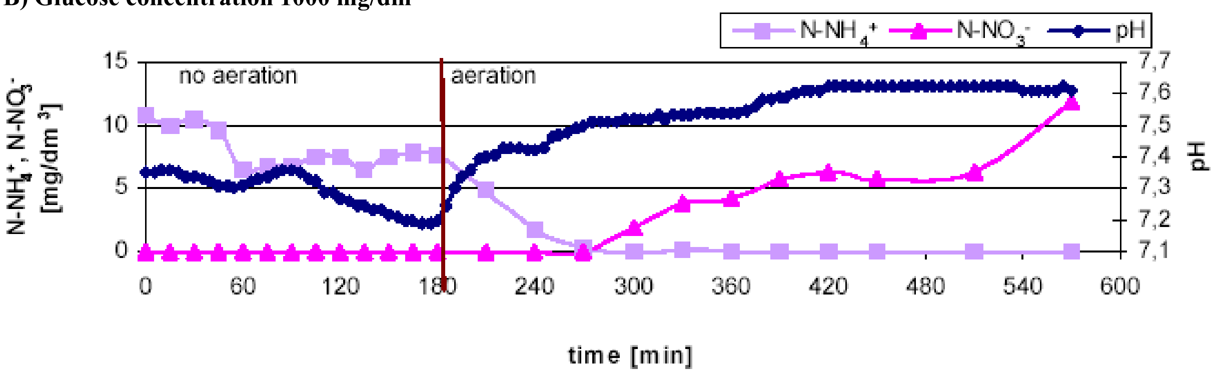
In aerobic phase the remaining VFA are easily degraded which results in the pH increase. Such run of pH curve is possible in the case when glucose is a main substrate.

The pH parameter is very sensitive for any disturbances and if for example phosphorus release in the anaerobic phase is disturbed, it is immediately reflected in the pH curve run.
This is clearly visible in Figs 4 and 5. Run of pH curve shows that generation of VFA is weakened and simultaneously, phosphorus release is weaker.

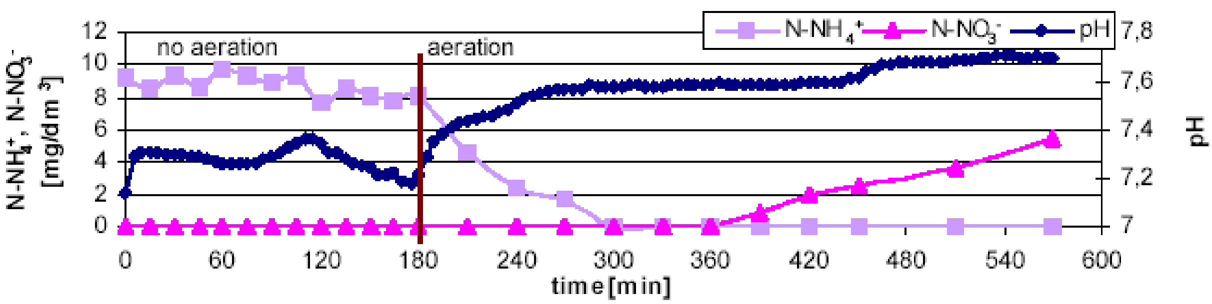
**A) Glucose concentration 750 mg/dm$^3$**




**B) Glucose concentration 1000 mg/dm$^3$**




**C) Glucose concentration 1500 mg/dm$^3$**




**D) Glucose concentration 2000 mg/dm$^3$**

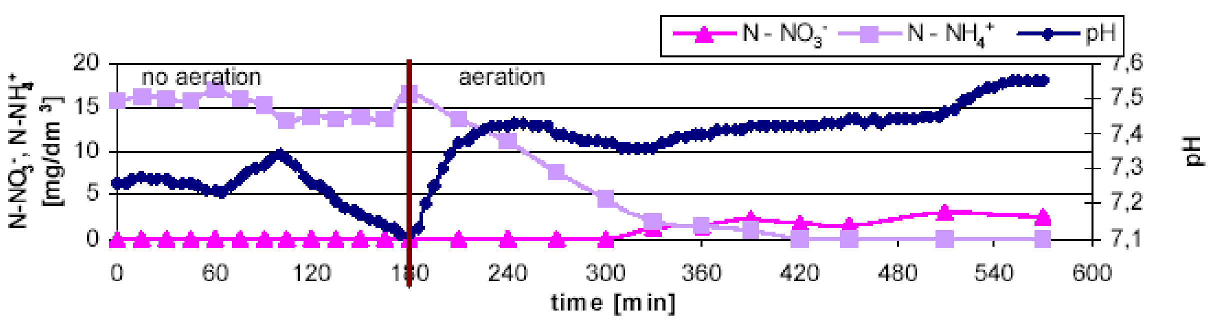
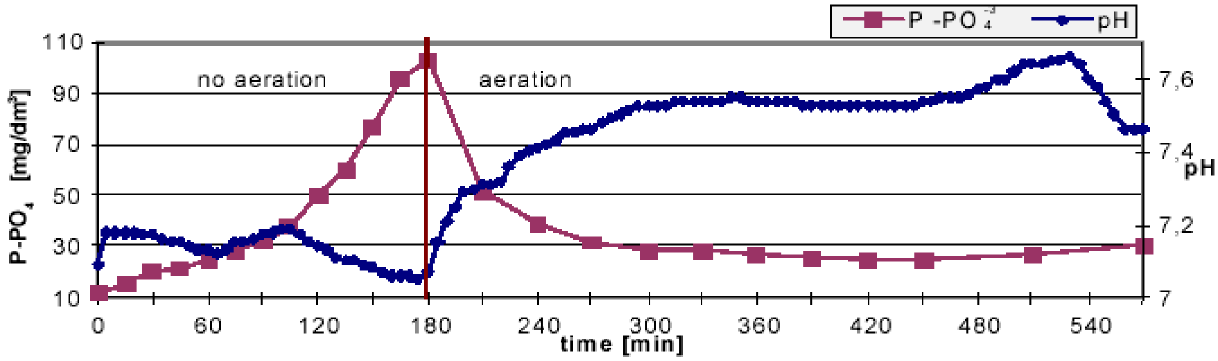
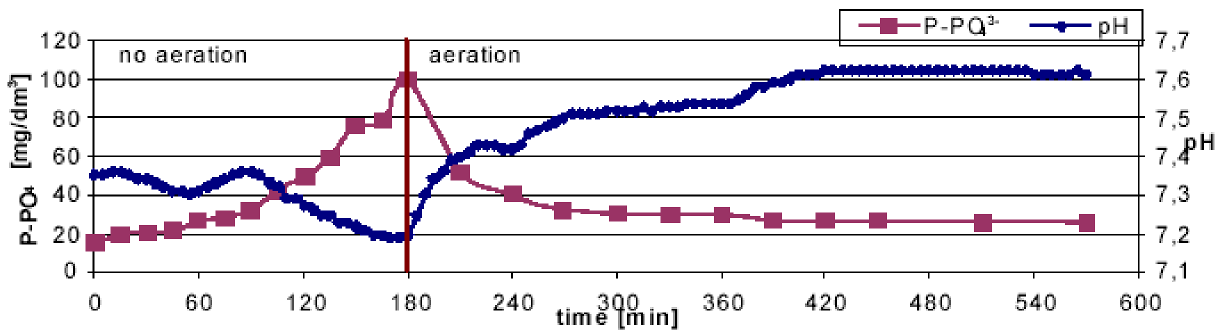



**Fig. 2.** N-NO$_3$, N-NH$_4$, and pH dependence on time.

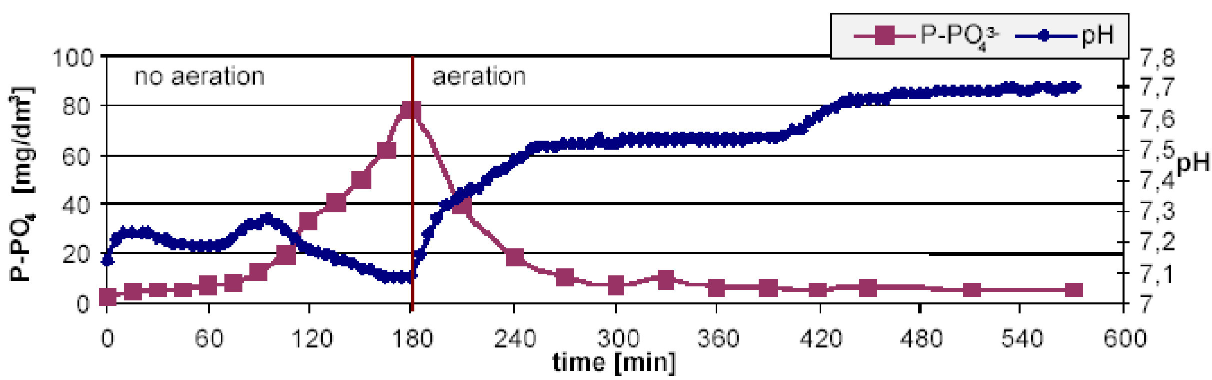
**A) Glucose content 750mg/dm$^3$**




**B) Glucose content 1000mg/dm$^3$**




**C) Glucose content 1500mg/dm$^3$**




**D) Glucose content 2000mg/dm$^3$**

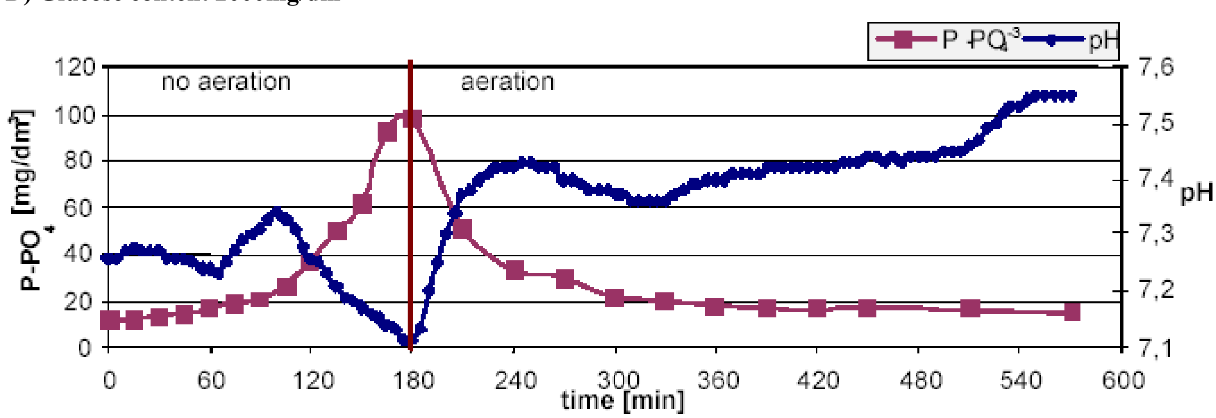



**Fig. 3.** Phosphates concentration and pH changes with time

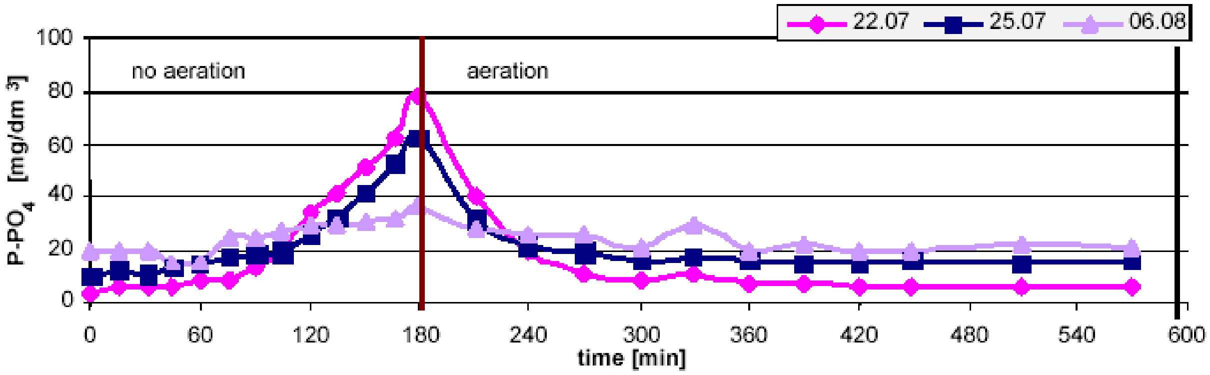



**Fig.4.** Phosphates concentration changes with time

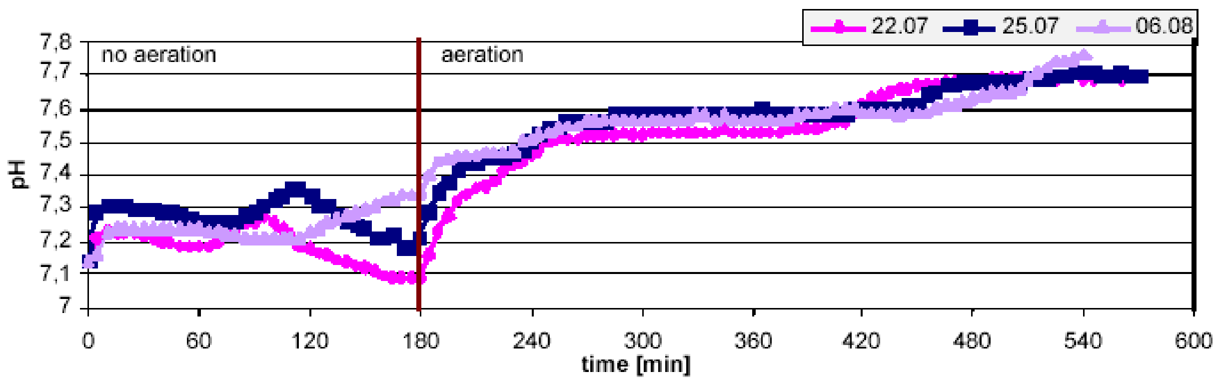



**Fig.5.** pH changes with time

Further, we have tried to compare the pH changes with changes of other parameters, conductivity and redox potential.

In Fig. 6 there are compared curves for pH and conductivity.

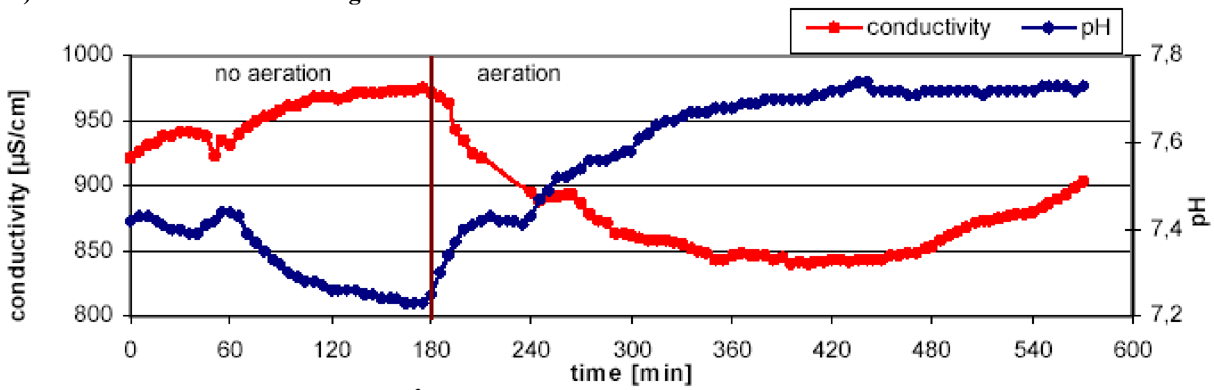
It is obvious that conductivity depends on the concentration of all types of ions and this is reflected in its mean value. However, it is clearly visible that both curves seemed to be a mirror reflection of each other. This suggests that the change of conductivity is proportional to the change of $H^+$ ions concentration.

In Fig.7 the relations of pH and redox potential are compared.

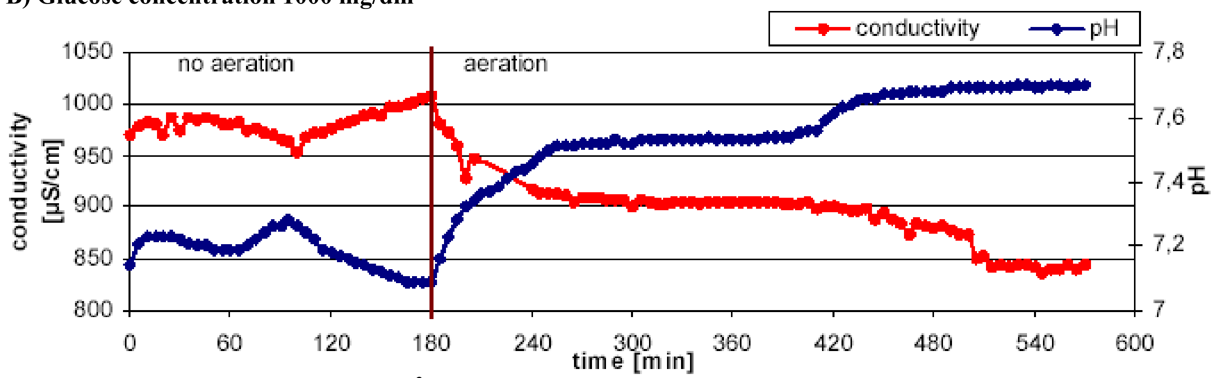
On redox curve there are characteristic two break points in non aerated phase.

The first collapse point on redox curve appears at the same point as the minimum on pH curve and the second collapse point relates to the maximum on pH curve. This is clearly visible in each case. At the end of anaerobic phase both curves have minima.

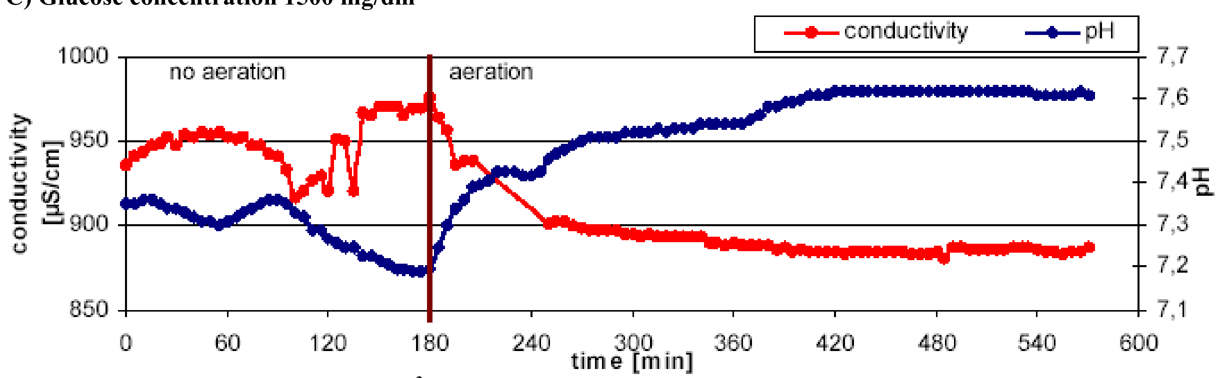
**A) Glucose concentration 750 mg/dm$^3$**




**B) Glucose concentration 1000 mg/dm$^3$**




**C) Glucose concentration 1500 mg/dm$^3$**




**D) Glucose concentration 2000 mg/dm$^3$**

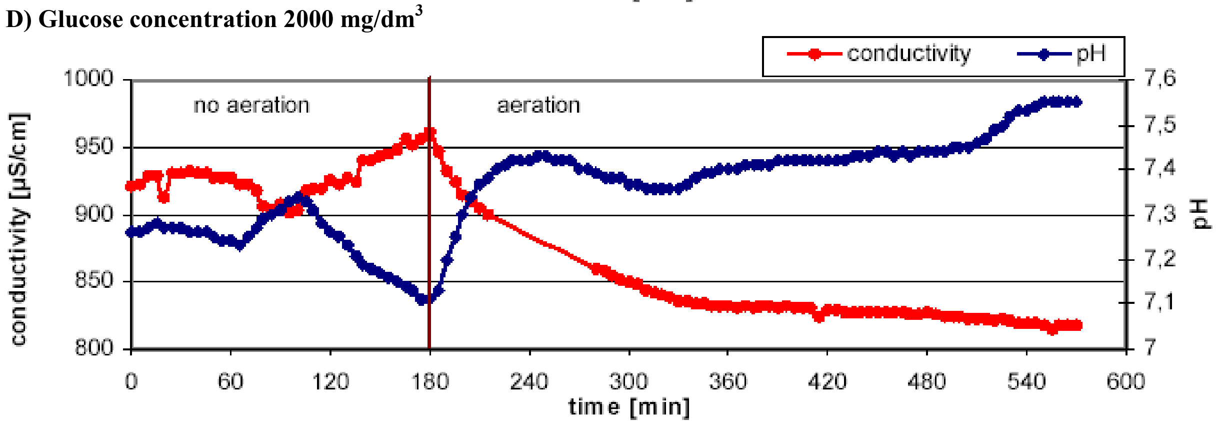



**Fig. 6.** Conductivity and pH dependence on time

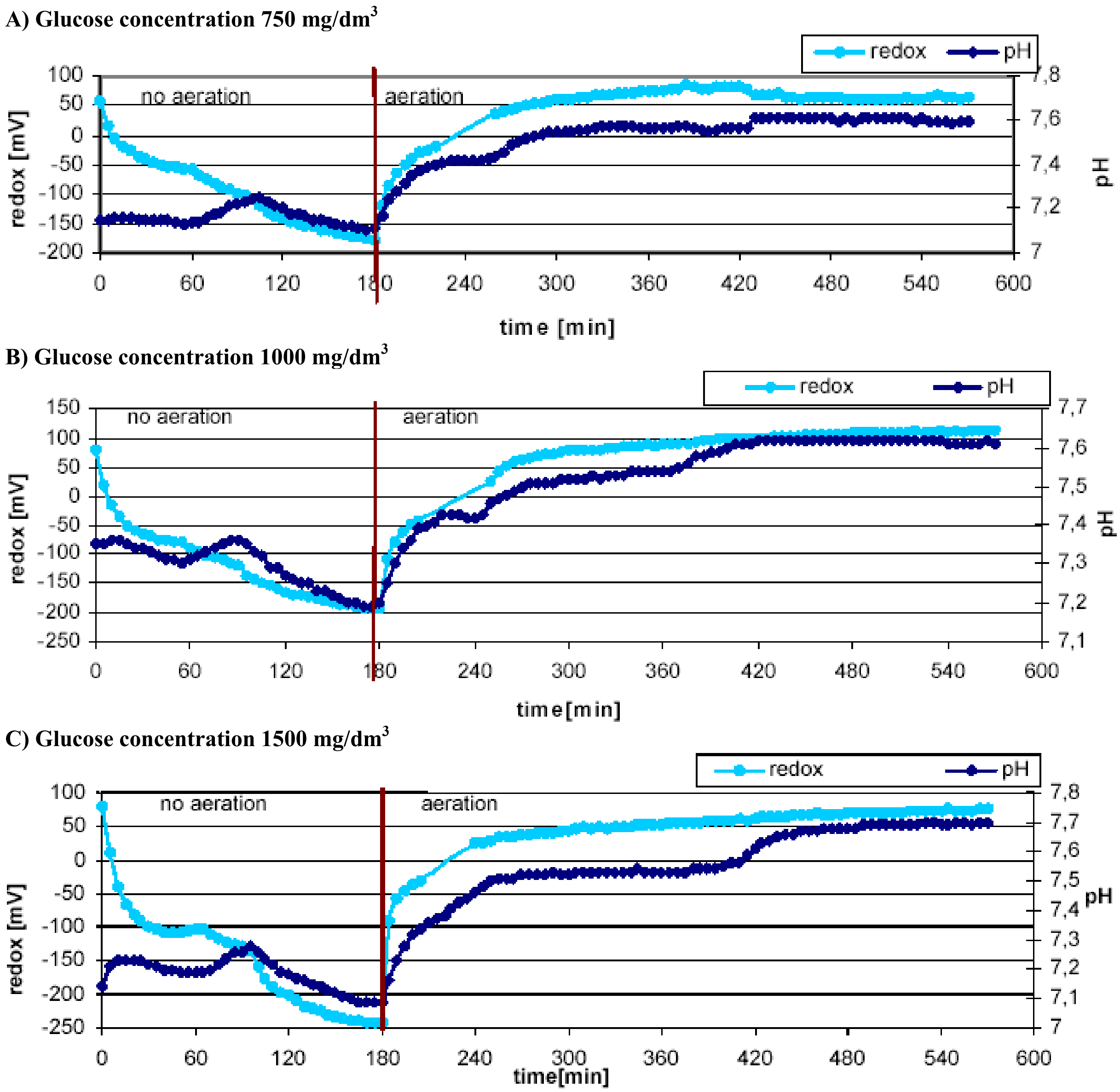



**Fig. 7.** Potential redox and pH changes with time

Usually, redox potential changes are attributed to transformations of nitrogenous compounds during process. The fluctuations of this parameter can also be applied in a control system for bioreactor with alternate denitrification (Czerwionka and all.). Analysing the shape of redox curves, and the interpretation by other scientists, one can expect that denitrification process should proceed in these experiments. However, this was impossible as the concentration of nitrates was zero during this phase of the process (0 – 180 min).

When analyzing our results it is hard to find the correlation of redox and $NH_4$-N or $NO_3$-N concentrations.

On the basis of other results (not presented here) it can be stated that much easier is to correlate the redox potential with $PO_4$-P, Dziecielska et. al.) and pH curves (Fig.7)

## CONCLUSIONS

For all processes which run without any disturbances the pH curves are very similar and characteristic minima and maxima in the anoxic/anaerobic phase are observed. The pH curves show very strong correlations with $PO_4$-P curves and are a regular reflection of the conductance-time relationships. The correlations were not found with nitrogenous compounds concentration changes as well, as with COD reduction.

In the aerobic region the pH curve does not show any visible correlations with other parameters, as it is in the anoxic/anaerobic phase. However, the more important is control of the process during these two phases, which decide about de-phosphatation and de-nitrification and may affect the development of filamentous growth.

In cases when for any reason the process is disturbed e.g. as presented in figure 4, where phosphorus release is going not properly, the pH curve is different from presented earlier. This makes a chance to exploit the pH measurements for the control of the process and it can help to learn immediately about disturbances in the process. If it is realistic it will be known after further investigations. For example, the experiments should be performed at conditions where denitrification also proceeds.

However, it has been found that when substrate was saccharose or starch instead of glucose, the pH curves shape was different. It should be also underlined that in real wastewater reactor the changes of all parameters are not so sharp as in the case of model wastewater. Besides, usually in the anaerobic phase pH rises and after a certain time of aeration pH decreases, accompanying to the decrease of $NH_4$ –N and increase of $NO_3$ –N. The repeatable changes of pH can be used for the following the process run, however, the results obtained for model wastewater show that process is more complicated than it seems from observations of real wastewater treatment. Thus, the experiments with model wastewater should be continued.

REFERENCES

Czerwionka K., and Geneja M., (2002). Application of redox potential measurement for control of alternate denitrification process in activated sludge chamber. *Proceedings of the I International Scientific and Technical Conference on Technology, Automation and Control of Wastewater and Drinking Water Systems, TiASWiK'02, p.141-146.*

Dziecielska D. and Jakusz G., (2004). Poszukiwanie korelacji między parametrami mierzonymi podczas oczyszczania ścieków zawierających węglowodany w komorach SBR z zastosowaniem osadów o różnych właściwościach sedymentacyjnych. *MSc thesis, Gdańsk University of Technology, Chemical Faculty, Gdańsk.*

Mędrzycka K., Tomczak-Wandzel R. And Cytawa S., (2002). Indirect determination of nitrogen removal from wastewater in biological treatment plants. . *Proceedings of the I International Scientific and Technical Conference on Technology, Automation and Control of Wastewater and Drinking Water Systems, TiASWiK'02, p.137-140.*

Podedworna J., (1999). Potencjał redox a ocena przebiegu oczyszczania ścieków w reaktorze SBR w świetle badań własnych. *Gaz, Woda i Technika Sanitarna, 2/1999, p.53-57.*