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A new synthetic polymers used in removal of pollutants from industrial effluents

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ABSTRACT

Chemical products synthesised using polymer waste have a great significance in industry. Chemical modifications of this type of waste make it possible to obtain products having new properties and at the same time to decrease the amount of usually dangerous waste in the environment. The products can be used in the processes reducing environmental micro-pollutants and in particular in wastewater treatment processes. There are more and more possibilities to use new synthetic polymers in industrial effluents treatment due to dynamic development of the technology of water and sewage treatment. Besides, technological changes of production processes make it necessary to carry out research on new polymers used in the processes of industrial effluents treatment. Despite the fact that in wastewater treatment technologies small amounts of organic polyelectrolytes are used, their global consumption is still quite big. A new generation of chemical products: flocculants synthesised from polymer waste ware used in coal mine pit waters treatment with good results. In the chemical modification of polystyrene waste as well as of post-production waste of phenol–formaldehyde resins, the products of specific flocculation properties and reducing the indicators of macro and micro-pollutants in industrial effluents were obtained. The products appeared to be effective flocculants supporting the coagulation process of coal mine pit waters.

Keywords: New synthetic polymers; Industrial effluents; Wastewater treatment

1. Introduction

The interest in new materials and various solutions aiming at fastening wastewater treatment processes increases due to a growing demand for water. Besides, the state of water purity gets worse and there are increasing requirements concerning the quality of water used in industry. Therefore, economical water management and using the same water several times have become a necessity. Wastewater and water pollution in industry can be in the form of suspensions or solutions, including colloidal solutions, usually of

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negative charge. The frequently used coagulation process involves the use of supportive agents (flocculants). Coagulation depends on numerous parameters, such as physicochemical composition, temperature of wastewater, a type and dose of the coagulant, a type of the process supporting agents as well as hydraulic and other parameters. Coagulation is a complex process, but it is possible to optimise the parameters in order to increase its efficiency [1–4].

Together with an increase in the concentration of organic compounds, nitrogen and phosphorus compounds as well as heavy metals in wastewater both chemical and biological methods are used in parallel in order to decrease the concentration of pollutants in industrial effluents discharged to the receiving water. Chemical wastewater treatment by means of metal salts (Fe and Al) increases the amount of insoluble pollutants released from sewage which are in different state of dispersion [5–7]. In the sewage coagulation process, flocculants (polyelectrolytes) [8–16] are used together with aluminium sulphate and iron or calcium salts in order to support the process. Modernisation of wastewater treatment technology or water treatment and appropriate selection of a coagulant and flocculent often have an impact on cost reduction and lead to some significant improvement of the quality of wastewater.

One of the technologies that have environmental loading connected with sewage is the technologies of coal mining and dressing. This is strictly connected with creating two groups of sewage: pit waters and post-production effluents from coal mining and dressing [5]. Most of pit waters are formed in the Silesian Voivodeship, Poland, and their major pollution is high salinity [5]. Post-production effluents are created in the process of hydraulic transport and hydro-classification of coal. Their amount is significantly smaller but they are also loaded with suspensions to a great extent.

Currently in Poland, different treatment methods are used for this type of wastewater, e.g. not much salinated pit waters are used in the industry for wet gas dedusting, hydrotransport and maintenance of greenery on the premises of a coal mine after pretreatment (coagulation with aeration, sedimentation and filtration of the suspensions, and in the final stage, UV rays disinfection). Hydrotechnical and other methods are used for pit waters disposal. Post-production effluents are treated usually by sedimentation in big natural water reservoirs. Some new, economically beneficial solutions should be searched for due to the fact that the problem of waste water from coal mines is quite complex. In the case of salinity of pit waters of up to ten grams per litre, membrane methods are economically more advantageous. Electrodialysis is most frequently used for water treatment with salinity in the range of 10 g/L or reverse osmosis with low salinity. In Poland, there has also been developed the technology of using highly saline waters for the production of chlorine gas with the membrane method. The removal of pollutants in post-production wastewater in mining is also possible by clarifying in settlers where, previously, there are added polyelectrolytes e.g. polyacrylamide. Therefore, to meet this need, the research in order to use synthesised polymers from polystyrene waste and phenol–formaldehyde resins in the coagulation process has been carried out. Preliminary research proved that the polyelectrolytes could be used successfully in the coagulation process of mine wastewater treatment [17,18]. In this article, the analysis of the results of the research on using a selected group of synthesised polyelectrolytes from polymer waste as the agents supporting one of the stages of pit water treatment—coagulation in two coal mines has been presented.

2. Materials and research methods

2.1. Research substrates

The following substrates were used in the research: a coagulant, newly synthesised polyelectrolytes, commercial polyelectrolyte and pit waters from coalmines KWK1 and KWK2. In the research on the selected industrial waters treatment, aluminium sulphate was used as a coagulant $(Al_2SO_4)_3 \cdot 18H_2O$ pure for analysis, which is often used to eliminate colloidal pollutants in technological processes of water and wastewater treatment. On the basis of the results of the research carried out, it was found that the optimum dose of a coagulant for KWK1 pit water, respectively, for P1 and P2 was 50 mg/L and for P3 and P4 was 60 mg/L; for pit water KWK2, the optimum dose was 60 mg/L for P1 and P2 and for P3 and P4 was 70 mg/L.

2.1.1. New synthetic polymers—flocculants

In the research on the change of the value of the indicators in coal mine pit waters, the polymers synthesised from polystyrene waste as well as from post-production phenol–formaldehyde resins (novolac resins) were singled out. The way of obtaining polyelectrolytes as well as the characteristics of new flocculants selected for the research are described in the author's monograph on eco-polyelectrolytes [19].

In the preliminary research, several dozens of new polyelectrolytes were examined; however, the following products: sodium salts—sulphonate derivative of polystyrene waste and phenol–formaldehyde resin, as well as amine derivatives of phenol–formaldehyde resin made it possible to obtain the best effects of supporting the coagulation process of sewage and industrial waters [20].

The optimum doses of polyelectrolytes: sulphonate derivative of polystyrene waste (SPP), sulphonate derivative of novolac resins (PS-N-SE, PS-N-NS, PS-N-T) and amine derivatives of novolac resins (PS-N-SE, PS-N-NS, PS-N-T) were several dozen times smaller than the doses of a coagulant (0.1–2.5 mg/dm^3), similar to using commercial polyelectrolyte Praestol 2515 (0.5 and 1.0 mg/dm^3).

Polystyrene and novolac sulphonate derivatives contain sulphonic groups—SO_3H and amine derivatives—NH_2 groups.

2.1.2. Commercial polyelectrolyte—Praestol 2515

In the research on supporting the coagulation process, Praestol 2515 was selected from commercial polyelectrolytes. Due to its anion character, it was acknowledged that it is a polyelectrolyte, and its flocculation activity can be compared to the activity of newly synthesised polyelectrolytes, modified polystyrene waste and formaldehyde resins which also include active groups: sulphonic—SO_3H, amine—NH_2.

Table 1
Results of the physicochemical analysis of pit water from KWK1 coal mine

Indicator type	Value range*
Turbidity, NTU	115.0–132.0
pH	6.58–7.61
5 d biochemical oxygen demand, mg O_2/L	2.1–3.8
Oxygen consumption: dichromate method, mg O_2/L	35.6–91.9
Oxygen consumption, mg O_2/L	6.5–10.4
Ether extract, mg/L	2.0–2.5
Ammonia nitrogen, mg/L	0.62–2.47
Sulphates, mg SO_4/L	1,350.0–1,608.0
Chlorides, mg Cl/L	1,476.0–2,197.0
Total hardness, mg/L	1,706.0–2,507.5
Solvated parts: total amount, mg/L	4,410–6,910
Suspension: total amount, mg/L	30.8–50.6

*The most common value range.

Table 2
Results of the physicochemical analysis of pit water from KWK2 coal mine

Indicator type	Unit	Value range*
Turbidity	NTU	160.0–190.0
pH	–	7.90–8.20
5 d biochemical oxygen demand	mg O_2/L	2.6–6.2
Oxygen consumption: dichromate method	mg O_2/L	35.5–68.6
Oxygen consumption	mg O_2/L	5.9–11.5
Ether extract	mg/L	7.5–45.90
Ammonia nitrogen	mg/L	0.35–1.31
Sulphates	mg SO_4/L	41.0–594.0
Chlorides	mg Cl/L	3,196.0–6,071.0
Total hardness	mg/L	2,746.7–3,876.6
Solvated parts: total amount	mg/L	6,412.0–1,015.0
Suspension: total amount	mg/L	21.2–52.0

*The most common value range.

This flocculent is totally soluble in water, it is odour-free, it is characterised by density in the range from 0.6 to 0.75 g/cm^3 and viscosity of about 400 mPa*s (0.5% in distilled water). This agent is efficient in the pH range 3–13. Praestol 2515 is a commercial polyelectrolyte on the basis of polyacrylamide, it is provided as a white powder.

2.1.3. Characteristics of the examined waste water and industrial water

Pit waters from two coal mines belonging to Katowice Coal Holding (Tables 1 and 2) were used in the research. The above-mentioned waters were singled out for the research due to their physicochemical properties: i.e. a high content of sulphates and chlorides, the content of which in wastewater should be reduced, which is strictly connected with water supply and sewage effluent disposal contents.

The samples of pit waters were taken on the day of the research after 30 min sedimentation in order to remove settleable solids. Then, after decantation, the physicochemical properties of the examined sewage were designated (considering the selected pollution indicators).

2.2. The way of conducting technological research of coal mine pit water treatment

The research on the coagulation process of pit waters with the use of a coagulant and polyelectrolytes was conducted according to the below patterns of technological systems (Figs. 1 and 2) and the commonly used methodology of coagulation process research.

Presented patterns of technological systems include as an example turbidity and pH measurements. The same technological systems were used in the examination of the other below-mentioned sewage pollution indicators. The methods of testing indicators were presented in the monograph—appendix 1 [19].

The optimum dose of coagulant was determined as the minimum amount necessary to obtain maximum turbidity reduction after the coagulation and sedimentation processes.

Then, the minimum dose of particular newly synthesised flocculants and commercial flocculent was determined also in order to obtain maximum turbidity reduction.

The research into the flocculation process of pit waters was conducted using 1% solution of the coagulant and 0.1 and 0.01% solution of newly synthesised flocculants. To carry out the process, a mechanical stirrer was used. After adding the coagulant, the mixture was stirred for 1 min at the speed of 300 rpm and for 15 min at the speed of 90 rpm and, then, it was left to stand for 30 min. After sedimentation, the parameters were measured. After determining the dose of the coagulant, the dose of the flocculant was established. The way of conducting the research into the flocculation process was discussed in the publications [13,14].

Each turbidity measurement was done seven times. Turbidity was designated using Turb 550 IR device providing quick and reliable measurement. The measurement method applied in the device is compliant to ISO 7027/DIN 27027 standards, it is also compliant to the recommendations of US EPA.

The designation of the other physicochemical indicators of industrial effluents and waters was done in laboratories and according to the standards [19].

3. The use of newly synthesised polyelectrolytes in supporting the coagulation process of coal mine pit waters

The research aimed at establishing the influence of newly synthesised polymers as flocculants in the coagulation process on the change of the value of selected indicators of the examined coal mine pit waters. The relation between the effects and the type of used polymers in the coagulation process was to be determined. The theoretical basis and preliminary research confirm that there is a possibility to obtain polyelectrolytes of equally effective performance in the sewage coagulation process in comparison with commercial polymers synthesised on a great scale on the basis of polymers and acrylamide copolymers which is connected with high production costs.

In order to examine the influence of the selected group of new polyelectrolytes on selected indicators in coal mine pit waters (KWK1 and KWK2), firstly, the optimum dosages of a coagulant—aluminium sulphate were determined and then, respectively, the dosages of polyelectrolytes were determined. Four samples of pit waters sewage were taken in the research on supporting the coagulation process with newly synthesised polyelectrolytes, respectively, from KWK1 and KWK2 coal mines.

The analysis of the research proved that comparable effects of eliminating turbidity in the coagulation process of pit waters KWK1 were obtained in all the examined samples (Figs. 3–6).

Comparable results of reduction in turbidity were obtained also in case of the analysis of the results of four samples of mine water KWK2 (Figs. 7–10).

The analysis of the research proved that the best effects of eliminating turbidity in the coagulation

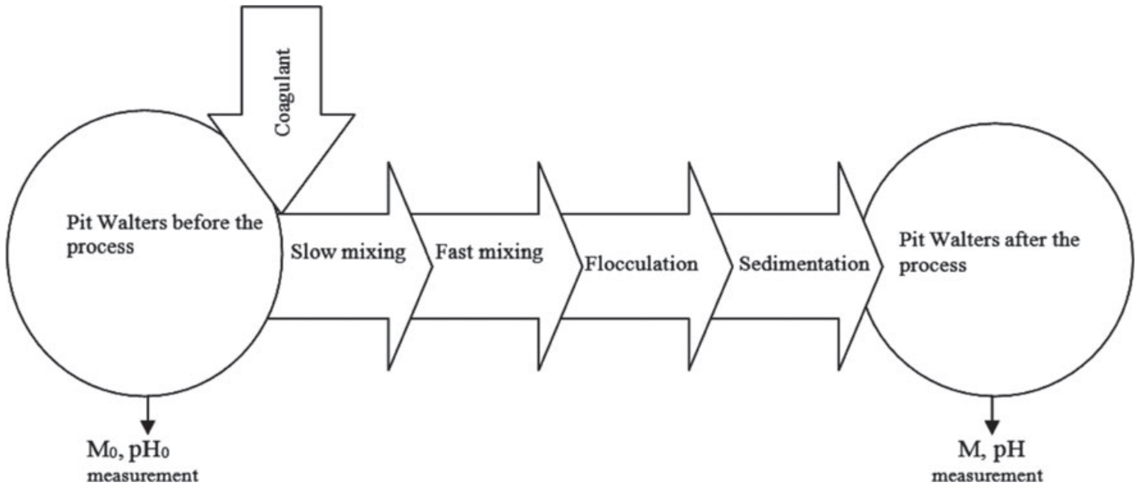

Fig. 1. A diagram of the technological system used in the examination of pit waters KWK1 and KWK2 coagulation process with the use of a coagulant. M_0—turbidity before the coagulation process, pH_0—reaction before the coagulation process, M—turbidity after the coagulation process, pH—reaction after the coagulation process.

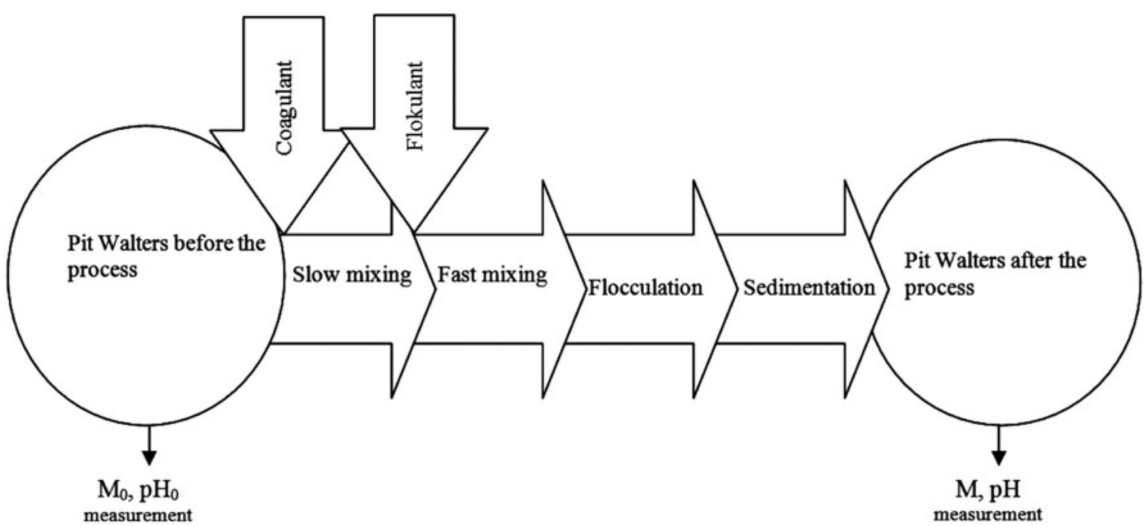

Fig. 2. A diagram of the technological system used in the examination of the pit waters coagulation process with the use of a coagulant and flocculent. M_0—turbidity before the coagulation process, pH_0—reaction before the coagulation process, M—turbidity after the coagulation process, pH—reaction before the coagulation process.

process of pit waters KWK1 and KWK2 were observed when a coagulant and polyelectrolyte PSP or commercial flocculent were used. In almost all the trials turbidity, reduction was above 90%, and in the case of other polyelectrolytes used in the coagulation process KWK1 and KWK2 turbidity reduction was also relatively significant and it was over 80%.

The analysis of the research of other sewage and industrial waters indicators carried out according to the current standards proved that using chemically modified polymer waste, both sodium salts—sulphonate derivative of polystyrene waste and phenol–formaldehyde resins waste, as well as amine derivatives of phenol–formaldehyde resins leads to a significant decrease in almost all analysed indicators, although the observed decrease was not identical for all the flocculants (Figs. 11 and 12).

The reductions of the value of chlorides, sulphates, ammonia nitrogen, 5 d biochemical oxygen demand, oxygen consumption: the dichromate method, oxygen consumption, solvated parts and suspension were especially important and noticeable. On the basis of

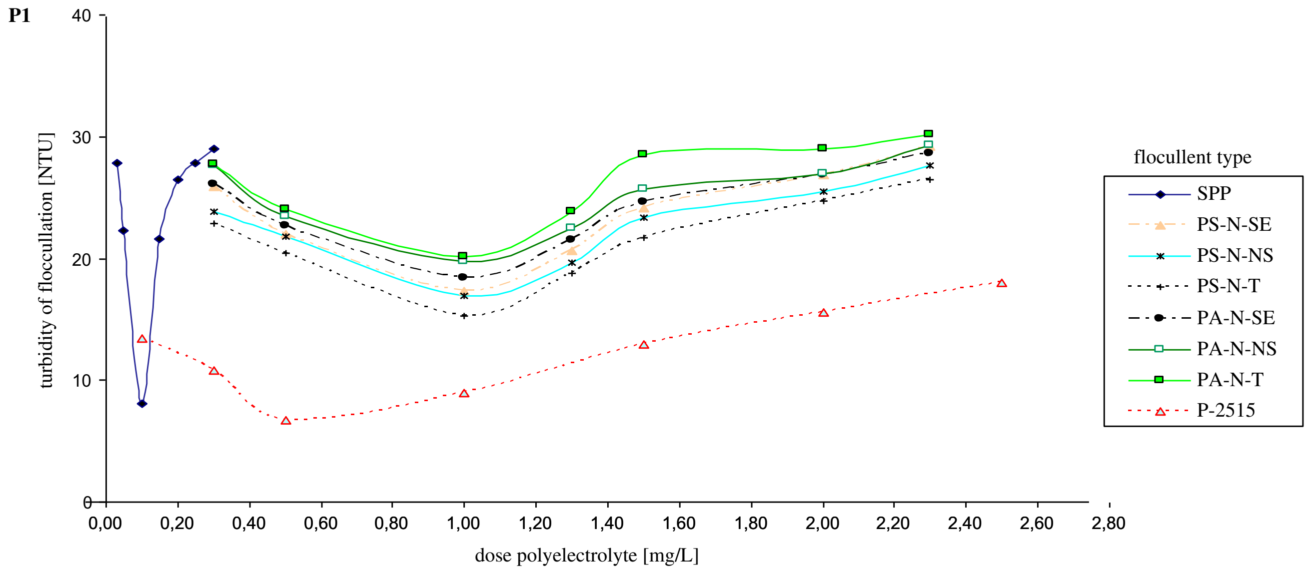

Fig. 3. The changes of turbidity depending on the dose of polyelectrolytes applied in purification of mine water KWK1 (P1—M_0 = 120,5 NTU).

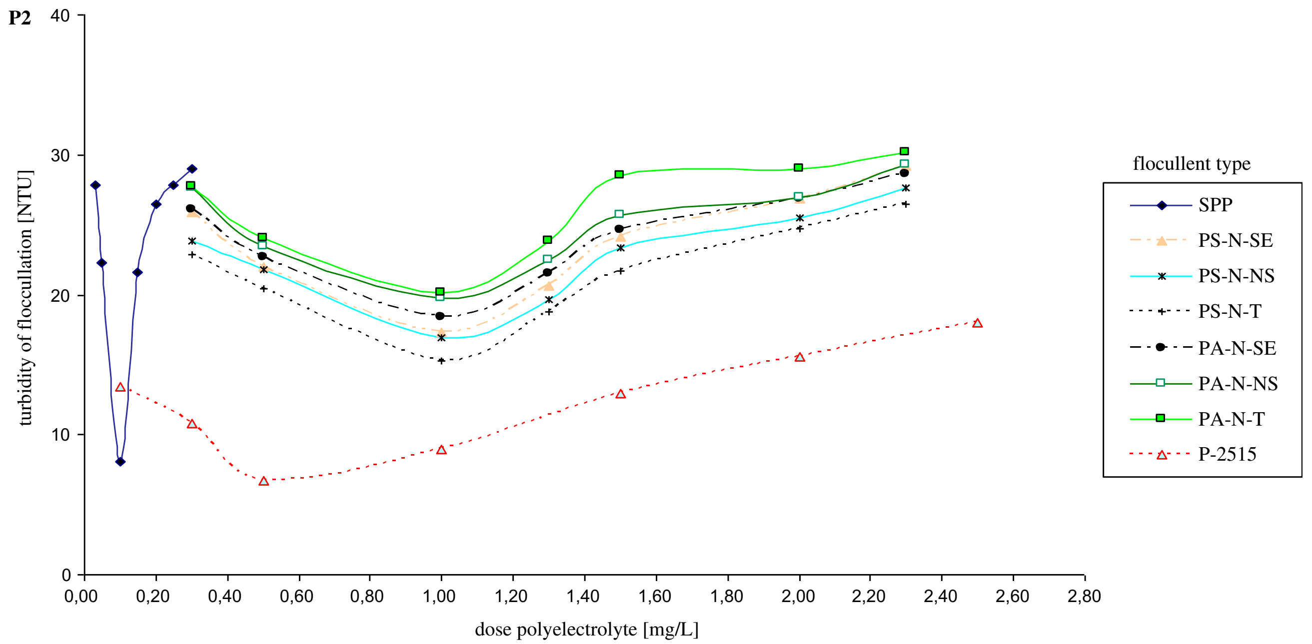

Fig. 4. The changes of turbidity depending on the dose of polyelectrolytes applied in purification of mine water KWK1 (P2—M_0 = 123 NTU).

the obtained results concerning the changes of values of pollution indicators of the analysed sewage and water after the coagulation process carried out with the use of a coagulant and chemically modified polymer materials waste, it can be said that comparable results of coal mine pit waters treatment were obtained concerning the examined polyelectrolytes, and in some cases, much better results were obtained than when using commercial polyelectrolyte. Usually, in the coagulation process there is not observed the effective removal of chlorides, sulphates and ammonia nitrogen, but the use of new polymers may bring

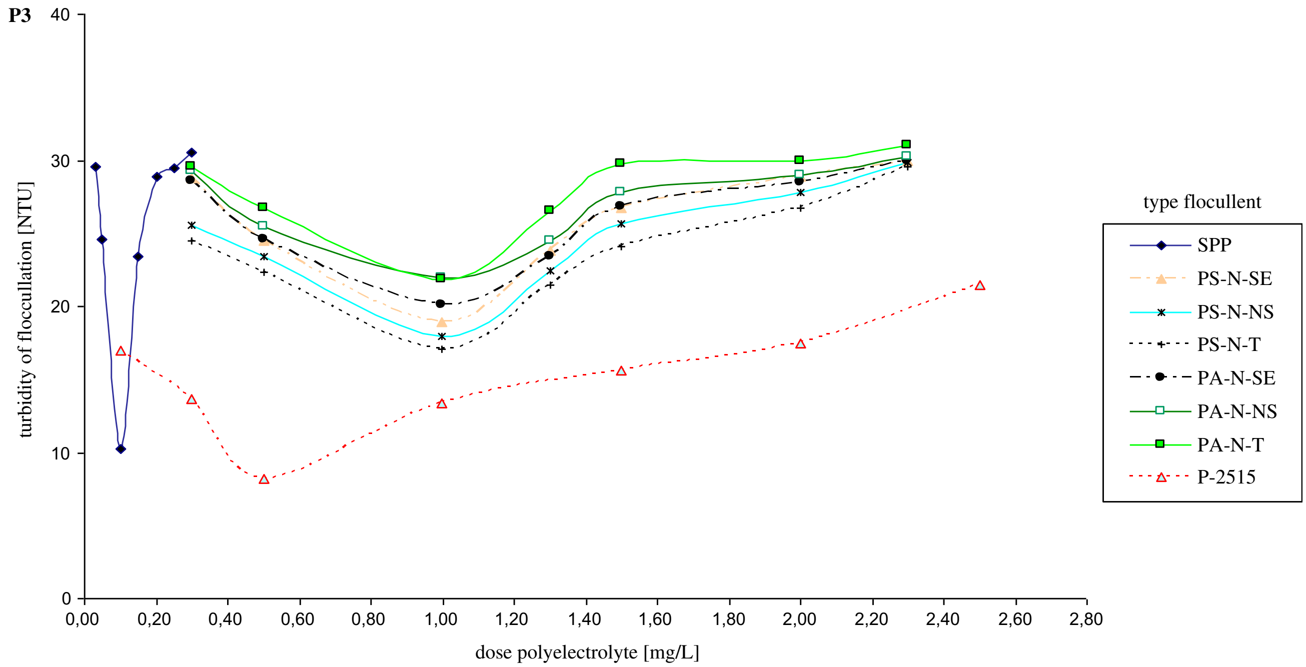

Fig. 5. The changes of turbidity depending on the dose of polyelectrolytes applied in purification of mine water KWK1 (P3—M_0 = 125,1 NTU).

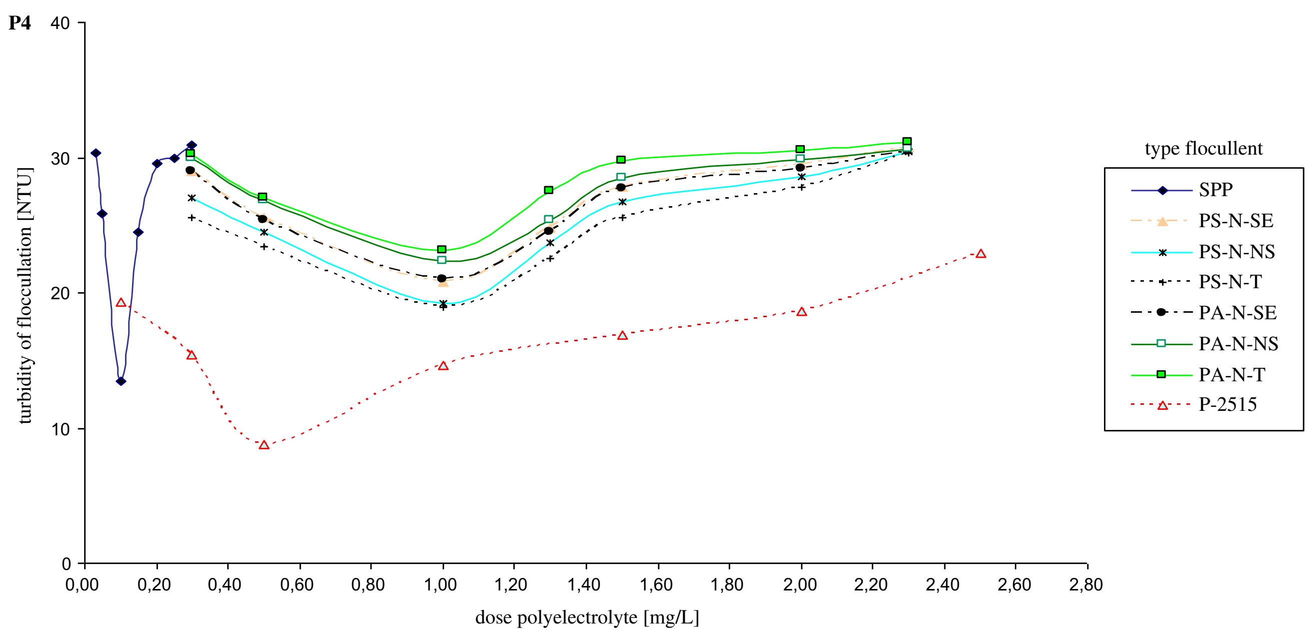

Fig. 6. The changes of turbidity depending on the dose of polyelectrolytes applied in purification of mine water KWK1 (P4—M_0 = 130,2 NTU).

about some reduction in these indicators, too. It is believed that ion exchange or occlusion take place. Some portions of the polymer, depending on pH, the chemical composition of the solution can be rolled up in the form of the bundle and their functional groups are not available and, therefore, changing the conditions is followed by the release and activation of the functional groups. It follows that the

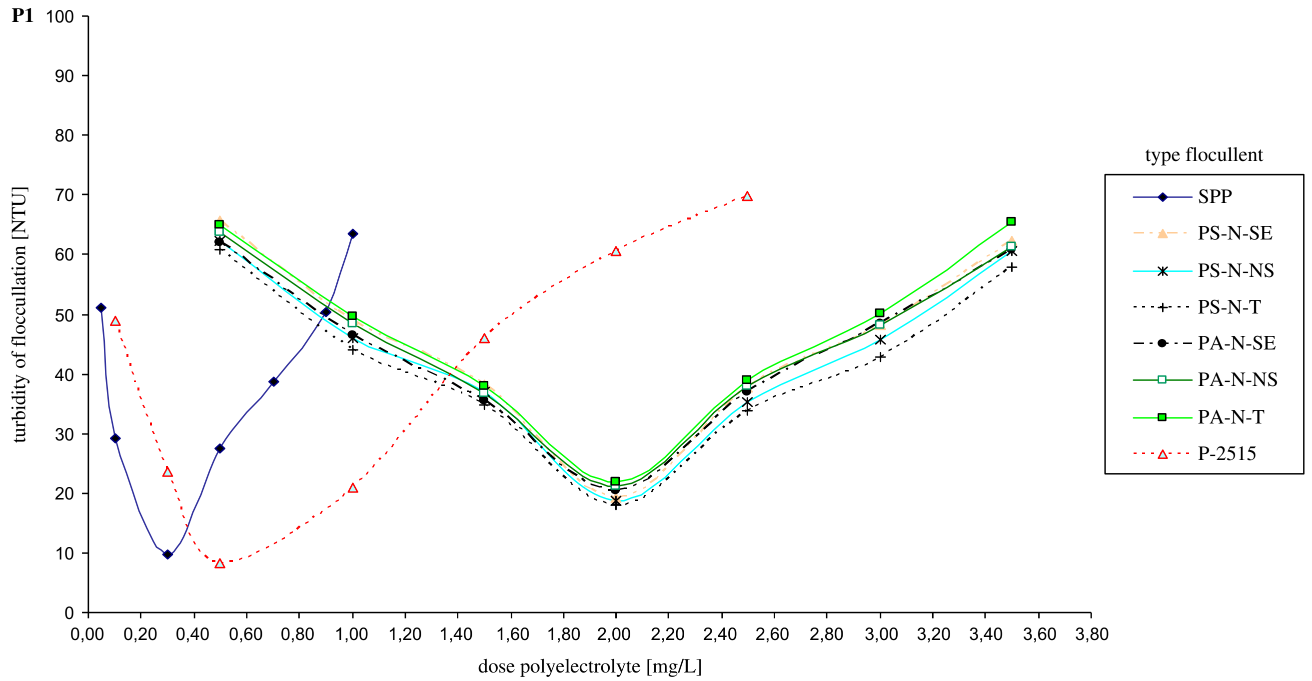

Fig. 7. The changes of turbidity depending on the dose of polyelectrolytes applied in purification of mine water KWK2 (P1—M_0 = 161,2 NTU).

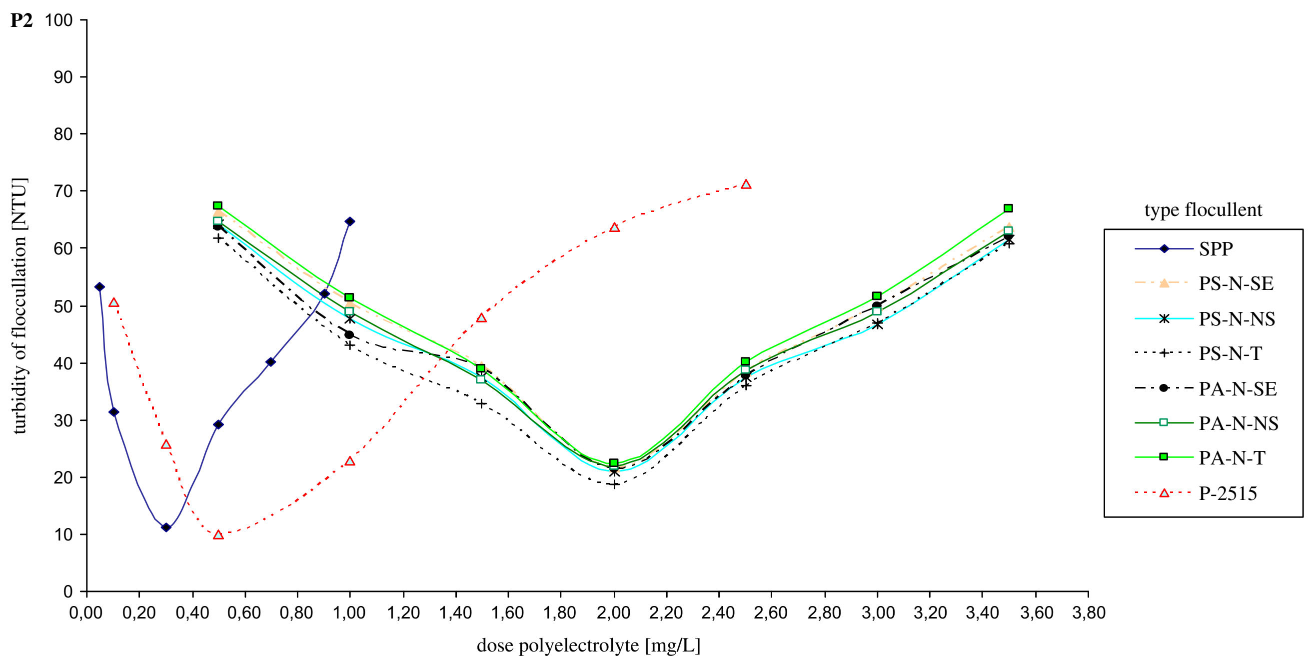

Fig. 8. The changes of turbidity depending on the dose of polyelectrolytes applied in purification of mine water KWK2 (P2—M_0 = 165,4 NTU).

polyelectrolyte structure is more complex and the mechanism of action requires more precise physico-chemical testing [21].

Also a decrease in pH value was observed as the result of using the examined flocculants in the flocculation process.

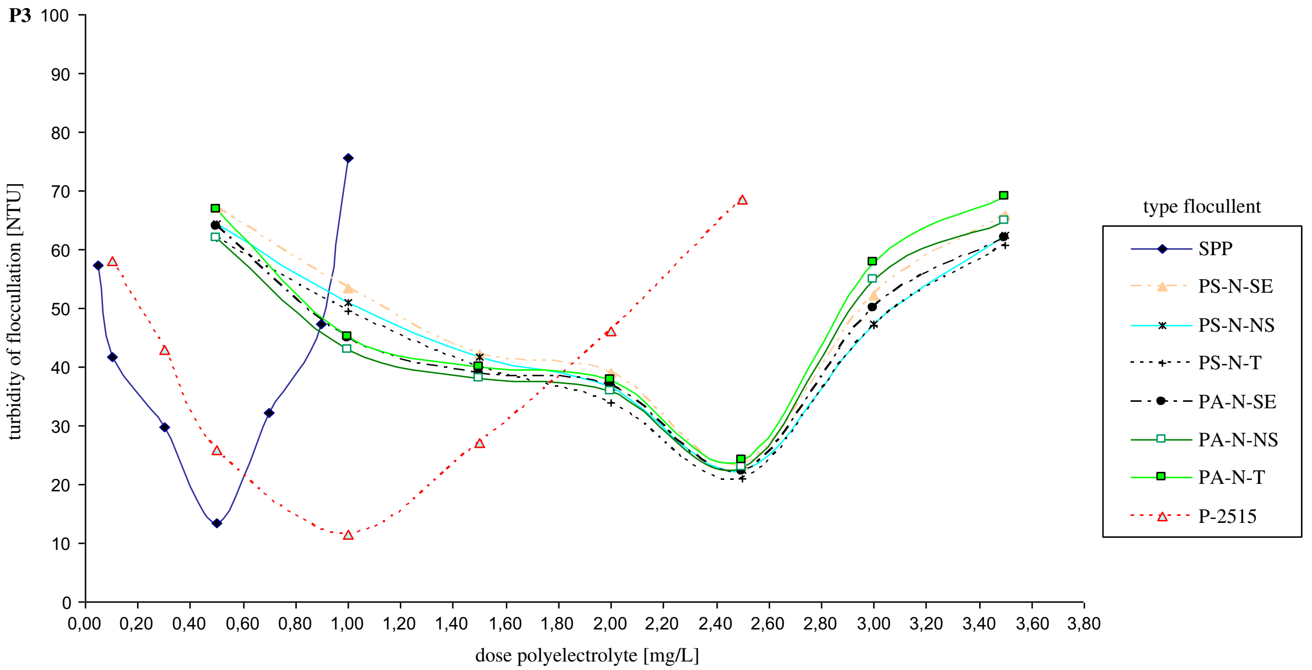

Fig. 9. The changes of turbidity depending on the dose of polyelectrolytes applied in purification of mine water KWK2 (P3—M_0 = 182,2 NTU).

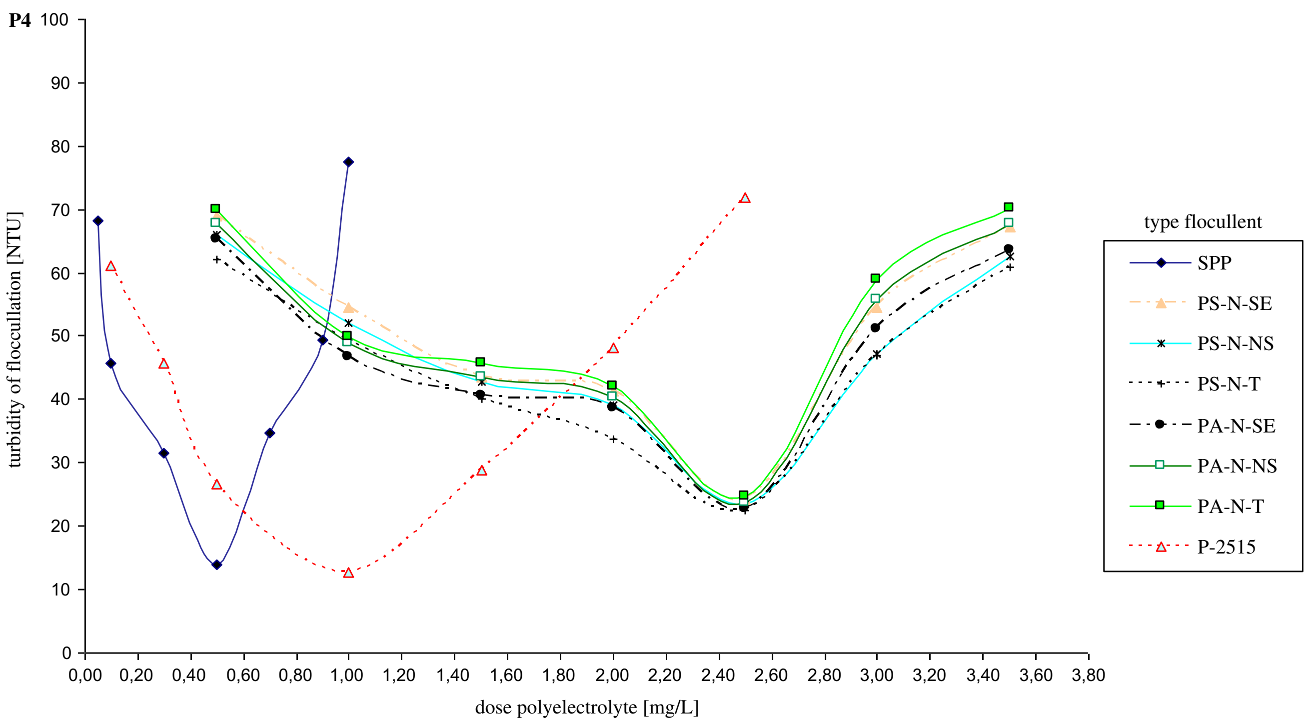

Fig. 10. The changes of turbidity depending on the dose of polyelectrolytes applied in purification of mine water KWK2 (P4—M_0 = 189,4 NTU).

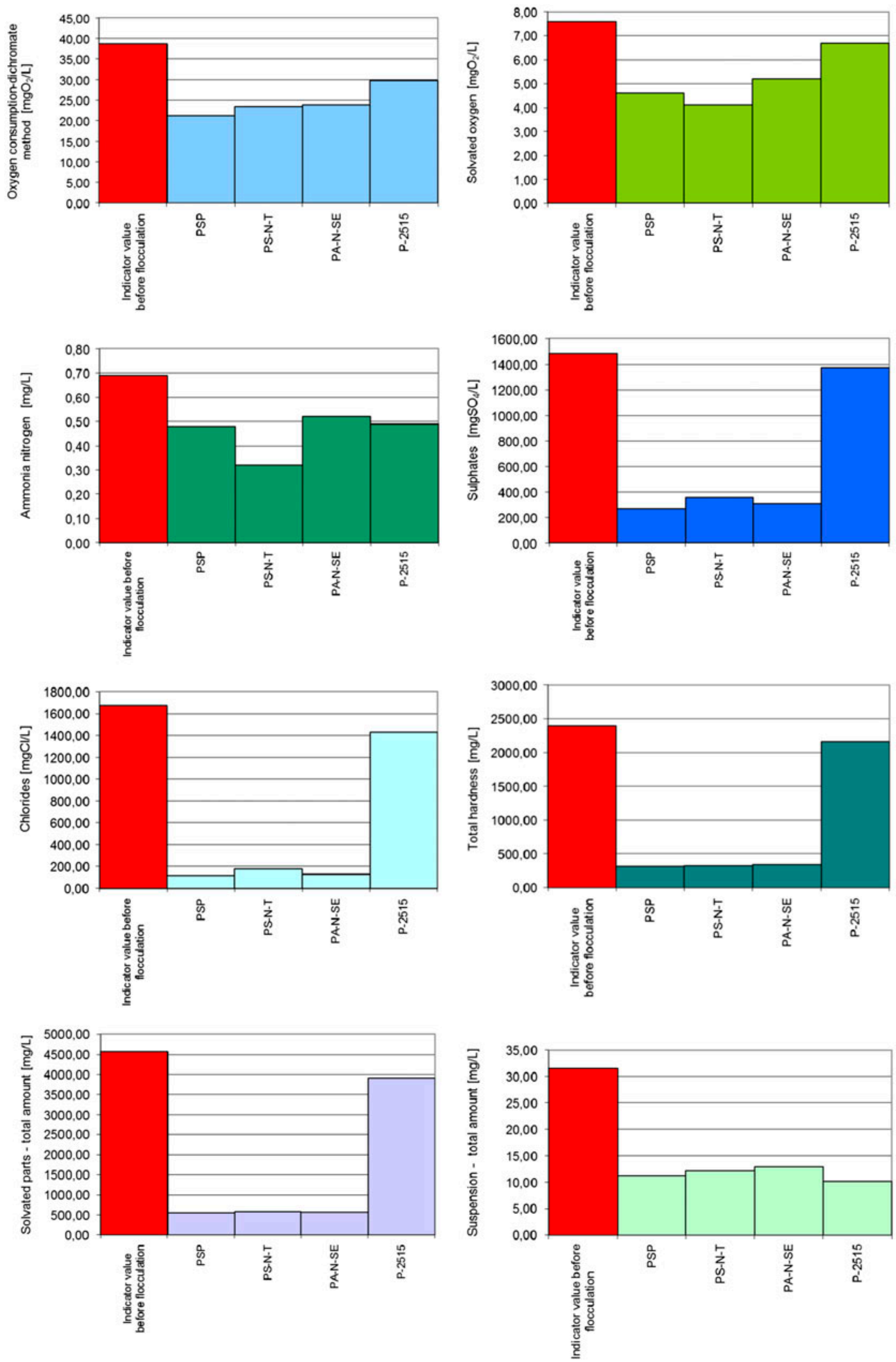

Fig. 11. The relation between the change of values of the selected pit water KWK1 indicators (P1—M_0 = 120,5 NTU) and the type of applied polyelectrolyte.

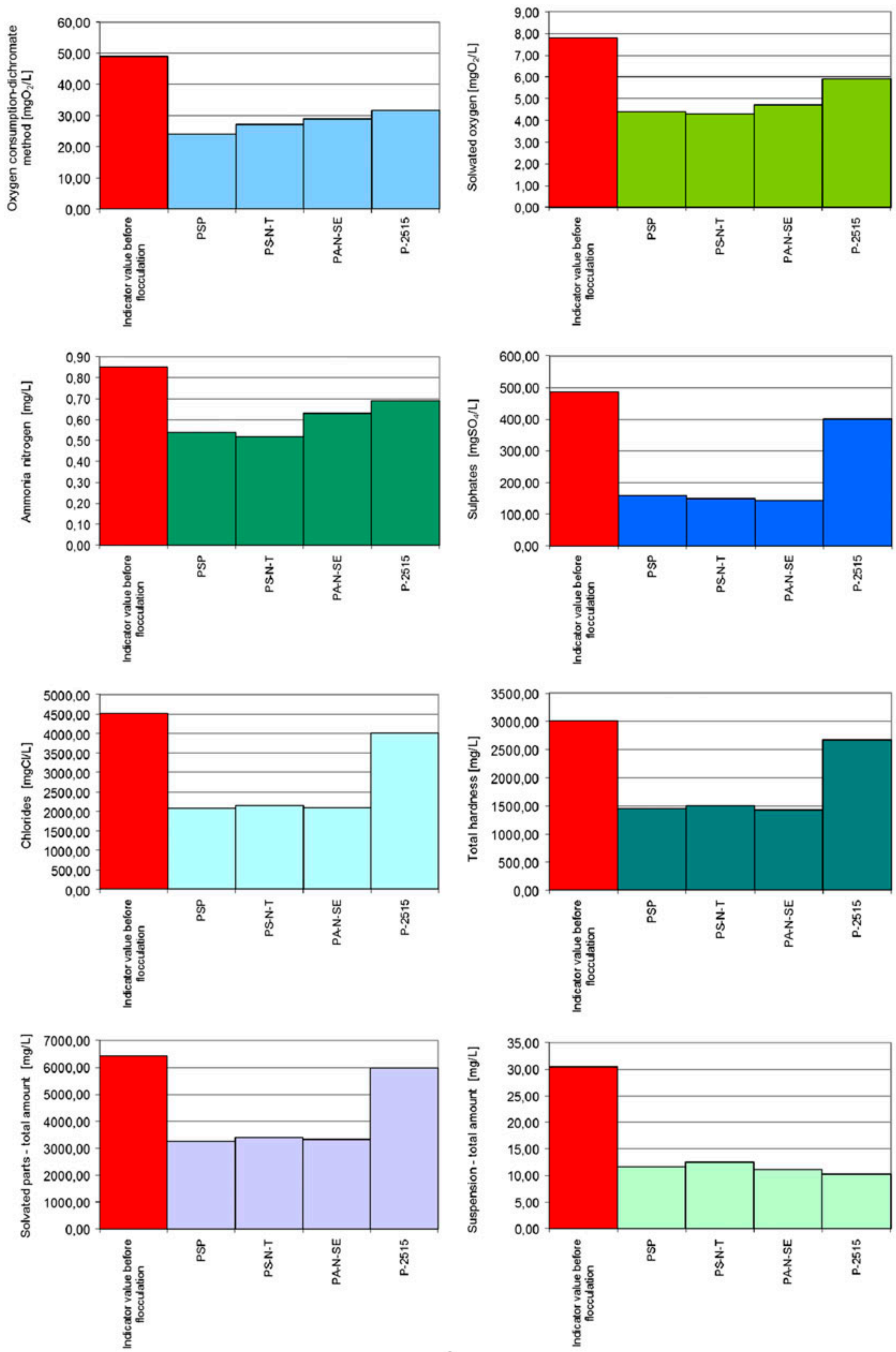

Fig. 12. The relation between the change of values of the selected pit water KWK2 indicators (P1—M_0 = 161,2 NTU) and the type of applied polyelectrolyte.

However, the examination of pH parameter of pit waters proved that the use of the coagulant and, then, flocculant in the coagulation process brought about the pH reduction, though, only in decimals.

4. Summary

Thanks to great improvement in industrial sewage and water treatment, we can limit the contamination of natural watercourses. However, despite such activities in some parts of watercourses still "dead," impaired wastewater drains are created. At present, more and more industrial plants are forced to rationalise water management. They are supposed mostly to use closed water circuits, which makes it necessary to search for new, effective methods of wastewater treatment so that the treated wastewater could be used for particular purposes in the plants. Coal mine industry contaminates the main river catchments of the Vistula and Odra rivers, among others, with other salinificated pit waters coming from several dozens of coal mines in Poland. Salt utilisation and the use is a very efficient method to eliminate the problem. Approximately 60% of load can be utilised in the scale of the whole of Poland. Also, many other methods are used, which are more beneficial from the economic point of view. It results from the research carried out that the flocculants synthesised from polymer waste supporting the water coagulation process can be effectively used in salinificated pit waters treatment. The new flocculants applied made it possible to reduce the examined pit water pollutants selected for examination in two coal mines even by 90%. In particluat, good results of the analyses were obtained as regards eliminating chlorides and sulphates which lead to the conclusion that they might be used in the treatment of wastewater created in coal mining and dressing.

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