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TRANSFORMATIONS OF NITROGEN AND PHOSPHORUS IN SOIL PLANTED WITH WILLOW IRRIGATED WITH WASTEWATER

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PRZEMIANY AZOTU I FOSFORU W GLEBIE NAWADNIANEJ ŚCIEKAMI PO DRUGIM STOPNIU OCZYSZCZANIA – POD UPRAWĄ WIERZBY

Celem pracy było określenie możliwości wykorzystania gleby organicznej w uprawie wierzby do oczyszczania ścieków z nadmiaru azotanów i fosforanów oraz określenie przydatności potencjału redoks do oceny przemian związków azotowych w badanej glebie. Wykazano przydatność gleby organicznej w uprawie wierzby w procesie oczyszczania ścieków w warunkach obiektu doświadczalnego „Hajdów". Wyznaczono również istotne zależności pomiędzy potencjałem oksydoredukcyjnym a przemianami azotu zachodzącymi w glebie nawadnianej ściekami po drugim stopniu oczyszczenia.

Summary

The objective of the study was to determine the possibility of using organic soil under willow for wastewater purification of excess nitrate and phosphates, and to estimate the applicability of redox potential for the assessment of transformation of nitrogen compounds in the soil under study. The study showed the suitability of organic soil and willow for wastewater purification under the conditions of the „Hajdów" experimental object. Also, significant relationships were shown between redox potential and nitrogen transformation occurring in soil irrigated with wastewater after 2[nd] stage of treatment.

INTRODUCTION

Wastewater, as well as organic and inorganic wastes infiltrating surface waters, ground waters and soils constitute a potential hazard not only to the functioning of ecosystems but also to human health [20].

Phosphates occur in municipal wastes at high concentrations. Conventional mechanical-biological treatment plants remove phosphorus compounds only at the rate of about 15%. Chemical transformation of phosphorus in water frequently leads to its precipitation and accumulation in bottom sediments. Phosphate ions are easily sorbed on the surface of suspensions and sediments.

Processes of nitrogen and phosphorus transformations between water and bottom sediments mainly depends on the oxygen conditions, temperature, reactions, redox potential, and the surface of bottom sediments [5].

The accession of Poland into the structures of the European Union imposes on us the obligation of draining wastewater to the ground and surface waters in accordance with the standards in force in the EU, i.e. in the case of nitrogen 15 g N m^{-3}.

Soil is the primary receiver of wastes generated in nature. Sewage and wastes treatment by means of soil and plants is the effect of complex processes – chemical, physicochemical, biochemical – taking place in the aeration and saturation zones. The use of wastewater for irrigation of muck soils and dried peats is worthy of recommendation.

In Poland root treatment plants began to appear and develop towards the end of the 70's of the last century, in the coastal region near the city of Gdańsk. In the years 1991–1993 successive objects of the type were established, in Wawrowo, Brzeziny, Golczewo, Rokitno, Małyszyn and Gralewo, among other places [12]. Currently in Poland there are about 300 sewage treatment plants of this type in operation, while in the United States there are about 150 plants of the root-reed type in one of the State [2, 8, 14, 16].

The objective of the study was to determine the possibility of using an organic soil under red willow for purifying wastewater of excess nitrate and phosphate, and to estimate the applicability of redox potential for the assessment of transformation of nitrogen compounds in the soil under study.

DESCRIPTION OF THE OBJECT STUDIED

The study was conducted at an experimental object located in the Bystrzyca River valley on peat-muck soils with organic matter content of 32–36% and mineral-muck soils with organic matter content of 13.3–17.2%. Both sub-types of soils were developed from low sedge peat [7, 13]. The object was irrigated with wastewater from the town of Lublin treated at the Hajdów treatment plant. The whole area of the object (about 8 hectares) was divided into seven fields, and each of the fields into three sectors – A, B and C. Irrigation was applied on sectors B (single dose of wastewater, optimum for a given plant), and C (double the optimum dose), while sectors A were not irrigated and acted as control sectors. The field studied was planted with common willow (*Salix americana*) – Field 2 [7, 13].

METHODS

Chemical analyses of NO_3^--N, PO_4^{3-}-P and determinations of redox potential (Eh) were done for the following experimental materials: wastewater, soil solutions, and drainage waters. Irrigation with treated wastewater was applied at the following doses: – full single dose of 900 [mm], double dose of 1800 [mm], number of doses – 12 per year.

Soil solutions at the particular depths (10, 30, 50, 70, 100 cm) were collected by means of ceramic filters installed in the soil profile of each sector to the vacuum vessels in accordance with the irrigations cycle. Drainage water filtrates were taken from the individual outlets. Detailed analysis of transformation of nitrate(V) was performed on the basis of their mean concentrations from all the flooding performed in the first year of the study, after 3 hours and after 2 and 7 days from the moment of wastewater application on the field under willow plantation as an effect of their action on the soil environment. At the same time, the analysis of the concentration of the ions under study in the drainage waters was conducted.

For redox potential determinations, three platinum electrodes were installed at the depths of 10, 30, 50, 70, and 100 cm in permanent soil pits, one in each sector. Redox potential measurements were taken with relation to a calomel electrode used a constant non-zero voltage reference electrode. The measurements within the object studied were taken with help of a portable apparatus, an Orion Ioanalyzer 404. Due to temperature variations during the measurements, corrections were applied to the values of the reference electrode potential, assuming for temperatures of 10, 15, 20, and 25°C potential values of 254, 251, 247 and 244 mV, respectively.

Determinations of nitrogen and phosphorus forms in the experimental material were done by means of a flow-type spectrophotometric analyzer, Foss Tecator FIA-Star 5010. Determination of NO_3^--N was performed by passing the sample tested through a column filled with copper plated cadmium to reduce nitrate(V) to nitrate (III). Next, sulfanilamide was added to create diazo bonds. Diazo compounds, reacting with N-(1-naphthyl)-ethylenediamine hydrochloride, yield diazo red whose absorbance was measured at wavelength of 540 nm. Determination of PO_4^{3-}-P was done according to the following method: the sample containing ortho-phosphate reacted with ammonium molybdate to form heteropoly molybdophosphoric acid. The acid was reduced in a second step to phosphomolybdenum blue by stannous chloride in a sulphuric acid medium. The intensive blue color of the formed heteropoly compound was measured at 690 nm.

The differences between replications did not exceed 12%.

RESULTS AND DISCUSSION

Concentrations of nitrate(V) and phosphorus forms in the treated wastewater used for irrigation of fields show a high level of variation – the concentration of NO_3^--N varies from 20.2 to 38.4 g m^{-3}, and that of PO_4^{3-}-P from 3.1 to 6.8 g m^{-3}, pH value ranged from 6.47 to 8.41, COD 30.1–56.3 g O_2 m^{-3} and BOD_5 8.3–22.6 g O_2 m^{-3} [7, 13].

Transformation of nitrate (V) in field planted with willow

Figure 1 presents the concentration of nitrate(V) in the control sector A and in sectors B and C in the period from 3 hours till 7 days after soil flooding. A slight accumulation of nitrate(V) in the soil solution from the control sector was observed at the depths of 50 and 70 cm, which may be related to the lower biological sorption in that part of the soil profile. Mean concentration of NO_3^--N in the soil profile was approximately 5 g m^{-3}, with the highest value of 6.7 g m^{-3} recorded at the depth of 50 cm.

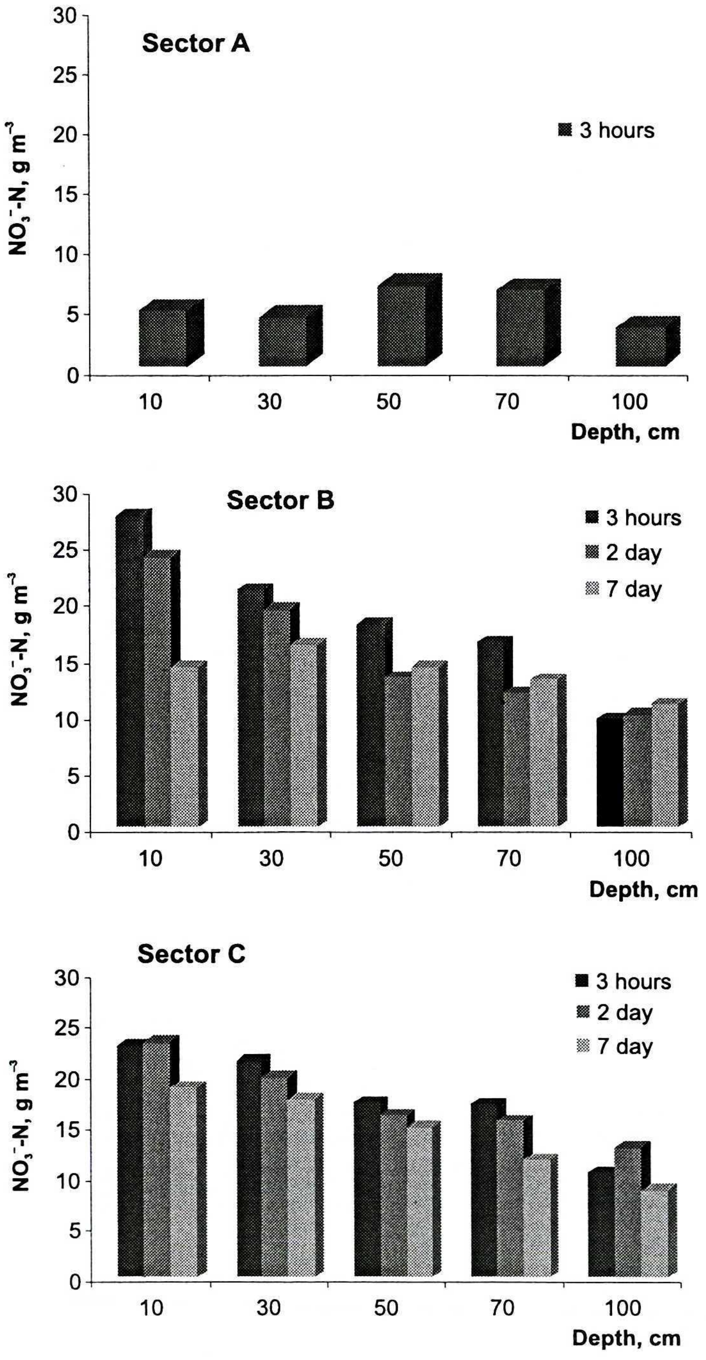

Fig. 1. Concentration of NO_3^--N in soil solution under willow plantation in control sector (A), in sector irrigated with single dose of wastewater (B) and in sector irrigated with double dose (C) in relation to depth and to the irrigation time

Introduction of treated wastewater modifies the chemical environment of plant and microbial life. Mean concentration of nitrate(V) form introduced with the wastewater was about 29 g m^{-3}.

Concentrations of NO_3^--N in the soil solution similar to those in the treated wastewater were noted in the 3rd hour in sector B at the depth of 10 cm, and a slightly lower concentration in sector C. With increasing depth and passage of time from the moment of irrigation with wastewater, the concentration of nitrate(V) decreased. Under conditions of anaerobiosis caused by high soil moisture or total flooding, bacteria use nitrate(V) or nitrate(III). Those organisms use oxidized forms of nitrogen as alternative electron acceptors instead of free oxygen. When during dissimilative reduction of nitrates molecular nitrogen (N_2) or (N_2O) is produced, the process is called denitrification. Sometimes, however, reduction of nitrates leads to the production of ammonia or nitrate(III), especially at low values of Eh. Generally, it can be stated that the rate of denitrification increases after the addition of nitrates [1, 17].

The distinct decrease in the concentration of NO_3^--N at the depth of 50–100 cm could have been related to dissimilative reduction of nitrate(V) involving the activation of the dissimilative path reductases which use NO_3^--N as electron acceptors alternative to O_2 [15].

Figure 2 illustrates the concentration of NO_3^--N in drainage waters with relation to the time of filtration and to the irrigation dose in willow plantation. The highest concentrations of nitrate(V) in the drainage waters were observed after 3 hours from irrigation with wastewater, which confirms the high mobility of the ion in the soil profile. After two successive days of analysis the concentration of the ion under study decreased slightly. The irrigation dose had virtually no effect on the concentration of NO_3^--N in the drainage waters.

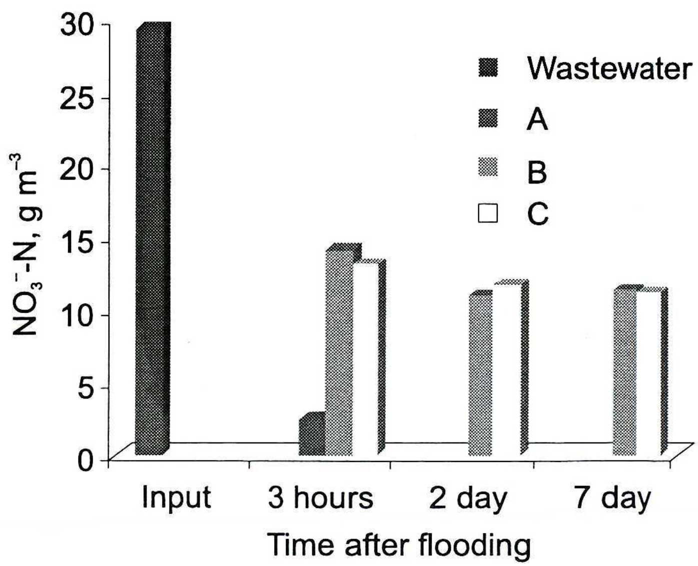

Fig. 2. Concentration of NO_3^--N in wastewater (input) and in drainage waters under willow plantation in relation to depth and to time elapsed from flooding (symbols as in Fig. 1)

High concentration of nitrate(V), several times higher than in the control object, more than four-fold (NO_3^--N concentration from the seventh day after flooding was divided by control concentration), persisted for a period of 7 days after the application of irrigation with wastewater. However, it did not exceed 15 g N m^{-3}, i.e. the limit value accepted by the EU. With relation to the amount of N introduced with the wastewater, the concentration of NO_3^--N decreased, on average, by 2- to 2.5-fold. The effectiveness of the soil-root filter, expressed as percentage decrease in the amount of NO_3^--N introduced to the soil with the wastewater, was approximately 61% for sectors with the single and double irrigation doses.

Transformation of phosphorus in field planted with willow

Figure 3 illustrates the concentration of PO_4^{3-}-P in the drainage waters in relation to the time of filtration and to irrigation dosage in the willow plantation. The concentration varied from 1.11 to 0.91 mg PO_4^{3-}-P m^{-3} for the second day of analysis, and from 0.78 to 0.43 mg PO_4^{3-}-P m^{-3} for day 6, for sectors B and C, respectively. Taking into account the level of phosphate-P concentration in surface waters permitted in Poland, which is 0.2 in class I, 0.5 in class II, and 1,0 mg PO_4^{3-} dm^{-3} in class III [11], the six-day period of operation of the soil-root filter appears to be insufficient to discharge water in class III of purity. Therefore, having in mind the protection of waters against excessive amounts of phosphates, lower irrigation doses should be applied.

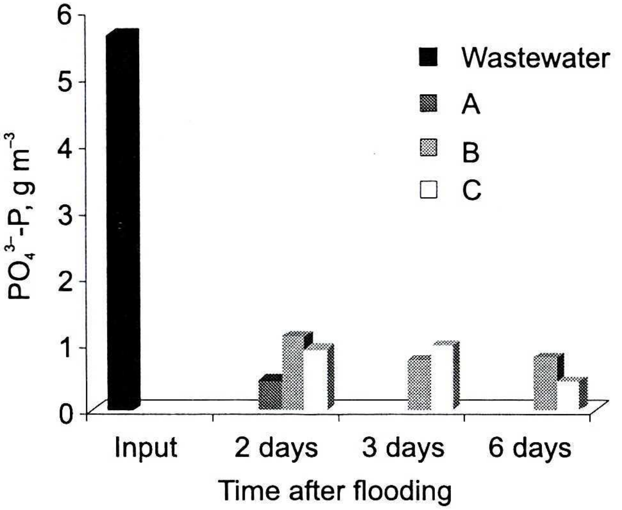

Fig. 3. Concentration of PO_4^--P in wastewater (input) and in drainage waters under willow plantation in relation to depth and to time elapsed from flooding (symbols as in Fig. 1)

The highest concentration of phosphate-P in drainage waters was recorded after 2 days from irrigation with wastewater. On the following days of the analysis the concentration of the ion in question decreased notably in the case of a single irrigation dose. This tendency was kept over subsequent 3 days. In the case of the double dose of wastewater, the concentration of phosphates-P decreased notably on day 6 of the analysis. It is noteworthy that already on the second day from wastewater application the concentration of the ion in question dropped more than five-fold with relation to that in the wastewater.

The effectiveness of the process of wastewater purification of excess phosphates was greater than in the case of nitrate ion and reached 86.1% for sectors with single irrigation dose and 92.4% in the case of the double dose. Studies by Brandyk [3] conducted on peat soils showed very good effects of wastewater purification and good results of grassland production.

Dynamics of redox potential changes

Introduction of wastewater to soil in amounts causing its complete flooding radically alters the air-water relations in the soil. As shown by studies of numerous authors [6, 10], under the conditions of soil flooding with water oxygen depletion occurs within several hours, causing a number of changes in the soil. In particular, the redox potential of the soil decreases, the decrease in Eh value below +300 mV being caused by soil reduction and activation of redox couples other than the O_2/H_2O system, for example NO_3^-/NO_2^- [6].

Gliński and Stępniewski [6] found out that soil flooding with water caused a gradual decrease of redox potential until a certain fairly stable level was reached. The rate of the decrease and the value of Eh depend on the intensity of the process of reduction, determined by temperature and by the content of easily decomposable organic substrate, and by the content of oxidized inorganic compounds acting as electron acceptors, including nitrate(V) [4, 6].

Redox potential in the control soil profile was fairly constant down to the depth of 50 cm and varied from +440 mV to +460 mV, i.e. within the range of oxygen oxidation of carbon [18]. At the depth of 70 cm the value of Eh dropped suddenly by about 200 mV, reaching negative values at the depth of 100 cm, close to the process of methanogenesis (Fig. 4). Such a rapid drop of redox potential was related to the appearance of ground water from the level of 50–60 cm.

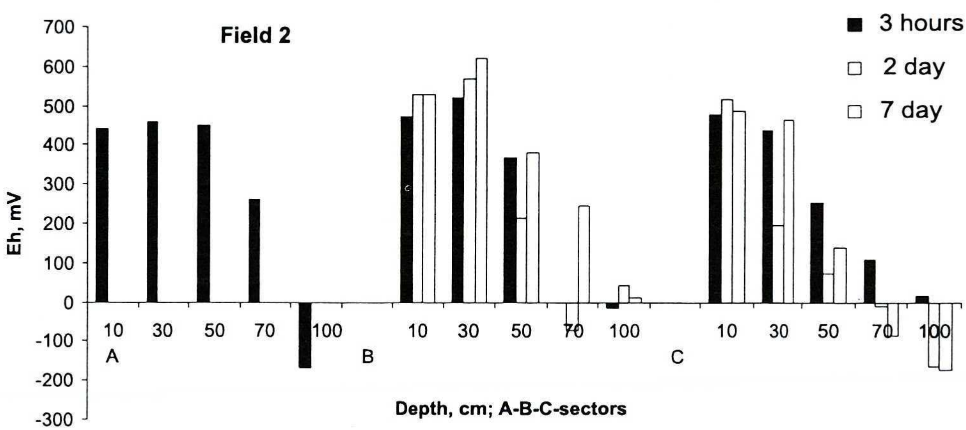

Fig. 4. Values of Eh in soil profile in relation to depth, irrigation dose, and time of irrigation after 3 hours, and 2 and 7 days (symbols as in Fig. 1)

Analysis of changes in the oxygenation status of sectors A, B, C down to the depth of 30 cm in the third hour from irrigation showed a slightly higher value of Eh in the irrigated combinations than in the control sector (A), which may have been related to the lower ground water level (70 cm) in sectors B and C. In the deeper parts of the soil profile of field 2, at the depth of 50 and 70 cm, the value of Eh in sectors B and C decreased in relation to the control.

Generally, it can be stated that the value of redox potential in the third hour from flooding decreased with depth. The decrease depended more on the level of the ground water table than on the application of wastewater.

Wastewater introduced to the soil migrates down the profile at varying rates, depending on the profile structure and filtration coefficient, causing changes in the air-water relations. The soil studied is characterized by varied air and water permeability, both between the fields and within a field, depending on the depth. This feature of the soil is related to the dynamics of the decrease in redox potential, and to the reoxidation of the soil profile. The observed phenomenon is also connected with the migration of the wastewater and with the improvement of the aeration conditions in the soil. Analysis of the oxygenation status of the field under willow plantation, down to 30 cm at the single irrigation dose, showed a slow increase in the value of Eh from the third hour to the seventh day after flooding, which may indicate an improvement in the air-water relations and the beginning of the process of reoxidation, observed already from day 2 after flooding with wastewater. The process could have also been affected by the water permeability of the soil, whose filtration coefficient increases at the depth of 20–40 cm [13]. On the other hand, the process of reoxidation of lower horizons of the soil (from 50 to 70 cm) took place with a certain delay, which was likely related to the migration of the wastewater within the soil profile. The process was marked by its absence at the depth of 100 cm, i.e. below the ground water table. In sector C a distinct effect could be observed of the double dose of wastewater on the redox status of the soil. The process of soil profile reoxidation was slowed down, and the effect was observable already from the depth of 30 cm. At depths from 30 to 50 cm a strong decrease in the value of Eh was observed on the second day of the experiment, by 243 and 182 mV, respectively, with an increase occurring only on the 7th day. Slowing down of the process of soil reoxidation in sector C must have also been affected by the much lower filtration coefficient – of about 45 cm day^{-1} – as compared to sector B, where it was approximately 140 cm day^{-1} [12]. At the depth of 70 and 100 cm redox potential, very low at the moment of flooding with wastewater, dropped drastically on 2nd and 7th day after the flooding, down to the values of -83 and -173 mV, respectively.

The character of nitrogen transformation is closely related to the soil oxidation status. Analysis of the dynamics of the transformation of nitrate(V) in relation to the depth in the soil profile and to the dosage of irrigation with wastewater indicated an overall decreasing tendency of their concentration. Characterization of the oxygenation status of the soil through the determination of redox potential values creates the possibility of indication which biochemical path may be taken by nitrate(V). Down to the depth of 50 cm, the control sector was characterized by relatively high redox potential, close to the value of +400 mV or even considerably higher. Eh values above +400 mV are characteristic of well aerated soils, where oxidation reactions predominate. One should assume, therefore, that under those conditions nitrates took the path of duction, where nitrogen was reduced by plants or microbial activity to the ammonium form prior to being built into the cells. Enzymes of the reductase group take part in the process. Redox potential decrease below 400 mV has been adopted conventionally as the limit of the reduction of nitrates on the path of dissimilative reduction, where nitrates are a respiratory substrate. Also nitrate reductases get activated in the process, though those of the dissimilative path that is inactive in the presence of oxygen. We should assume, therefore, that below +400 mV the drop in concentration of NO_3^--N was caused by the process of denitrification. Literature reports indicate that the beginning of the process of denitrification in various soils occurs at different values of Eh, sometimes even below +200 mV [9, 19]. Under favorable conditions (e.g. low Eh, available organic matter) nitrate(V) enters the path of dissimilative reduction where the end product is ammonium ion temporarily increasing its concentration in the soil profile, especially in the lower horizons.

Nitrate(V) concentration and redox potential in soil flooded with single and double doses of treated wastewater

Soil flooding may cause a gradual decrease of redox potential until a certain fairly stable level is reached. The rate of decrease and the minimum value of Eh depends on the intensity of the processes of reduction, on conditional temperature and on the amount of easily decomposable organic matter and of bioreducible oxidated inorganic compounds acting as electron acceptors. The presence of those compounds maintains redox potential on a certain constant level which e.g. in the case of nitrates is from +100 to +200 mV [6].

In the study reported here, an attempt was made at determining the correlation between the concentration of nitrate(V), introduced with the single and double doses of wastewater irrigation, and the value of redox potential. The relations obtained are presented on the example of mean values of concentration of NO_3^--N and values of Eh recorded in the fields in the first year of flooding.

Analysis of regression of the relation studied in the control sectors showed a lack of relationship between the concentration of nitrate(V) and the value of Eh.

On the other hand, observation of the relationship between content of nitrate(V), introduced with the wastewater, and the value of Eh proved to be interesting. The relation is described with two mathematical functions – linear ($y = a + bx$) and logarithmic ($y = a \ln x + b$). In all the cases analyzed the functions are positive, which means that a higher concentration of NO_3^--N corresponds to a higher value of Eh (Fig. 5). A higher correlation was noted in sector C, where the coefficient of determination R^2 reached values above 0.95 ($P < 0,001$), on days 2 and 7 after the flooding, and a lower correlation in sector B.

Analysis of the graphs presented here indicates that until the 2nd day after irrigation with wastewater in all the analyzed cases Eh values at the level of +200 mV was maintained within the range of concentrations of 10–20 g m^{-3} NO_3^--N. At high soil moisture, that concentration could provide protection of the soil against the process of reduction. Włodarczyk [19] confirmed that nitrate content decrease in the range from about 100 to approximately 10 mg NO_3^--N kg^{-1} redox potential dropped from 250 to 190 mV. The limit value for mineral soils, at which a distinct drop in Eh value occurs, is the level of about 100 mg NO_3^--N kg^{-1}. The highest diurnal reduction of nitrates coincided with Eh values within the narrow range between 200 and 210 mV.

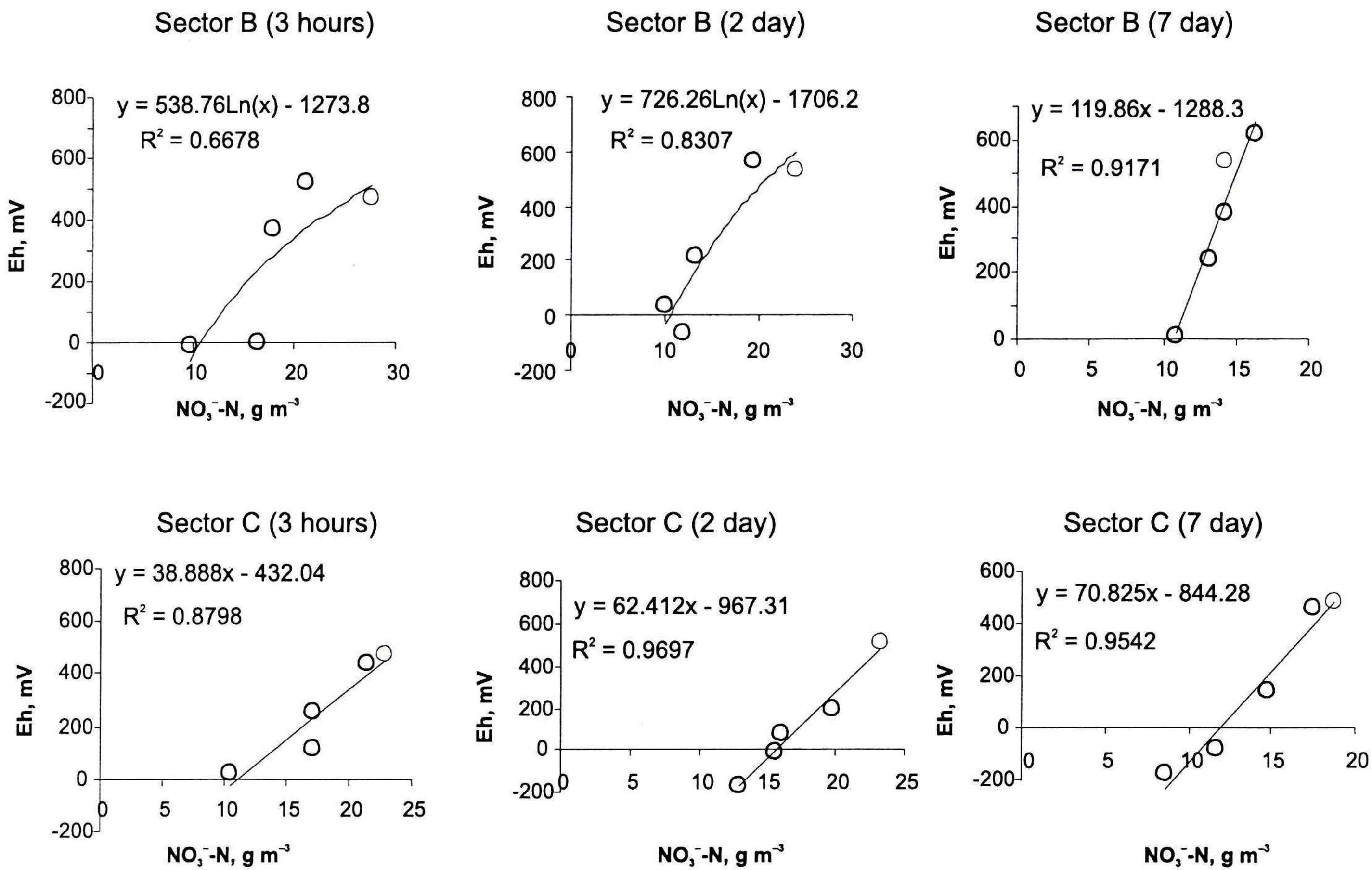

Fig. 5. Values of Eh as a function of concentration of NO_3^--N in soil solution after 3 hours and 2 and 7 days from irrigation with treated wastewater (symbols as in Fig. 1)

CONCLUSIONS

1. In the first year of the study, application of wastewater increased the average concentrations of NO_3^--N and PO_4^{3-}-P ions in drainage waters in relation to control sectors, thus only partially fulfilling the role of supplementary filter for wastewater purification.
2. Higher effectiveness of the soil-root filter was obtained in relation to the phosphate ion and lower in relation to the nitrate ion.
3. Application of treated wastewater had a significant effect on the value of redox potential.
4. Significant correlation was shown between redox potential and nitrogen transformation occurring in soil irrigated with wastewater after 2^{nd} stage of treatment.
5. No correlation was found between the concentration of nitrate(V) of the control sector (A) and the value of Eh.
6. Higher coefficient of correlation was noted in fields flooded with the double dose of wastewater.
7. In all analyzed cases Eh value on the level of +200 mV was maintained when concentration of NO_3^--N was within the range of 10–20 g m^{-3}.
8. Organic soil used as a biofilter showed an ability of reoxidation.
9. Application of wastewater at doses lower than the single dose may constitute a valuable source of nitrogen in cultivation of plants for industrial purposes.

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